An Introduction to the Principles of
PHYSICAL CHEMISTRY

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BY

O. MAASS
Macdonald Professor of Physical Chemistry,
McGill University

AND

E. W. R. STEACIE
Associate Professor of Chemistry, McGill University

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PREFACE TO SECOND EDITION

IN THE present edition, in addition to minor alterations the following main changes have been made:

(*a*) New chapters have been added on atomic structure, the phase rule, and colloidal systems.

(*b*) The chapter on the rate of chemical reactions has been entirely rewritten and brought up to date.

(*c*) A number of modifications has been made in the chapter on electrolytic dissociation, and a section on the Debye-Hückel theory has been added.

(*d*) The treatment of electrochemistry has been greatly extended and made more exact.

(*e*) A large number of questions on the material of each chapter has been included.

It is hoped that these additions and alterations will result in an improvement of the book and an enlargement of its usefulness, without sacrificing the viewpoint and objectives of the original edition.

O.M.
E.W.R.S.

February, 1939

PREFACE TO FIRST EDITION

This book is intended for a first course in physical chemistry for students who have had elementary courses in chemistry, physics, and mathematics. A course of about fifty lectures has been given at McGill University for the past twenty years in this form to a class composed of those intending to make chemistry their profession, chemical engineers, and students intending to enter medicine and the biological sciences. These students have either not had calculus, or are taking courses in it concurrently with physical chemistry. In the case of students intending to specialize in chemistry it has been found advisable to bring in an elementary course such as this at the earliest possible stage in their training. This makes possible a better appreciation of more advanced and detailed courses in physical chemistry, since the student thus has several years in which to assimilate the fundamental ideas.

In the following pages the object has been to develop an understanding of the basic principles of physical chemistry. An attempt has been made to present the subject as rigorously as possible consistent with the inculcation of its real significance, rather than the accumulation of a large amount of rule-of-thumb knowledge. The first chapter especially emphasizes this viewpoint. The real significance of this chapter will be realized after the student has completed the book.

O. Maass
E. W. R. Steacie

Montreal, Canada
February, 1931

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AN INTRODUCTION TO
THE PRINCIPLES OF PHYSICAL CHEMISTRY

CHAPTER I

INTRODUCTION

The Objects and Limitations of Science.—A casual observation of the phenomena of nature is sufficient to show that matter is continually undergoing changes. These changes are of various kinds: changes of position, changes of state, changes of composition, etc. The object of science is to systematize these changes, explain their cause, and predict their occurrence. The practical aim of science is to foretell the largest possible number of future events from the smallest possible number of observations.

In this attempt to systematize and explain natural phenomena, however, it must be remembered that absolute knowledge is impossible. All our explanations and predictions must necessarily be incomplete. Thus, for example, we can never determine the ultimate constituents of matter, although we can continually come closer to them. At first sight, matter appears to be made up of an almost infinite number of different constituents. The atomic theory and the experiments on which it is based reduced the number of basic constituents to the 92 elements. According to modern ideas all these elements are made up of a few fundamental components, such as protons, electrons, and neutrons. We have thus achieved a tremendous simplification in reducing the number of "unknowns" to three or four. We are, nevertheless, as far as ever from the ultimate constituents, since we are now faced with the question, What are the component parts of the electron, the proton and the neutron? The fact that our knowledge of natural phenomena can never be complete is, however, no ground for discouragement. The further our knowledge progresses, the more we can explain, and the more we can foretell. It is always possible, therefore, to know more than we do at present, and the fact that we can never know everything about natural phenomena is of little consequence.

The Scientific Method.—Science is based on observation and experiment. During the last century the number of workers and the amount of data accumulated have increased with great rapidity. As a result science has become so complicated that subdivision into a large number of branches has become essential. If it were not for the possibility of classifying and systematizing knowledge, further advance would be virtually impossible. Fortunately it is possible to effect a great simplification by the subdivision of science into separate branches which include groups of related phenomena. Two important branches of science will be considered here, viz.: physics and chemistry. Each of these branches has been subdivided again. Thus chemistry consists of four main divisions: analytical, inorganic, organic, and physical. Each of these has again been further subdivided. Thus physical chemistry includes electrochemistry, colloid chemistry, photochemistry, thermochemistry, etc. At the beginning of the last century it was possible for an individual to study "natural philosophy," and to become thoroughly conversant with all phases of science. Today specialization in a fairly narrow field is necessary. Although this is true, it is nevertheless essential that phenomena which apparently differ widely should be correlated as much as possible. Hence, in order to pursue one branch of science successfully, it is necessary to have a working knowledge of all related subjects.

The diffusive effect of continual subdivision of knowledge into narrow branches, if carried to extremes in the future, would lead to stagnation. This effect is, however, offset by the coordination which is effected by general principles which apply to all branches of science, and by the correlation of facts and the discovery of general laws of nature.

After investigating a large number of phenomena which appear to possess certain similarities, the results are examined to see if any regularity can be found. If so, the observed regularity is put in the form of a concise statement called a law. An example of such a generalization is the law of the conservation of mass. This can be stated as follows: The matter in a definite system has a definite mass irrespective of any chemical or physical changes that may take place in the system. This "law" is merely a concise statement of the fact that in a large number of experiments no change has ever been observed. A law must therefore be looked upon merely as an empirical shorthand expression. It sums up experimental results and allows the results of other experiments to be predicted when they are carried out under specified conditions. It should be emphasized that nature makes the law, not man. The experimenter merely guesses at the best way of summing up the workings of nature. In other words, nature does not have to obey the law—the law must obey nature. Law in science therefore has an entirely different meaning from the same word used in a legal sense.

The more concise the expression of a law, the easier it is to apply. The most concise statement is usually in the form of algebraic symbols. This is generally the most useful form because it lends itself to mathematical operations. In certain cases, such as the law of the conservation of mass, nothing is gained by mathematical expression. In most cases, however, such as the gas laws, a very great simplification results from the mathematical expression of a law.

After a number of experiments have been performed, and have been successfully expressed as a law, the next step of the human intellect is to ask the question "Why?" Is it possible from the structure of the system investigated to arrive at an explanation of the observed facts? Is it possible to imagine some simple structure for the system which would logically lead to the complex observed behaviour? This imaginary picture of the system need not be rigorously accurate. It must however, lead to the observed facts, and it must be simpler. The simplicity may arise in two ways: either the imaginary system is simpler in itself, or else it is simpler because it has properties about which more is known. Very often, for example, a structure may be imagined which can be dealt with by the laws of mechanics, which when applied lead to the observed facts. The essential feature is that the "explanation" must be more easily understood than the phenomenon being explained. For instance, the statement that chemical reaction is explained by atoms of certain elements having an affinity or liking for one another is worthless, since it is just as difficult to understand the " likes " of atoms as it is to understand their reactions. On the other hand, imagining that a gas has a discontinuous structure and applying Newton's laws of motion to the component parts in order to derive the gas laws comprise an "explanation" of great value, as will be shown later.

For our purpose a supposed explanation of a set of phenomena which leads to the laws observed will be called an hypothesis. The process of formulating an hypothesis follows the empirical formulation of a law whenever possible. In certain cases more than one explanation or hypothesis has successfully explained a law. This naturally leads to uncertainty. When it is possible to perform additional experiments which eliminate all but one hypothesis, the latter obviously approaches nearer to certainty. Such an hypothesis, viz., one which is unique, will be termed a theory. More strictly the word theory should be used only for an hypothesis which not only is unique, but which also can be used to predict phenomena which were not contemplated when the underlying law was first formulated. In practice the words *hypothesis* and *theory* are often used interchangeably and we shall follow the customary usage in each individual case. Even with the above definition of a theory, it should not be looked upon as an ultimate truth, but merely as an hypothesis, which, for the present, explains the observed facts, and predicts new ones. A theory exists only as long as it proves of value and is not contradicted by any experimental fact. Once it is shown to be in conflict with experiment it must be abandoned or modified. The adherent of a scientific theory should not have the viewpoint of a "fundamentalist."

Half-truths and Inexact Laws.—Laws are the result of the classification of experimental results and consequently they are dependent on the accuracy with which the experiments have been performed. In the majority of cases it has been necessary to modify the laws when greater precision in measurement has been attained. Thus the early measurements on the pressure, temperature, volume relationships of gases led to the gas law. This is now referred to as the "ideal gas law" because refinements in experimentation have shown that the law does not accurately represent the facts for any real gas. Modifications of the law, such as that of van der Waals, are in better accord with both hypothesis and experiment, but further refinements in measurement again gave rise to discrepancies.

The law of the conservation of mass was long regarded as one of the "infallible" laws. Recent work in radioactivity, however, has shown that it is not rigorously true. Although it is beyond the scope of chemical measurements, we now know that when 32 grams of oxygen react with 4 grams of hydrogen to form water there is a loss in weight of about 10^{-8} gram.

It may therefore be wondered whether these laws are of any value since they are known to be merely half-truths. The answer is that, although they are not rigorously true, they are approximations and hold within certain limits. Thus the ideal gas law is only an approximation. In spite of this, however, it gave rise to the hypothesis of the discontinuous structure of gases, which has proved of tremendous value. The modifications introduced by van der Waals' equation have really confirmed, rather than weakened, the original hypothesis. The hypothesis, therefore, is of very great value, although the search for the exact modification of the gas law is not yet ended. Inexact laws are of value from the purely practical point of view as well. The ideal gas law, for example, can be used in many calculations where extreme accuracy is not required. Again, for all ordinary purposes, the law of the conservation of mass may be assumed to hold rigorously. This discussion, together with the developments in the chapters to follow, is intended to bring out the necessity of caution in the application of laws. It is essential to know the limitations of a law and the manner in which it may be arrived at theoretically. Intelligent application cannot be made by rule-of-thumb methods, but only through a thorough knowledge of the underlying assumptions and limitations.

This exposition of the limited validity of experimental laws must be kept in mind in the later development of the subject matter of this book. The behaviour of gases, for example, will be approached from the point of view of the ideal gas law because from it the hypothesis of the discontinuous structure of gases was first deduced. It is unnecessary to bring in complications at first which would only obscure the point at issue without in any way invalidating the result. Later, when discussing the properties of gases, the limitations of the gas law will be described in detail. Very often the historical development of a subject is the most convenient because in many cases the fundamental facts were first discovered and the confusing side-issues were not encountered till later when more accurate investigations were possible. To illustrate this we may consider Dalton's atomic hypothesis. In this hypothesis it was assumed that all the atoms of an element have equal weights. On this basis the four gravimetric laws were explained very successfully. We now know that so-called isotopes of elements exist, the atoms of which have different weights. This, however, does not invalidate the conclusions of the atomic theory, and it is convenient to develop the theory in its simple form and to deal with the complicating factors later.

The question now arises, Are there any laws which have no limitations? In other words, Is it possible to sum up the results of human experience with the accuracy of an algebraic equation? Naturally no positive answer can ever be given to the question. There are, however, cases in which the laws deduced from experiments seem to be more accurate than the experiments themselves, and further refinement in experimental technique does not lead to discrepancies. Foremost among these laws, and the basis of all branches of science, is the first law of thermodynamics, or the law of the conservation of energy. No human experience has ever thrown doubt on the validity of this law, and it is therefore assumed to be absolutely accurate.

The Empirical and the Mechanistic Points of View.—As we have seen previously, the attempt is made to explain natural phenomena by imagining a structure of simple unit parts which leads logically to the observed facts, usually by means of statical or dynamical treatment. This mechanical analogy, by means of which facts are visualized, is referred to as the "mechanism" of the process. The governing factor in the employment of this mechanism is not its truth but its utility. The use of mechanistic reasoning is entirely justified if we can progress further by means of it than would be possible by the empirical classification of facts and the formulation of laws. The empirical method possesses the great disadvantage that it cannot lead beyond the boundary of direct experience. The mechanistic method, however, can often predict the result of a quite novel experiment. This furnishes its complete and its sole justification. In every case, of course, we try to find the true explanation of the facts, and unquestionably we often do find it, but it should always be remembered that usefulness is the sole criterion of a successful hypothesis.

Ostwald, one of the founders of physical chemistry, at one time started a school of thought whose object was to eliminate mechanistic reasoning. His idea was to apply the generalizations of physics, if possible in symbolic form, to physicochemical systems treated as homogeneous media, without reference to the structure of the systems. Ostwald soon abandoned this idea as impractical, just as Lord Kelvin was forced to abandon the elastic theory of gases. These attempts to avoid mechanistic reasoning were of value, however, because they combated the tendency to go to the other extreme and to defend a mechanism, not from the point of view of utility, but dogmatically as infallible. Although dogmatic adherence to hypotheses is highly objectionable, there is no question that progress would have been greatly retarded had the attempt been successful to use only thermodynamics, and to discard all possible theories of the structure of matter.

The mechanistic method has been justified both from the viewpoint of the investigator and as a method of teaching. It will therefore be the standpoint of this book to adopt it whenever possible and convenient. This does not mean that the value of thermodynamics and symbolic representation should be overlooked. Every process must be regarded as being absolutely subject to the laws of thermodynamics; and, in addition, symbolic representation is of value because it lends itself to quantitative calculations and to the use of mathematical manipulations.

After emphasizing the mechanistic viewpoint, it may be of interest to point out certain cases in which progress has been made without its use. In some branches of physiology, for example, the conditions are so complex that it is impossible at present to assign any mechanism, no matter how complicated or artificial. In the meantime, therefore, it is necessary to proceed empirically.

The States of Aggregation.—Any portion of matter possesses certain properties by means of which it can be described, viz.: density, colour, form, etc. By suitable changes in the temperature of the environment, matter may be made to suffer marked changes in properties, which are reversed when the temperature changes are reversed. A general classification has been made and all portions of matter may be described as belonging to one of three "states": solid, liquid, or gaseous. A solid has a definite volume and shape, and owing to gravity it exerts pressure at its points of support. A liquid has a definite volume but its shape is adapted to that of the container. At every point of contact with the container pressure is exerted due to gravity, the magnitude of the pressure depending on the depth below the surface. A gas has no definite volume or shape and completely fills its container. It exerts a uniform pressure on every part of the surface of the container, even against the action of gravity. As an example we may consider water. At ordinary temperatures water is a liquid with a definite volume but adapting itself to the shape of its container. When it is cooled to a low temperature it changes to ice, which is a solid and maintains its shape when removed from its container. If the ice is heated it melts to form water with the original properties of the liquid state. If water is heated to a higher temperature it forms steam. Steam is a gas and it uniformly and completely fills any container in which it is confined. If the steam is cooled it condenses to the original liquid.

Each of the states of aggregation has marked properties which are general in nature, and are more or less independent of the particular portion of matter under consideration.

Physical and Chemical Changes.—The two sciences, physics and chemistry, deal with matter and the changes which it undergoes. It is difficult to give definitions which distinguish between the two with exactness in all cases. In general, however, we may say that physics is primarily concerned with energy changes in material systems, whereas the main interest of chemistry is matter *per se.* This difference in viewpoint is well exemplified by the way in which text-books of the two subjects are subdivided. Thus in physics the divisions usually are: heat, light, sound, electricity, etc., i.e., various forms of energy. In textbooks on elementary chemistry, however, the divisions are usually the elements: oxygen, hydrogen, the halogens, etc., i.e., different forms of matter. The general tendency of physics is therefore to consider large generalizations, such as the law of the conservation of energy, which are independent of the particular kind of matter concerned. Chemistry, on the other hand, tends to be more descriptive and somewhat to overlook general principles in its search for detailed knowledge.

Physical chemistry is concerned with the application of the generalizations of physics to chemistry. It deals with the effect of various kinds of matter on physical properties, and conversely with the effect of physical factors on chemical reactions. Thus the inorganic chemist is satisfied when he has summed up a reaction in the form of an equation which expresses the stoichiometric relations of the substances concerned. Physical chemistry, however, seeks further information concerning the energy change which accompanies the reaction, the rate at which the substances react, the effect of temperature and pressure on the equilibrium, etc.

As an example we may consider the two reactions:

$$N_2 + O_2 \rightleftarrows 2NO$$

$$N_2 + 3H_2 \rightleftarrows 2NH_3.$$

In the first of these heat is absorbed when nitric oxide is formed, whereas in the latter heat is evolved in forming ammonia. An increased temperature causes the equilibria to shift in such a way that more nitric oxide is formed, but less ammonia. Increased pressure has no effect on the nitric oxide reaction, whereas it causes an increased yield of ammonia. There are thus a large number of physical factors whose effects on chemical reactions require explanation. It is one of the main purposes of physical chemistry to predict and interpret such phenomena.

The Use of Mathematics.—Among the prerequisites for a comprehensive study of physical chemistry mathematics takes an important place. It does so from two rather different points of view. Of these, the ability to utilize mathematical manipulations in specific problems in physical chemistry is perhaps of less importance than the training in exact thinking and in certain logical systems of reasoning.

Apart altogether from its usefulness for specific problems, the value of the study of mathematics cannot be overemphasized. Mathematics may be regarded as a short-hand method of representing a large number of facts, marshalling these facts in order, and deriving logical conclusions from them in a recognized way. The value of such an acquirement to the student of physical chemistry is therefore obvious. On the other hand, apart from the training derived, too much must not be expected from mathematics. In its actual application it is a tool of great value, and, in general, it serves to condense and to simplify facts, but no amount of mathematical manipulation will give results which are not inherent in the premises.

QUESTIONS

1. Define the term law as it is used in science. Discuss this definition and illustrate by examples the various points emphasized (conciseness of expression, infallibility, etc.).
2. Distinguish between hypothesis and theory.
3. Describe the scientific method, and illustrate it by an example.
4. Define physical chemistry, and discuss its objectives.

CHAPTER II

THE STRUCTURE OF MATTER

THE object of the present chapter is to present the experimental evidence which is necessary to develop the atomic structure of matter in its simplest form. The scientific method, previously outlined, will be followed, i.e., we will proceed from experiment to law, and then to hypothesis.

The idea of the discontinuity of matter was one of the early speculations of the Greeks. At first sight it appears almost unbelievable that such an hypothesis could have been put forward at a time when scientific knowledge was so slight. It must be remembered, however, that the original hypothesis of Leucippus was based on no experimental evidence, and that it was merely one of a large number of vague speculations concerning natural phenomena.

The more modern ideas of the atomic molecular structure of matter are based on three main lines of experimentation: experiments on gases which led to the gas laws; experiments on chemical reactions which led to the four gravimetric laws; and experiments on the volume relations existing in gas reactions which led to Gay-Lussac's law of reacting gas volumes. These three subjects will now be considered in some detail.

(A) Experiments on Gases.—The gaseous state was the last of the states of aggregation of matter whose existence was recognized. Van Helmont, in the seventeenth century, was the first to discover the ponderability of gases and vapours. Boyle first made quantitative measurements with gases and investigated the relation between the volume of a gas and the pressure under which it exists.

The type of apparatus employed by Boyle is shown in Fig. 1. A U-tube, as shown, leads through a stopcock to a mercury reservoir. A gas, for example air, is confined in the right-hand arm of the tube above the mercury. The other arm is evacuated. The right-hand arm of the tube is graduated so that the volume of the gas may be read. The pressure on the gas may be varied by running mercury in or out of the tube from the reservoir. The following represent a set of typical observations obtained with an apparatus of this kind.

Pressure, cm. of Mercury	Volume, c.c.	pv
10	100	1000
20	50	1000
30	33	990
40	25	1000
50	20	1000
60	17	1020

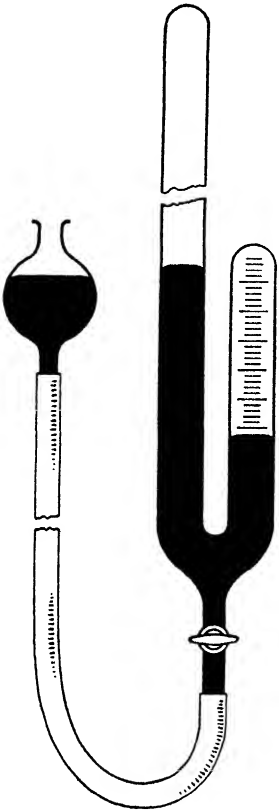

FIG. 1.

The original experiments were accurate only to within a small percentage. It is immediately obvious that the volume decreases as the pressure increases. By trial (i.e., guesswork) it was found that the volume of the gas was inversely proportional to the pressure under which it existed, the temperature remaining constant. This statement is usually known as Boyle's law. Expressed in symbolic form we have, where p is the pressure and v the volume,

$$v \propto 1/p, \quad \text{or} \quad pv = \text{constant} = K_1.$$

The last column in the above table shows that this is true, within the accuracy of these experiments. It should be noted that this law is true only provided the temperature of the gas is kept constant during the experiments.

Somewhat similar experiments were made later by other workers to determine the effect of varying temperature. These were made in two ways. In one set of experiments the gas was heated to various temperatures by immersing the U-tube shown in Fig. 1 in a water or oil bath. At each temperature the pressure, in centimetres of mercury, was read, which was necessary to maintain the volume constant at some fixed mark on the graduated scale. It was found that the pressure increased as the temperature was raised, the volume of the gas being maintained at a constant value. The experimental results thus obtained were summed up by Charles and by Gay-Lussac in a law which is known either as Charles' law or as Gay-Lussac's law. Some sample observations are given below.

VOLUME KEPT CONSTANT AT 100 C.C.

Pressure, cm. of Mercury	Temperature, °C.	Pressure, cm. of Mercury	Temperature, °C
273	0	473	200
303	30	243	− 30
333	60	213	− 60
373	100	173	−100

These results may be summed up in the symbolic form

$$p = p_0(1 + \alpha t) \quad \text{(Volume constant),}$$

where p is the pressure of the gas at a temperature $t°$ C., p_0 is the pressure at 0° C., and α is a constant which is found to have the numerical value 1/273.1. Similar experiments were also performed in which the pressure was maintained constant and the volume of the gas was allowed to vary as the temperature changed. These experiments led to a very similar mathematical expression:

$$v = v_0(1 + \alpha t) \quad \text{(Pressure constant),}$$

where v is the volume of the gas at a temperature $t°$ C., v_0 is the volume at 0° C., and α is a constant which was found to have the same numerical value as before, viz.: 1/273.1.

In the two above expressions the temperatures referred to are those on the Centigrade scale. A certain simplification is possible in the symbolic form of the laws if we can find a temperature scale which eliminates the constant α. This elimination of the constant will be of value, if it can be accomplished, since the simpler the form of a law, the more useful it becomes.

Suppose that we adopt a temperature scale on which a degree represents the same temperature increment as it does on the Centigrade scale, but that we adjust the zero of the new scale in such a way that $t°$ on the Centigrade scale represents the same temperature as $(t + 1/\alpha)°$ on the new scale (usually called the Absolute scale).

Then, if t = temperature in °C.,

T = temperature in ° Absolute,

we have $(t + 1/\alpha) = T$, or $T - 1/\alpha = t$, $T - 273.1 = t$. Hence 0° on the Centigrade scale is equal to 273.1° on the Absolute scale.

With this new notation Charles' law can be immediately simplified. The expression

$$p = p_0(1 + \alpha t) \quad \text{becomes} \quad p = p_0\left\{1 + \alpha\left(T - \frac{1}{\alpha}\right)\right\},$$

or $$p = p_0 \alpha T,$$

or $$p = \frac{p_0 T}{273.1}. \quad \text{(The volume being constant.)}$$

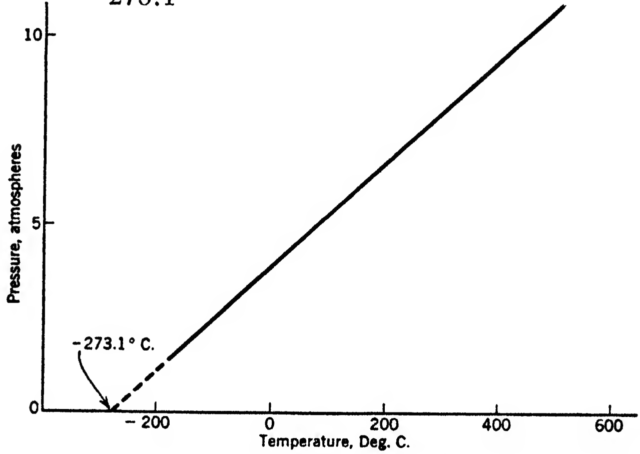

FIG. 2.—The Variation in the Pressure of a Gas with Temperature.

This result may also be arrived at graphically in a very simple manner. Figure 2 shows the variation in the pressure of a given volume of air as the temperature is varied. It will be seen that a straight line is obtained when the pressure is plotted against the temperature in °C. The results indicated in the diagram cover the temperature range from 600° C. to −180° C. If the line is extrapolated it cuts the temperature axis at −273.1° C. This means that if air could be cooled without liquefaction or solidification occurring its pressure would become zero at −273.1° C. Experiments with other gases lead to similar results, and it may therefore be concluded that the pressure of any gas would be zero at −273.1° C. It follows that the pressure of a gas is directly proportional to its distance from $-273.1°$ C. Or,

$$p = K(t + 273.1) = KT,$$

where t denotes the temperature in °C. and T that in °Absolute. Similarly, for the volume-temperature expression we obtain

$$v = \frac{v_0 T}{273.1}. \quad \text{(The pressure being constant.)}$$

If we denote 0° C. (or 273.1° Abs.) by T_0, we have

$$\frac{p}{T} = \frac{p_0}{T_0},$$

or

$$\frac{p}{T} = K_2. \quad \text{(Volume constant.)}$$

Similarly

$$\frac{v}{T} = \frac{v_0}{T_0}$$

or

$$\frac{v}{T} = K_3. \quad \text{(Pressure constant.)}$$

From Boyle's law we also have

$$pv = K_1. \quad \text{(Temperature constant.)}$$

If we are dealing with the same mass of gas, these three equations * may be combined into one expression by means of a well-

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* The three expressions to be combined are condition equations, i.e., they only hold under specified conditions, when some factor remains constant. We cannot combine them therefore by multiplication. We can accomplish this, however, by proceeding as follows: Let the initial pressure, volume, and temperature of a certain mass of gas be p_0, v_0, and T_0, respectively. Suppose that the conditions are altered so that the final values of the three variables are p_1, v_1, and T_1. We can imagine that the process occurs in two stages.

(1) Maintain the volume constant at v_0. Change the temperature from T_0 to T_1. Suppose that the pressure under these conditions is p. Then we have from Charles' law:

$$\frac{p_0}{p} = \frac{T_0}{T_1}. \quad \text{(Volume} = v_0 = \text{constant.)}$$

(2) Now let the temperature be maintained constant at T_1, and expand the gas from v_0 to v_1. Applying Boyle's law we have:

$$pv_0 = p_1 v_1 \text{ (temperature} = T_1 = \text{constant),}$$

or

$$p = \frac{p_1 v_1}{v_0}.$$

Substituting for p in the equation above gives

$$\frac{p_0 v_0}{T_0} = \frac{p_1 v_1}{T_1},$$

or

$$pv = KT.$$

known algebraic operation dealing with condition equations. This gives the expression

$$\frac{pv}{T} = \frac{p_0v_0}{T_0} = K,$$

or

$$pv = KT,$$

where K is a new constant.

This expression sums up the results of the above three equations and is therefore much simpler and more convenient to apply. It should be noted, however, that the process of combining the three equations into one is purely mathematical. By the combination we have not learned any new facts about the behaviour of gases, but have merely summed up our former knowledge in a more concise form.

Not long after Boyle's experiments an explanation of the behaviour of gases was suggested. In its modern form this explanation or hypothesis may be summed up as follows:

A gas is composed of discrete particles (molecules), which have the form of spheres and which are perfectly elastic. These are in continual motion in all directions and obey Newton's laws of motion. The pressure which a gas exerts on the walls of the containing vessel is due to the hits recorded by the moving molecules. In virtue of this motion the gas has a certain amount of intrinsic energy which manifests itself in the form of heat. The temperature of the gas is thus a measure of the kinetic energy of the molecules.

This hypothesis immediately leads to a qualitative explanation of the gas laws:

(1) $pv = K_1(T = Const.)$.—The molecules of the gas are supposed to be in motion and to hit the walls of the container. In order that this bombardment may lead to a steady pressure, the number of particles must be exceedingly large and they must strike the walls with great frequency. Since the molecules are assumed to be perfectly elastic there will be no loss of energy by friction, and the pressure will remain constant over an indefinite period.

Compressing the gas, i.e., decreasing its volume, increases the number of molecules per unit volume, and hence increases the number of impacts in unit time on the walls of the containing vessel. The pressure will therefore increase when the volume of the gas is decreased. We thus have a qualitative explanation of Boyle's law.

(2) $p/T = K_2 (v = \mathit{Const.})$.—Raising the temperature of a gas at constant volume increases the average energy (or velocity) of the molecules. Hence the force with which they strike the walls, i.e., the pressure, is increased. Thus the assumption that the temperature is a measure of the intrinsic energy of the gas molecules leads qualitatively to the observed relationship between pressure and temperature.

Furthermore, light is thrown on the meaning of the zero of the Absolute scale of temperature. We can imagine the velocity of the molecules being decreased continually, the decrease being manifested as a decrease in the temperature of the gas. Finally, a condition will be arrived at where the molecules are absolutely stationary. At this point they have no kinetic energy, and the zero on the Absolute scale of temperature has been reached. If the molecules are motionless the pressure must be zero, as required by the above equation. As a further consequence, it follows that it is impossible to have a temperature lower than 0° Absolute or $-273.1°$ C., since we cannot imagine a negative kinetic energy.

(3) $v/T = K_3 (p = \mathit{Const.})$.—This follows from similar lines of reasoning. Raising the temperature increases the velocity of the molecules. Hence fewer hits are required to maintain the same pressure, and this condition can be produced by increasing the volume.

After the above qualitative reasoning, which shows that the hypothesis is at least a plausible one, the next step is to show that it leads quantitatively to the concise expression connecting the pressure, volume, and temperature of a gas, viz.: $pv = KT$. This may be accomplished as follows:

Consider a single molecule moving about in a cubical container (Fig. 3). Suppose that the mass of the molecule is m, its velocity parallel to the two side walls of the container is u, and that the length of side of the container is l. Then the force exerted by the molecule on a wall during a single collision will be equal to the change of momentum suffered during the collision.* The momentum before the collision will be equal to $m \cdot u$. The momentum after is $m(-u)$. Hence the change in momentum during a collision $= 2mu$.

The average force, during the period of time considered, exerted on the pair of walls by the molecule = (change in momentum) (number of hits in unit time)

$$= 2mu \cdot u/l$$

$$= \frac{2mu^2}{l}.$$

The actual motion of the molecule in the container will, of course, not be merely back and forth between two walls, but will be in all directions. We can, however, resolve the motion into three velocity components at right angles to one another, and parallel to the sides of the container. Let the actual velocity of the molecule at any moment be x, and let its three components be u, v, and w as shown in the diagram.

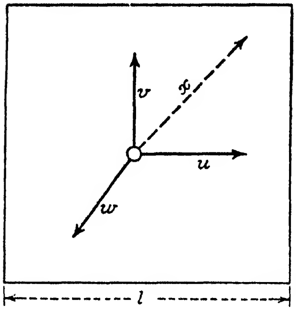

FIG. 3.

Then the average total force on all six walls of the cubical container, due to the single molecule, will be

$$\frac{2mu^2}{l} + \frac{2mv^2}{l} + \frac{2mw^2}{l},$$

$$= \frac{2m}{l}(u^2 + v^2 + w^2).$$

From the parallelepiped of velocities this is equal to

$$\frac{2mx^2}{l}.$$

---

*According to Newton's second law, force is equal to mass-acceleration. Acceleration is the change in velocity per unit time. Hence, since the mass of the particle remains constant, the force it exerts is equal to the change of momentum per unit time.

The pressure on the walls of the container is equal to the force per unit area. Hence

$$p = \frac{2mx^2}{l \cdot 6l^2}$$

$$= \frac{mx^2}{3l^3}.$$

If we assume that, instead of a single molecule, there are actually n molecules in the container, we have, since each exerts its pressure independently,

$$p = \frac{mnx^2}{3l^3}$$

$$= \frac{mnx^2}{3v},$$

where v is the volume of the cube.

Hence

$$pv = \tfrac{1}{3}mnx^2.$$

Now the kinetic energy of a molecule is equal to

$$\tfrac{1}{2}mx^2.$$

Hence the kinetic energy of n molecules

$$= \tfrac{1}{2}mnx^2.$$

Hence we have

$$pv = \tfrac{1}{3}mnx^2$$

$$= \tfrac{2}{3} \text{ (kinetic energy of all the molecules)}.$$

But it is one of the assumptions of the molecular hypothesis that the temperature is a measure of the kinetic energy of the molecules.

Hence

$$pv = KT,$$

where K is a constant.

It is thus apparent that the assumptions of the molecular hypothesis, when applied by means of the laws of dynamics, lead quantitatively to the gas law.

Certain assumptions regarding molecules have been made in the above derivation. It was tacitly assumed that they have no volume, i.e., that they may be regarded as mathematical points; that they have no influence on each other; and that they are perfectly elastic spheres. The excellent agreement between the theory and the earlier experiments shows that these assumptions were justified. The discussion of the inaccuracies which result from these assumptions will be reserved for a later section dealing with the general properties of gases.

The most important fact brought out by the foregoing discussion is that the hypothesis of the structure of matter based on discontinuity, i.e., matter made up of discrete parts, will explain the properties of an apparent continuum such as a gas.

(B) Experiments on Chemical Reactions.—As we have seen from the preceding section, the behaviour of gases can be satisfactorily explained by the assumption of discrete particles. Gases can be condensed to form liquids and solids, which may again be converted into gases by raising the temperature. It would therefore be expected that there should be no fundamental difference in the ultimate structure of the different states of matter. We will therefore examine the evidence for the discontinuous structure of matter in general, irrespective of its state of aggregation. The main evidence of this kind is furnished by the quantitative investigation of chemical reactions.

There are an almost infinite number of diverse forms of matter. These diverse substances can be transformed one into another by interaction, temperature change, etc. Pure substances, i.e., those whose properties are homogeneous throughout, may be divided into two classes, elements and compounds. Compounds are substances which can be split up into simpler ones by chemical processes, whereas elements cannot be resolved into simpler substances. This idea of certain fundamental substances has existed since the days of Aristotle, but it remained for Boyle to give the above clear definition.

An enormous number of experiments have been performed in connection with the building up and breaking down of chemical substances. Those of a quantitative nature have led to the following four laws of chemical combination.

(1) *The Law of the Conservation of Mass.*—Lavoisier originally showed that the fundamental property of matter is its gravitational attraction, and that the amount of matter in a closed system, as measured by its mass, remains constant

throughout all transformations of the matter. One of the most accurate verifications of this is found in the experiments of Landolt.

In Landolt's experiments two substances which would react with one another were placed separately in the two arms of an H-shaped tube. The side arms of the tube were than sealed off so that the system was completely enclosed. The H-tube was then very accurately weighed, turned upside down so that the reagents could mix and react, and then weighed again. Landolt took very great precautions to eliminate all possible sources of error, and came to the conclusion that no change in weight, greater than the experimental error, occurred when a chemical reaction took place. Thus in the 15 different reactions he investigated the change in weight due to the reaction was always less than one part in a million. In no case was this change in weight greater than the probable error in weighing (about ± 0.03 milligram).

These experiments have been summed up in the law of the conservation of mass, which may be stated as follows: The matter in a definite system has a definite mass, irrespective of any chemical reactions or physical changes that may take place within the system.

(2) *The Law of Constant Composition.*—A large number of experiments have shown that a chemical compound always has the same composition no matter how it is prepared. Thus, for example, the analysis of four different samples of nickel bromide, prepared in different ways, gave the following results:

Sample	Grams of Nickel Combined With One Gram of Bromine
I	0.36728
II	0.36722
III	0.36726
IV	0.36725

The composition of nickel bromide is therefore constant within the experimental error.

Thousands of experiments of a similar nature have given similar results with other substances. The results of all such experiments may be summed up in the law of constant composition: The composition of a compound is definite, and is independent of the amount of substance present and of its method of preparation.

(3) *The Law of Multiple Proportions.*—At first sight there appear to be numerous exceptions to the law of constant composition, since substances are known which have different properties but which are composed of the same elements. The explanation is that two elements may form more than one compound, but each of these compounds has a constant composition. Through an examination of such compounds a surprising relationship was found concerning the relative amounts of the substances combined.

Consider, for example, the two oxygen-hydrogen compounds: water and hydrogen peroxide. Water contains, by weight, 11.11 per cent hydrogen and 88.89 per cent oxygen. Hydrogen peroxide contains 5.88 per cent hydrogen and 94.12 per cent oxygen. Expressing this another way, we may say that 1 gram of hydrogen combines with 8.00 grams of oxygen to form water; and with 16.00 grams of oxygen to form hydrogen peroxide. The amounts of oxygen combined with 1 gram of hydrogen in the two compounds are in the ratio of 16 to 8, i.e., 2 to 1, or small whole numbers.

As another example we may consider the two oxides of sulphur: sulphur dioxide and sulphur trioxide. It is found by experiment that 1 gram of sulphur combines with 1.00 grams of oxygen in forming sulphur dioxide, and 1 gram of sulphur combines with 1.50 grams of oxygen in forming the trioxide. Hence the relative quantities of oxygen combined with 1 gram of sulphur are in the ratio of 2 to 3, again small whole numbers.

All experiments of a similar nature can be summed up in the law of multiple proportions: If two elements, A and B, unite to form more than one compound, the different amounts of A which combine with a fixed amount of B are in the ratio of small whole numbers.

These results are, to say the least, surprising. The law of constant composition was almost to be expected, but it would certainly not be anticipated that the relative quantities of one element combining with a fixed quantity of another should be *exactly* in the ratio of small whole numbers.

(4) *The Law of Reciprocal Proportions.*—Even more unexpected are the results obtained when we consider the relative amounts of substances combining with one another to form different compounds. These results have led to the law of reciprocal proportions, which is one of the foundations of modern chemistry. The experimental results on which the law is based may be illustrated as follows: Consider the three compounds: carbon tetrachloride, hydrogen chloride, and methane. The hydrogen and chlorine in hydrogen chloride are combined in the proportion of 1 gram of hydrogen to 35.5 grams of chlorine. In methane, hydrogen and carbon are combined in the proportion of 1 gram of hydrogen to 3 grams of carbon. In carbon tetrachloride we have carbon and chlorine in the proportion of 3 grams of carbon to 35.5 grams of chlorine. That is, the weights of chlorine and carbon which will combine with 1 gram of hydrogen are also the weights which will combine with one another to form carbon tetrachloride.

As another example we may consider the compounds hydrogen sulphide, water, and sulphur dioxide. Here we have

Hydrogen sulphide:
1 gram of hydrogen to 16 grams of sulphur.

Water:
1 gram of hydrogen to 8 grams of oxygen.

Sulphur dioxide:
16 grams of sulphur to 16 grams of oxygen.

Hence the amounts of oxygen and sulphur which combine with one another to form sulphur dioxide are small whole-number multiples of the amounts of oxygen and sulphur which will combine with 1 gram of hydrogen.

These and all similar results lead to the law of reciprocal proportions: If various elements combine with one another, then the relative amounts of any two which combine with a fixed amount of the third, chosen arbitrarily, will also combine with one another, or with small whole-number multiples of one another.

All the experiments which have been performed on the weights of substances entering into chemical reactions have been summed up in the above four laws. In this case the laws can be stated more clearly by words than by symbolic representation, on account of the type of phenomenon with which they are concerned. In formulating an hypothesis to explain these laws use is made of the basic principle of discontinuity (i.e., discrete particles), which was found adequate in the explanation of the structure of gases. For the present we will leave aside the question of whether the particles involved in the explanation of the behaviour of gases are related to the units occurring in chemical reactions. The following hypothesis, first clearly stated by Dalton, can be shown to give a satisfactory explanation of the above four laws.

The Atomic Hypothesis.—All matter is composed of small definite particles called atoms, which are indivisible by chemical processes. The atoms of the same element are alike in weight and in all other properties. Chemical combination consists of the union of one or more atoms of one element with one or more atoms of another element to form each and every one of the larger particles of which the compound is composed.*

We will now consider the gravimetric laws one by one in the light of this hypothesis.

The Law of the Conservation of Mass.—Since, according to the atomic hypothesis, a chemical reaction consists merely in a rearrangement of atoms, and since the weight of an atom is constant, the law of the conservation of mass follows directly from the theory.

The Law of Constant Composition.—All atoms of the same element are assumed to be identical. A particle of a chemical compound is assumed to consist of a definite small number of atoms. Hence it follows that the composition of the compound will be constant, and will be independent of the amount of substance present.

The Law of Multiple Proportions.—Consider two elements, A and B, which combine to form more than one compound.

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* It should be noted that the term molecule is not being used for an aggregation of atoms at this stage in the development of the theory. For the moment the term atom is employed for the smallest indivisible portion of an element, and particle is used to denote the structural unit of a compound. The relation between the atom and the molecule will be discussed later.

Suppose that the individual particle of one of these compounds is composed of one atom of A and one atom of B. In another compound suppose there are two atoms of B to one of A. Since all atoms of B have the same weight, the relative amounts of B combined with a fixed amount of A will obviously be in the ratio of 2 to 1. That is, they are in the ratio of small whole numbers, as stated on the law of multiple proportions.

The Law of Reciprocal Proportions.—Consider three elements A, B, and C. Suppose that these react to form compounds AB, AC, and BC, each of which contains only 1 atom of each constituent in the structural unit. Suppose that an atom of A weighs W_A grams, one of B weighs W_B, and one of C weighs W_C. Then we have:

In the compound AB:
A and B are combined in the proportion of $W_A : W_B$.

In the compound AC:
A and C are combined in the proportion of $W_A : W_C$.

In the compound BC:
B and C are combined win the proportion of $W_B : W_C$.

Hence the relative quantities of B and C combined with W_A grams of A are in the ratio of $W_B : W_C$, i.e., in the ratio in which they occur in the compound BC.

Hence we can again explain the properties of matter in bulk by the assumption of a discontinuous structure. The question arises as to the connection between the molecules of a gas and the atoms of Dalton's hypothesis. The simplest view, and the one that was originally held by Dalton, was that the two were identical. This question will be considered in the following section.

(C) Experiments on Gas Reactions.—Even before Dalton's hypothesis had been put forward, experiments had been carried out by Gay-Lussac and by Humboldt on the volumes of gases which enter into chemical reactions. These experiments were of no great significance at the time, but they later proved to be of very great importance as a means of clearing up the question of the difference between atoms and molecules. They thus brought simplicity and uniformity to the whole question of the structure of matter.

As a typical experiment of this kind we may consider the investigation of the reaction between hydrogen and oxygen to form water. Measured quantities of hydrogen and oxygen are introduced into the graduated tube shown in Fig. 4. The gases are confined by means of mercury. The whole apparatus is heated to 100° C., or slightly higher, so that the water formed when the gases react will be in the gaseous state (steam). A spark is then passed between the two terminals, an explosion takes place, and steam is produced. The amount of steam formed is determined from the graduations on the tube. Experiments of this kind have shown that when the initial gases are present in the exact proportion of 2 volumes of hydrogen to 1 of oxygen, they react completely to form steam, no residue of uncombined hydrogen or oxygen being left. If the gases are present in any other proportion a residue of one or the other is left, depending upon which is in excess. The volume of the steam formed is found to be exactly equal to the original amount of hydrogen. The results of the experiment can thus be concisely represented as:

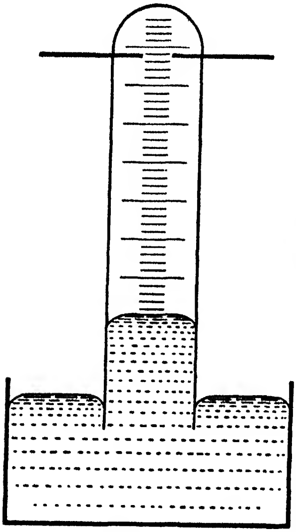
FIG. 4.

hydrogen + oxygen = steam.
2 vols. 1 vol. 2 vols.

Similar results are found with other gas reactions, thus:

hydrogen + chlorine = hydrogen chloride,
1 vol. 1 vol. 2 vols.

hydrogen + nitrogen = ammonia.
3 vols. 1 vol. 2 vols.

The *exactness* of the ratios, 2 to 1, 3 to 1, etc., should be particularly noted. Within the accuracy of the experiments these ratios are always found to be exactly integral. The results may be summed up in the law of reacting gas volumes: When two or more gases react, the volumes of the reacting gases and of the products formed, if gaseous, are in the ratio of small whole numbers.* In order to explain the results summed up in the above law, the following hypothesis was suggested by Avogadro:

Equal volumes of all gases under similar conditions of temperature and pressure contain equal numbers of molecules. These molecules are composed of one or more of the atoms of Dalton's hypothesis. In the case of the molecules of gaseous elements the atoms are of the same kind; in the case of gaseous compounds they are of different kinds.†

In order to illustrate the manner in which Avogadro's hypothesis fits the experimental facts, we will again consider the hydrogen-oxygen reaction.

	hydrogen +	oxygen =	steam
Volumes of gas	2	1	2
Number of molecules	$2N$	N	$2N$
Denote the number of atoms to the molecule by	n_1	n_2	n_3

By the law of the conservation of mass and the atomic theory, since atoms cannot be created or destroyed, we have

$$2Nn_1 + Nn_2 = 2Nn_3,$$

or

$$2n_1 + n_2 = 2n_3.$$

Here we have only one equation, but there are three unknowns. We cannot, therefore, obtain a general solution of the equation, but by trial it is possible to find the simplest possible solution, remembering that n_1, n_2, and n_3 must be integral. If we put $n_1 = n_2 = 2$, then $n_3 = 3$, and we can write the reaction

$$2H_2 + O_2 = 2H_2O.$$

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* If measured under identical conditions of temperature and pressure, etc.

† Dalton originally suggested that equal volumes of all gases contain equal numbers of *atoms*, in the case of elements, or of the larger particles (molecules) in the case of compounds. According to this view we have

$$\begin{array}{ccc} \text{hydrogen} + & \text{oxygen} & = \text{steam.} \\ \text{2 vols.} & \text{1 vol.} & \text{2 vols.} \end{array}$$

Therefore

$$2N \text{ atoms} + N \text{ atoms} = 2N \text{ particles},$$

or

$$2 \text{ atoms} + 1 \text{ atom} = 2 \text{ particles}.$$

Hence we would obtain 2 unit particles of steam from 1 atom of oxygen, which is impossible according to the atomic theory. Consequently Dalton's original form of the above hypothesis was untenable.

It must be borne in mind that this is merely the simplest possible solution, not the only one. Thus the experimental facts given above could be equally well represented by

$$2H_4 + O_4 = 2H_4O_2.$$

One way in which this ambiguity can be cleared up is by the investigation of a large number of different reactions. If we find that a certain value, for hydrogen, say, will always fit the experimental facts, we are then justified in assuming that this is the true value. Thus for example we have

	hydrogen	+	chlorine	=	hydrogen chloride
	1 vol.		1 vol.		2 vols.
Number of atoms to the molecule.......	n_1		n_0		n_3
Then	Nn_1	+	Nn_0	=	$2Nn_3$
or	n_1	+	n_2	=	$2n_3$

Since there must be at least 1 atom of hydrogen and 1 atom of chlorine in a molecule of hydrogen chloride, the simplest solution possible is $n_1 = n_2 = n_3 = 2.$

That is, the molecules concerned are H_2, Cl_2, and HCl, or some multiple of these values. Again, we have

	hydrogen	+	nitrogen	=	ammonia
	3 vols.		1 vol.		2 vols.
Number of atoms to the molecule..............	n_1		n_2		n_3
Then	$3Nn_1$	+	Nn_2	=	$2Nn_3$
or	$3n_1$	+	n_2	=	$2n_3$

Since one molecule of nitrogen gives two molecules of ammonia, there must be at least two atoms to the nitrogen molecule, and the simplest possible solution is therefore

$$n_1 = n_2 = 2,\ n_3 = 4.$$

In every case it is found that the assumption that the molecules are made up as H_2, Cl_2, NH_3, N_2, H_2O, etc., fits the experimental facts, and these values are therefore assumed to be the true ones. Avogadro's hypothesis thus gives a logical explanation of the facts.

Atomic Weights.—The relative weights of the atoms of elements constitute one of the most fundamental properties of matter, since these govern the weights of substances which enter into chemical reactions. Because of the many compounds in which oxygen occurs it has been chosen as the standard, and the atomic weights of the elements are referred to the weight of the oxygen atom, which is arbitrarily given the value 16.

By analytical methods it is possible to determine the weight in grams of an element which will combine with 16 grams of oxygen. The compound formed in this way may contain more than one atom of one of the constituents in its molecule, and hence the weight of the element combining with 16 grams of oxygen is not necessarily the atomic weight, but may be a simple multiple or fraction of it. Oxygen never forms a simple compound with another element such that there are more than two atoms of that element to one of oxygen. The weight of an element which combines with 8 grams of oxygen is therefore either its atomic weight, or a simple fraction of the atomic weight, but not a multiple of it. This weight is called the equivalent weight of the element.

Extraordinarily accurate methods for the determination of the equivalent weights of the elements have been devised, especially by Stas, Richards, and their co-workers. In some cases the accuracy of these methods exceeds one part in 5000.

After determining the equivalent weight of an element it is necessary to find the number of atoms of the element which will combine with one atom of oxygen. In the case of gaseous compounds, this may be done as indicated in the previous section. This may also be accomplished by other methods, some of which will be described later. Once the atomic weight of an element has been determined, it can be used as a standard in determining the atomic weights of other elements, when the use of an oxygen compound is inconvenient.

The Structure of Matter.—In the foregoing pages the object has been to develop the hypothesis of the discontinuous structure of matter in some detail. To show the relative parts played by the various experiments, laws, and hypotheses, the preceding discussion is recapitulated in the table on page 30.

The three hypotheses, taken together, constitute the atomic-molecular theory of the structure of matter. Since the motion of the molecules is of paramount importance, this is often called the "kinetic theory."

As pointed out in the introduction, the value of an hypothesis is greatly enhanced if it is unique and if it leads to unexpected developments. The chapters to follow will show that the latter is true. With regard to the former, it can be stated

EXPERIMENT	LAW	HYPOTHESIS
The pressure, volume, temperature relationships of gases.	Boyle's law. Charles' law. $pv = KT$	The molecular hypothesis.
Quantitative experiments on chemical reactions.	The four gravimetric laws.	The atomic hypothesis.
Volume measurements on reactions between gases.	Gay-Lussac's law of reacting gas volumes.	Avogadro's hypothesis.

that no other hypothesis of a simple nature has been suggested which will adequately explain the experimental facts.

It may be well to recapitulate in some detail the distinction between the atom and the molecule. A molecule refers to the smallest particle of a gas which undergoes independent motion. This molecule is composed of one or more atoms. These atoms are of the same kind in the case of an element, and are of different kinds in the case of a compound. Chemical reactions are due to the combination or interchange of atoms to form molecules. When gases condense to form liquids or solids, the rôle of the atom in chemical reactions is unchanged. The molecules, however, are brought closer together. The question of the changes which take place under these circumstances, from the point of view of the molecule, will be left to the chapters dealing with the liquid and solid states of aggregation.

The above theory is, of course, only a bare outline of the basic ideas regarding the structure of matter. In applying it to various phenomena further detail is necessary in regard to the size, shape, etc., of atoms and molecules. It will be found that such additional assumptions are reasonable and do not detract from the simplicity and ubiquity of the fundamental principles involved.

QUESTIONS AND PROBLEMS

1. Fifty c.c. of a gas under a pressure of 120 cm. of mercury are allowed to expand at constant temperature until the volume is 110 c.c. Calculate the pressure. *Ans.* 54.5 cm. of mercury.

2. A given volume of gas exerts a pressure of 546 cm. of mercury at 273° C. If the pressure is 333 cm. at 60° C., calculate the pressure at 0° C., and the value of the constant α in Charles' law. *Ans.* 273 cm. $\alpha = 1/273$.

3. A given mass of gas at 50° C. has a volume of 100 c.c. under a pressure of 2.5 atmospheres. Calculate the temperature at which its volume and pressure will be 50 c.c. and 1 atmosphere, respectively. *Ans.* −208.4° C.

4. Iron and sulphur combine to form two different compounds in which the weight percentages of the constituents are (*a*) 63.53 per cent iron and 36.47 per cent sulphur; (*b*) 46.52 per cent iron and 53.48 per cent sulphur. Show that the law of multiple proportions holds.

5. The percentage compositions by weight of methane, carbon dioxide, and water are as follows:

methane—74.86 per cent carbon, 25.14 per cent hydrogen;
carbon dioxide—27.29 per cent carbon, 72.71 per cent oxygen;
water—11.22 per cent hydrogen, 88.78 per cent oxygen.

Show that the law of reciprocal proportions is obeyed.

6. For complete combustion, 200 c.c. of ethane require 700 c.c. of oxygen. In the combustion, 400 c.c. of carbon dioxide and 600 c.c. of water vapour are formed. The reaction is carried out at 120° C. and 1 atmosphere pressure, so that all the constituents are gaseous. The oxygen molecule contains two atoms, that of carbon dioxide 3 atoms, and that of water 3 atoms. Find the number of atoms in the ethane molecule.

7. State Boyle's law, and describe the experiments on which it is based.

8. State Charles' laws, and describe the experimental evidence on which they are based.

9. Show how the three laws may be combined, and define the absolute temperature scale.

10. State the molecular-kinetic theory, and show that it leads qualitatively to the gas laws.

11. Derive the gas law from the assumptions of the molecular theory.

12. State the law of the conservation of mass, and describe the experimental evidence on which it is based.

13. State the law of constant composition, and describe the experimental evidence on which it is based.

14. State the law of multiple proportions, and describe the experimental evidence on which it is based.

15. State the law of reciprocal proportions, and describe the experimental evidence on which it is based.

16. State the atomic hypothesis of Dalton, and show that it offers an explanation of the four gravimetric laws.

17. Describe the experiments which led to Gay-Lussac's law of reacting gas volumes.

18. State Avogadro's hypothesis, and show clearly that it offers an explanation of the law of reacting gas volumes.

19. Explain the term atomic weight.

20. State the atomic-molecular theory of the structure of matter, and give an outline of the experimental evidence on which it is based.

CHAPTER III

THE GASEOUS STATE OF AGGREGATION

Having developed an hypothesis of the structure of matter, we are now in a position to examine the various properties of matter in the light of the atomic-molecular theory. In the following three chapters we will deal with the properties of matter in its three states of aggregation: gaseous, liquid, and solid. Of these the gaseous state is by far the simplest.

Whether a substance exists as a gas, liquid, or solid depends solely on the temperature and pressure conditions which happen to prevail in its environment. Consequently every substance can exist in the gaseous state. However, since a high temperature may be required to obtain an appreciable volatilization, and since chemical decomposition tends to occur with rise in temperature, it is not possible to investigate the properties of all substances in bulk in the gaseous state.

When a liquid or solid volatilizes it is customary to call the resulting gas a vapour. It is convenient to restrict the term vapour to a gas which is in a low enough temperature environment for the coexistence of the liquid or solid state. The early experiments on the pressure, volume, temperature relationships of gases were carried out with relatively few substances. It is now possible to investigate a large number of substances in the gaseous state.

The simpler properties of gases, which can be discussed without any additional assumptions regarding the molecule, will first be considered. It will then be shown that there is need for more detailed specifications of the properties of the molecule as regards size, shape, etc., in order to explain those properties which are more complicated, or which have been more accurately investigated. These additional assumptions can best be approached indirectly, by first showing that there is an apparent discrepancy between the hypothesis and the experimental facts. It will then be shown that this discrepancy instead of weakening the hypothesis really strengthens it, in view of the reasonable and obvious factors that have to be taken into consideration.

The Densities and Molecular Weights of Gases.—It is possible to introduce Avogadro's hypothesis into the symbolic representation of the gas law $pv = KT$. In this equation the value of the constant K depends on the amount of gas under consideration. It is obviously proportional to the amount of gas. Thus, if the mass of gas is doubled, the temperature and pressure remaining constant, the volume of the gas would be doubled, and hence the value of K would also be doubled. Hence in the above expression the value of K has no particular significance, except for the special system under consideration. By introducing the hypothesis of Avogadro, we can change the gas law into a more convenient form involving a universal constant, which is independent of the nature of the gas and of the mass of gas under investigation.

From the experiments in connection with the law of reacting gas volumes it has been found that there are two atoms to the hydrogen molecule. Two grams of hydrogen at atmospheric pressure and a temperature of 0° C. have been found to have a volume of 22.41 litres. The constant K therefore has the value

$$\frac{1 \times 22.41}{273.1}$$

$$= 0.0821 \text{ litre-atmosphere,}$$

where the pressure is expressed in atmospheres, the volume in litres, and the temperature in degrees absolute.

According to Avogadro's hypothesis, equal volumes of all gases under similar conditions of temperature and pressure contain equal numbers of molecules. Since there are two atoms to both the hydrogen and oxygen molecules, the relative weights of a molecule of hydrogen and a molecule of oxygen are in the ratio of 2 to 32. Hence there are the same number of molecules in 32 grams of oxygen as in 2 grams of hydrogen. The volume occupied by 2 grams of hydrogen under standard conditions is 22.41 litres. Hence 32 grams of oxygen must also occupy a volume of 22.41 litres under these conditions. Consequently for 32 grams of oxygen we again have

$$K = \frac{1 \times 22.41}{273.1} = 0.0821 \text{ litre-atmosphere.}$$

Two grams of hydrogen is called arbitrarily the "gram-molecular" weight of hydrogen. Since there are two atoms to the molecule for both oxygen and hydrogen, and since the atomic weight of oxygen is 16 times that of hydrogen, the gram-molecular weight of oxygen is 32.*

In the same way, from the atomic weights and the number of atoms to the molecule, we can calculate the gram-molecular weight of any gas. As shown above for oxygen and hydrogen, when dealing with this quantity of gas the value of the constant K is 0.0821 litre-atmosphere. This is a universal constant for all gases and is usually represented by R. Hence *for the gram-molecular weight* of any gas we have

$$PV = RT.$$

If we are dealing with some arbitrary amount of a gas, weighing w grams, and if M is the molecular weight of the gas, then the number of gram-molecules, n, is w/M. Hence for *any* mass of gas we have

$$PV = nRT,$$

or

$$PV = \frac{w}{M}RT,$$

where R has the same value as before.

This equation gives the gas law in its most general and most convenient form, both for purposes of theoretical discussion, and for numerical calculations. It can be conveniently transformed to give the relation between the density of a gas and its molecular weight. Taking the density of any substance as the weight of 1 cubic centimetre, we have

$$d = \frac{w}{v},$$

---

* Of course oxygen is now used as the standard for atomic and molecular weights, but it is simpler to develop the argument with hydrogen, the original standard.

where w is the weight of the substance and v its volume in cubic centimetres. Or, letting V be the volume expressed in litres,

$$d = \frac{w}{1000V}.$$

Substituting for V in the gas law gives

$$d = \frac{PM}{1000RT}.$$

Hence, if we know the density of a gas under any set of conditions, we can calculate its molecular weight, and *vice versa.*

It should be noted that the density of a gas is thus proportional to its pressure and molecular weight, and is inversely proportional to the absolute temperature.

The Experimental Determination of the Density of Gases.—The gaseous state of aggregation differs markedly from the other two states in the matter of density. Under ordinary conditions gases are of the order of 1/1000 as dense as liquids. Thus 1 c.c. of water at 4° C. weighs 1 gram, whereas the same volume of air weighs only about 0.0013 gram. It is therefore apparent that the experimental determination of the densities of gases is beset with considerable difficulty, especially with substances which will volatilize only at very high temperatures. Three methods of measurement will be described, each of which has a particular range of application. The direct weight method is used for substances that are gaseous at room temperature; the Dumas method for substances that are liquid at room temperature; and the Victor Meyer method for liquids, and especially for substances which require very high temperatures for volatilization.

The Direct Weight Method.—This is the most obvious method. It consists of weighing a known volume of gas confined in a bulb. In practice, a glass bulb having a volume of about 200–300 c.c. is used. Sealed to the bulb is a stopcock, as shown in Fig. 5. The bulb is first connected to a vacuum pump and evacuated, and is then weighed. The end of the capillary is then placed under water, the stopcock is opened, and the vessel is filled with water. The stopcock is now closed, the water in the capillary is removed with filter paper, the bulb is dried externally and is weighed. The difference between this weight and that of the evacuated bulb gives the weight of water contained. From this we can calculate the volume of the bulb if we know the temperature of the water and its density.

The water is then removed from the bulb by means of a filter pump and the bulb is thoroughly dried. It is then filled with the gas whose density is to be determined, and is again weighed. We thus know the weight of the gas and its volume, and hence the density can be calculated for the conditions of temperature and pressure which prevailed during the determination, since we have

$$d = \frac{w}{v},$$

where d is the density of the gas, w is the weight of the gas, and v is the volume of the globe.

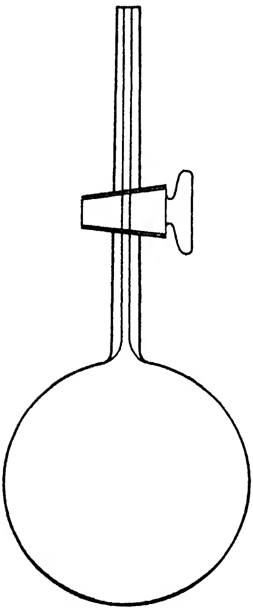

FIG. 5.

The direct weight method of determining the density of gases possesses two main limitations. In the first place its range of application is strictly limited, since it can be used only for substances which are gaseous at ordinary temperatures. Secondly, the main limitation from the point of view of accuracy is due to the fact that the bulb is very heavy compared to the gas which it contains. It is necessary to determine the weight of say 0.2 gram of gas in the presence of a container which may weigh over 100 grams. As a result the density has to be calculated from the very small difference between two comparatively large weights, and the method is not capable of an accuracy much greater than 0.5 per cent.

The Dumas Method.—As previously mentioned, this method is used for substances which are liquid at room temperature. The apparatus is shown in Fig. 6. It consists of a bulb, with a capacity of about 400 c.c., attached to a tube which is drawn out to a fine point. The bulb is first dried and weighed. This gives the weight of the bulb together with the air it contains. Let this weight be a. A few cubic centimetres of the liquid, whose vapour density is to be determined, are introduced into the bulb. It is then immersed in a bath, as shown in the figure, so that only the tip of the capillary projects out of the bath liquid. The bath is then heated to a temperature above the boiling point of the liquid within the bulb. The liquid boils, expels the air from the flask, and a jet of the vapour emerges from the capillary. When no more liquid is left in the flask, and the pressure of the vapour within it is therefore equal to that of the atmosphere, the tip of the flask is sealed off with a blow torch. The temperature of the bath and the atmospheric pressure are immediately read. The bulb is then removed from the bath, cooled, dried, and weighed. Suppose the weight of the bulb and vapour is b. The fact that the vapour has condensed to a liquid at the time at which it is weighed is, of course, of no consequence.

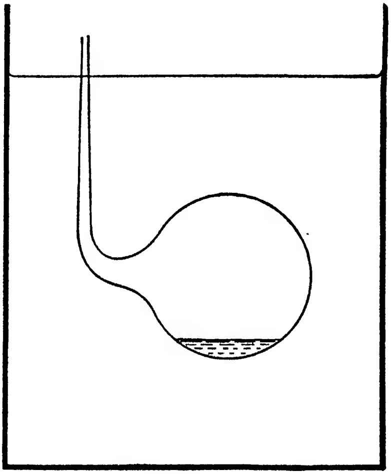

FIG. 6.

The tip of the capillary tube is then broken off under water. The water practically fills the bulb since the pressure in the bulb is less than that of the atmosphere. There will usually be a small amount of air in the bulb, but this may be neglected, or corrected for. The temperature of the water is read, and the bulb and water are weighed. Suppose this weight is c.

Then we have

$$\begin{aligned} \text{bulb} + \text{air} &= a \\ \text{bulb} + \text{vapour} &= b \\ \text{bulb} + \text{water} &= c. \end{aligned}$$

The weight of the air contained in the bulb is negligible compared to that of the water. Hence the weight of the water contained by the bulb is approximately equal to $c-a$. From this we can calculate the volume of the bulb. Suppose this is *d* c.c. Then the bulb plus *d* c.c. of air weighs *a* grams. Knowing the density of air under the conditions of the experiment, we can calculate the weight of the bulb alone. Subtracting this weight from *b* gives the weight of the vapour. We now have the weight of a known volume of vapour, and the density can be calculated for the conditions of temperature and pressure employed.

The essential point in the experiment is that the liquid contained in the bulb should be boiled away rapidly, and the flask sealed off immediately. If this is not the case, air will diffuse into the bulb along with the vapour, and the results will be vitiated. The main objection to the Dumas method is that it necessitates the use of extremely pure substances. Since most of the sample is boiled away, it follows that if a high boiling impurity is present in small amount it will be concentrated by the boiling. A small amount of impurity may thus cause a very large error in the results. The Dumas method is, however, useful over a wide range of temperature, and may be employed up to extremely high temperatures by the use of porcelain or silica vessels instead of glass. It is probably accurate to about 0.5 per cent when various corrections are applied, provided that we are dealing with a highly pure liquid.

The Victor Meyer Method.—This is the most common method for the determination of the vapour density of substances which are liquid or solid at ordinary temperatures. Here the volume of a weighed amount of the substance is determined by measuring the volume of air displaced by the vapour. The apparatus is shown in Fig. 7. It consists of a tube of about 1 cm. diameter with a bulb, having a capacity of about 100 c.c., sealed to its lower end. This tube is surrounded by an outer tube, in which some liquid is boiled in order to maintain the inner tube at a constant high temperature. The substance whose density is to be determined is placed in a very small bottle with a ground stopper, the weight of the liquid being determined. This bulb is placed in the top of the tube and is kept in position by means of a glass rod which slides through the hole in a rubber stopper in the side tube. Another side tube leads to a graduated burette, which is filled with mercury, and is connected to a levelling bulb.

The liquid in the outer jacket is boiled until the temperature of the air in the inner tube is constant. The level of the mercury in the burette is then read. The glass rod is pulled out, the small bulb drops to the bottom of the tube and is broken, or the stopper is driven out, and the liquid vaporizes practically instantaneously. The vapour formed displaces some of the air in the tube, which is driven over and collected and measured in the burette. Only air comes over into the burette, the vaporized substance remaining behind in the bulb. The volume of the air displaced is the volume which the vapour would occupy, if it were possible to have it as a gas at room temperature and barometric pressure. It is not necessary to know the temperature of the bulb, as long as we are sure that it is well above the boiling point of the liquid, and that it remains constant. Too much of the substance must not be used or some of it will get over into the burette and condense, which, of course, will invalidate the results. From the experiment we find the volume which a known weight of substance would occupy, if it existed as a vapour at room temperature and atmospheric pressure. Hence we can calculate the vapour density of the substance and its molecular weight. The method can be used up to very high temperatures by employing platinum vessels and an electric

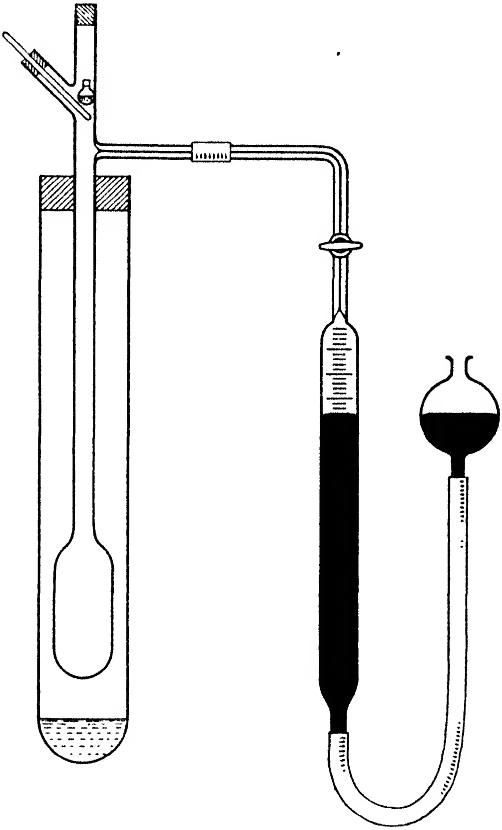

Fig. 7.

furnace. If the liquid used is not pure, we merely find the average molecular weight of its constituents. Consequently the presence of a small amount of impurity has very little effect on the results. The main objection to the method is its small sensitivity: it is not accurate to more than 3 or 4 per cent. A number of modifications of the method exist which give somewhat greater accuracy, but they will not be described here since they do not differ fundamentally from the Victor Meyer method.

The Diffusion of Gases.—The molecular hypothesis of the structure of gases was shown to lead to the relationship

$$PV = \tfrac{1}{3}mnx^2 = RT.$$

Since m and n are respectively the weight of a molecule and the number of molecules,

$$mn = M.$$

Hence we have

$$x = \sqrt{\frac{3RT}{M}}.$$

From this it is possible to calculate the velocity of the molecules of a gas. In addition we can draw a number of interesting conclusions. In the first place, the velocity of a molecule of a gas in a constant temperature environment is dependent on the temperature only, and is independent of the pressure and the volume of the gas. Furthermore, the velocities of the molecules of different gases differ, and are inversely proportional to the square roots of the molecular weights, or of the masses of the molecules. Thus if x_a and x_b are the velocities of the molecules of two gases A and B, then

$$\frac{x_a}{x_b} = \sqrt{\frac{m_b}{m_a}} = \sqrt{\frac{M_b}{M_a}},$$

where m refers to the mass of the molecule and M to the molecular weight. The kinetic definition of equal temperatures is the following: the energies of the molecules in systems at the same temperature must be the same. This follows directly from the above equation since we have

$$\tfrac{1}{2}m_a x_a^2 = \tfrac{1}{2}m_b x_b^2.$$

A numerical calculation shows that the velocity of a gas molecule is enormous under ordinary conditions. Thus for hydrogen at 0° C. we have

$$x = \sqrt{\frac{3 \times 273 \times R}{2}}.$$

In order that the velocity may be expressed in centimetres per second, R must be expressed in absolute units. Now

$$\begin{aligned} R &= 0.0821 \text{ litre-atmosphere,} \\ &= 0.0821 \times 1000 \text{ cm.}^3\text{-atmospheres,} \\ &= 0.0821 \times 1000 \times 76 \times 13.59 \text{ cm.}^3\text{-gr. per cm.}^2 \\ &\qquad \text{or gr. cm.,} \end{aligned}$$

(Since 76 cm. of mercury is atmospheric pressure and the density of mercury is 13.59.)

$$\begin{aligned} &= 0.0821 \times 1000 \times 76 \times 13.59 \times 980 \text{ dyne-cm.,} \\ &= 83.1 \times 10^6 \text{ ergs.} \end{aligned}$$

If we substitute this value for R in the above equation, we have for the hydrogen molecule a velocity of 1.8×10^5 cm. per second, or a little more than 1 mile per second. This high velocity explains why a gas uniformly fills its container even against the action of gravity, since this is negligible compared to such high velocities. One would naturally expect, therefore, that a very large number of molecules all moving with high speeds in a chaotic, i.e., not uniformly directed, manner would uniformly and completely fill any container, merely on the basis of chance.

It would be of great interest to follow the motion of one particular molecule amongst the others over a period of time. Such a movement is termed diffusion. It is, of course, impossible to observe a single molecule; but we can observe the phenomenon of diffusion macroscopically by observing the rates with which molecules of different species mix with one another. Suppose, for example, that a jar of hydrogen is inverted over a jar of oxygen, the two gases being separated by a ground glass plate. Then, if we remove the partition for a very short time and replace it again, we will find that both the upper and the lower jars now contain a uniform mixture of hydrogen and oxygen. This rapid diffusion, even against the action of gravity, is brought about by the rapid movement of the molecules amongst one another. Hence, any two gases, when brought into contact with one another, will form a uniform mixture in a short time. From this it is obvious that in addition to the very high velocity of the molecules, there must also be very considerable distances between them, in order that they shall mix with such great rapidity.

Suppose that we have a vessel filled with gas and connected, through a stopcock, to an evacuated space (Fig. 8). If we open the stopcock, the gas will rush through until both spaces are equally filled. The vacuum has merely a negative effect in this phenomenon. Those molecules which formerly struck the stopcock and were reflected back, pass through the opening into the other vessel as soon as the obstruction is removed. They will now move rapidly about both vessels until the gas is uniformly distributed.

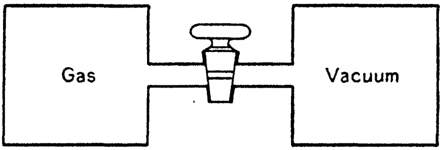

FIG. 8.

In the above case it is assumed that the opening between the two vessels is of moderately large dimensions. Huge numbers of molecules stream through this opening in the form of a jet, and the gas moves from one container to the other *en masse.* If the evacuated vessel is kept continuously evacuated, all the gas will rapidly leave the other vessel. Molecules will be able to get through such an opening as long as it is larger than the diameter of a molecule; but if we decrease the size of the opening another factor comes into play, i.e., the chance of a molecule hitting the opening becomes much smaller. The chance of a molecule getting through the opening depends on several factors, viz.: the number of molecules in the vessel, the ratio of the size of the opening to the surface of the walls of the container, and the number of hits made on the walls in unit time, i.e., the speed of the molecules.

It is practically impossible to make artificially a capillary, the diameter of which is small compared to the distance between two molecules. There are naturally occurring substances, however, such as meerschaum, which are full of minute capillary tubes whose diameters are of this order of size. If we join the two vessels shown in Fig. 8 by means of such a bundle of capillaries, the gas will *slowly* pass through. It is now possible to prove that the rate of diffusion is dependent on the velocities of the molecules. If we measure the amount of gas passing through from one vessel to the other in unit time at various temperatures, we find that it is proportional to $\sqrt{T}$. As previously shown, according to the molecular hypothesis the velocity of a molecule should be proportional to $\sqrt{T}$. A more striking experiment can be performed by measuring the rates of diffusion of different gases at the same pressure and temperature in the same apparatus. Here it is found that the relative rates of diffusion are inversely proportional to the square roots of the molecular weights. This is also in agreement with our previous conclusions regarding the velocities of molecules.

Another method of showing the same phenomenon is to place a mixture of equal volumes of hydrogen and oxygen in the apparatus. We then have the same number of molecules of each gas. According to the molecular theory the hydrogen molecule travels with four times the velocity of the oxygen molecule $(\sqrt{\frac{32}{2}})$. It will therefore have four times the chance of hitting an opening between the two vessels. Hence the gas effusing from an equimolecular mixture will contain four times as much hydrogen as oxygen. Similarly, the gas remaining behind will become richer in oxygen as the diffusion progresses. Both these facts have been proved experimentally and have been found to be in quantitative agreement with the theory. It would be extremely difficult to explain this process of separation by diffusion on any basis other than the discontinuous structure of gases. Apart from its theoretical interest, the process is of considerable practical value since it affords a method of separating different molecular species in the gaseous state. It has been used, for example, in separating the inert gases.

Temperature Changes in Gases.—When the volume of a gas is altered under conditions where heat cannot enter or leave the gas (i.e., adiabatically) various temperature changes are observed, which depend on the experimental conditions under which the volume change occurs. Consider the two systems represented in Fig. 9. In the apparatus marked *A* a rise in temperature occurs if the gas is compressed by means of a piston, whereas there is a fall in temperature if the gas is allowed to expand, moving the piston out before it. On the other hand, suppose that we have the gas in a chamber shown in *B*, next to which is an evacuated space. If the diaphragm separating the gas from the evacuated space is suddenly shattered, it is found that no noticeable temperature change occurs when the gas expands and fills the whole volume.

The molecular hypothesis of the structure of gases gives a ready explanation of these phenomena. The temperature of a gas is a measure of the kinetic energy of the molecules, and for any particular gas it depends solely on the velocity of the molecules. In the second experiment considered above, the molecules are moving about and colliding with the diaphragm between the gas and the evacuated space, from which they rebound. The removal of the diaphragm merely permits the molecules to move on into a space from which they were previously shut off. There is no reason why this should involve any alteration in their velocity. They merely move through greater distances and now collide with the new wall surface from which they rebound with unaltered velocity. The absence of a temperature change can therefore be predicted under these conditions. It should be noted that the total energy of the gas molecules is unaltered by this method of expansion. It follows therefore that the total energy content of a gas is independent of its volume.

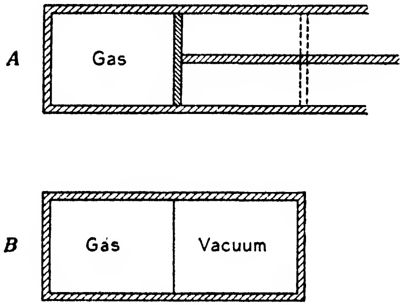

FIG. 9.

When a molecule rebounds from a stationary wall its velocity is therefore unaltered. It is obvious, however, that if the wall is made to move towards the approaching molecule, the velocity of the molecule will be increased by the collision. Conversely, if the wall is moving away from the molecule the velocity of the molecule will be decreased. A familiar analogy is the action of a tennis racquet on a ball. If the racquet is held stationary, the ball will rebound with practically its incident velocity. If the racquet is moved towards the approaching ball, the velocity of the ball is increased. If the racquet moves away, the velocity is decreased. Increased molecular velocity means a rise in temperature; a decreased velocity is equivalent to a fall in temperature. The phenomena observed when a gas is compressed or expanded by means of a moving piston are therefore clearly explained by the molecular hypothesis.

The above experiments can also be considered from the point of view of energy. In the case in which the gas expands into a vacuum through a ruptured diaphragm there is no change in energy external to the system. On the other hand, when a gas is compressed by means of a piston, the latter has to be forced in against the pressure of the gas by means of energy derived from some *external* source. This energy cannot be lost. It must therefore be stored up in the gas, which now has a higher energy content, i.e., a higher temperature. If the gas is allowed to expand and force the piston out, the piston acquires energy due to its motion. This energy can only be derived from the gas, whose temperature must consequently fall. This last explanation involves the tacit acceptance of the first law of thermodynamics (the law of the conservation of energy). The above considerations can be applied quantitatively, and the energy change can be obtained in the form of the work expended on the system, or the work performed by the gas. This work is given by the product of the pressure and the volume change occurring on expansion.* The exact calculations which permit the estimation of the temperature changes which occur are beyond the scope of this book.

A further point of interest in connection with these experiments is worth noting. The compression or expansion of a gas by means of a piston is a reversible process. The expansion through a shattered diaphragm is not a reversible phenomenon, since if we replace the diaphragm the gas will not again collect

* Work = (force) (distance)

$$
\begin{aligned}
\text{Work} &= (\text{force})\,(\text{distance}) \\
&= \frac{\text{force}}{(\text{distance})^2}\,(\text{distance})^3 \\
&= (\text{force per unit area})\,(\text{volume change}) \\
&= \text{pressure} \times \text{volume change.}
\end{aligned}
$$

in the original compartment. Again, the expansion through the shattered diaphragm occurs without any energy change. We could have performed this expansion, however, by means of a moving piston. We would then have obtained external work from the system. The expansion of a gas may therefore occur either with or without an accompanying performance of work external to the system. It is impossible to compress a gas, however, without the expenditure of work. The expansion of a gas may take place *spontaneously*. The compression of a gas never occurs spontaneously and it requires the expenditure of energy to bring it about. These considerations will be discussed in greater detail in Chapter VIII.

The Specific Heats of Gases.—The specific heat of a substance may be defined as the amount of heat, expressed in calories, which is required to raise the temperature of one gram of the substance one degree Centigrade.

Under ordinary conditions substances expand on being heated. In the case of gases, however, their temperature may be raised without any expansion taking place, i.e., under conditions of constant volume. The specific heat measured under these conditions is known as the specific heat at constant volume (c_v). If the pressure of the gas is kept constant and the volume is allowed to increase as the temperature rises, we obtain the specific heat at constant pressure (c_p). It is found experimentally that the two specific heats have considerably different values. The methods for the experimental measurement of these constants are described below.

The Measurement of the Specific Heats of Gases. (*a*) *The Specific Heat at Constant Pressure.*—This is usually measured by the method of Regnault. The apparatus is shown diagrammatically in Fig. 10. The gas whose specific heat is to be determined is confined in a large reservoir out of which it can flow at a constant pressure. The gas from the reservoir passes through a long spiral coil immersed in a heating bath which is kept at a constant temperature. The spiral is made sufficiently long to enable the gas to take up the temperature of the bath. Let this be denoted by T_G. After leaving the heating bath, the gas passes through another metal spiral immersed in the calorimeter, which is filled with water. The gas then escapes into the atmosphere. In the calorimeter the gas is cooled from the temperature, T_G, of the heating bath to that of the calorimeter.

Suppose that m is the mass of gas which flows through the calorimeter during the experiment; W the mass of water in the calorimeter; T_S the temperature of the calorimeter at the commencement of the experiment; and T_E the temperature of the calorimeter at the conclusion of the experiment.

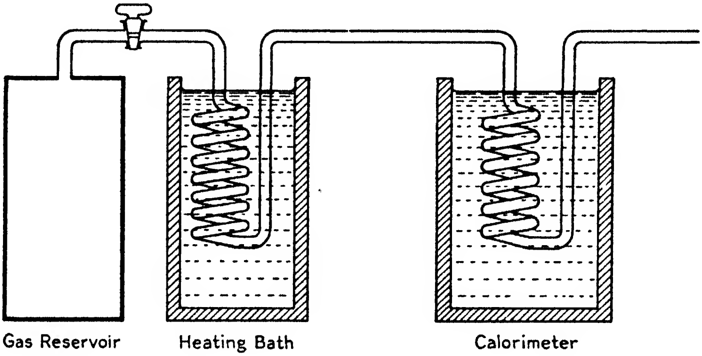

FIG. 10.

Then the heat lost by the gas during its passage through the calorimeter

$$= m \cdot c_p\left(T_G - \frac{T_S + T_E}{2}\right),$$

since $\frac{T_S + T_E}{2}$ is the average temperature of the calorimeter during the experiment.

The heat gained by the calorimeter

$$= W(T_E - T_S).$$

By the law of the conservation of energy these two quantities must be indentical. Hence

$$c_p = \frac{W(T_E - T_S)}{m\left(T_G - \frac{T_S + T_E}{2}\right)}.$$

In practice W represents, not the actual mass of water in the calorimeter, but what is called the water equivalent of the calorimeter. This represents the actual amount of water in the vessel together with a correction for the heat capacities of the metal spiral, thermometers, vessel, etc.

(*b*) *The Specific Heat at Constant Volume.*—This method was originally devised by Joly. The apparatus is represented diagrammatically in Fig. 11.

Two equal copper spheres are hung from the beam of a balance. One of the spheres is evacuated and the other filled with gas under fairly high pressure. The two spheres are suspended in a jacket into which steam can be admitted. The steam condenses on the two spheres, and gives up sufficient heat to raise their temperature to 100° C. The condensed water is collected in small drip pans suspended under the spheres. Since in one case the gas has to be heated as well as the sphere, more water is condensed on it. The difference in the weight of water condensed is determined by balancing the beam by means of weights. Let the initial temperature of the spheres be $t°$ C., the mass of gas in one sphere be m, the latent heat of evaporation of water be l, and the excess weight of steam condensed on the globe containing the gas be S. Then

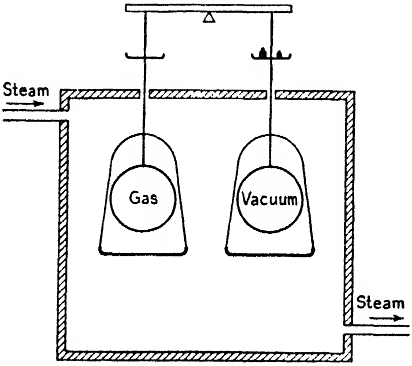

FIG. 11.

the heat given up by the steam in condensing

$$= Sl;$$

the heat absorbed in raising the temperature of the gas

$$= m \cdot c_v(100 - t).$$

Hence, equating these two quantities, we have

$$c_v = \frac{Sl}{m(100 - t)}.$$

The main experimental difficulty in the determination of c_v is due to the very large value of the heat capacity of the vessel compared to that of the gas under investigation.

(*c*) *The Ratio of the Two Specific Heats.*—In addition to the above, there is a third experimental method which is of importance; this was originated by Kundt and enables the ratio c_p/c_v to be evaluated experimentally. The great advantage of this method lies in the fact that only a very small amount of gas is required for the determination.

The velocity with which sound travels in a gas is given by

$$u = \sqrt{\frac{p}{d} \cdot \frac{c_p}{c_v}},$$

where u is the velocity of sound, p is the pressure of the gas, d is its density, and c_p and c_v have the usual significance. Hence, if we know the pressure and density of a gas and can determine the velocity of sound, we can calculate the ratio c_p/c_v. A sketch of the apparatus employed is given in Fig. 12.

FIG. 12.

It consists of a glass tube with a diameter of about 3 cm. and a length of about 1 metre, which is filled with gas. This is closed at both ends by corks through which pass pistons, *A* and *B*. The piston *B* is fixed firmly in place and is attached to a glass rod *C*. The piston *A* can be moved in and out. A small amount of lycopodium or some other light powder is sprinkled on the bottom of the tube between the two pistons. The rod *C* is rubbed with a piece of cloth until it vibrates strongly. Sound waves are thus set up which travel up and down the tube between *A* and *B*. The piston *A* is moved in and out until it is in such a position that the distance between *A* and *B* is an exact number of half wave lengths. As soon as it is in this position, stationary waves are set up and the powder is piled up into little heaps at the positions of the vibration nodes. The distance between the piles gives one half the wave length of the sound. The frequency of the vibration of C may then be determined by means of a set of tuning forks. We then have

$$\text{velocity of sound} = n\lambda,$$

where n is the frequency and λ is the wave length, and we can calculate c_p/c_v as given above.

In practice it is usual to avoid the determination of the frequency by comparing the wave length in the gas under observation with that produced in some standard gas, such as hydrogen, under the same experimental conditions. We then have

$$\frac{\text{velocity in unknown gas}}{\text{velocity in hydrogen}} = \frac{n\,\lambda_{\text{unknown}}}{n\,\lambda_{\text{hydrogen}}} = \frac{\lambda_{\text{unknown}}}{\lambda_{\text{hydrogen}}}.$$

Then, knowing the velocity of sound in hydrogen, we may calculate it for the unknown gas.

Experimental Results.—The experimental results which are obtained from the measurement of the specific heats of gases are of great interest. As we shall see, they can be interpreted on the basis of the molecular theory of gases provided that we add additional specifications regarding the molecules.

The first striking regularity is observed when we consider the specific heats of quantities of gases which contain equal numbers of molecules. The simplest way to compare such amounts of gases is to consider gram-molecular weights. The heat involved in raising the temperature of a gram molecule of gas 1° C. is referred to as its molecular heat. If we use capital letters to denote molecular heats and small letters for specific heats, we have

$$Mc_p = C_p \quad \text{and} \quad Mc_v = C_v.$$

It has been found experimentally that invariably, for all gases, we have the relation

$$C_p - C_v = 1.99 \text{ calories.}$$

The reason for this regularity is obvious when we consider the nature of the definitions involved. If we raise the temperature of 1 gram molecule of gas by 1° C., the final conditions will differ, depending upon whether the heating was performed at constant volume or at constant pressure. The difference between the values of C_p and C_v must be equal to the energy change involved in equalizing the two final conditions. Suppose the heating to be performed in the apparatus represented in Fig. 13, and that the piston is clamped in position and the temperature of the gas is raised 1° C. Then the heat required is obviously C_v. The pressure will now be greater than that of the atmosphere. It will be noted that no work has been done by the gas. If we were now to release the piston, it would move out, doing work against the atmosphere, and, as we have seen previously, the gas would be cooled. Consequently more heat would have to be supplied to heat the gas up again. When this process occurs continuously, as in the measurement of C_p, work is constantly done against a pressure of one atmosphere as the piston moves out. This work is equal to $P(V_2 - V_1)$, where P is the pressure, V_1 is the volume at a temperature $T°$, and V_2 is the final volume at a temperature $(T + 1)°$.

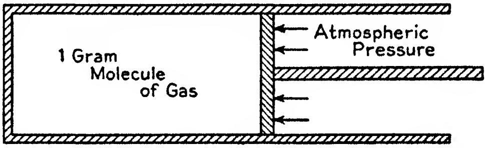

FIG. 13.

Hence we have

$$\begin{aligned} C_p &= C_v + P(V_2 - V_1), \\ &= C_v + R(T + 1) - RT \\ &= C_v + R. \end{aligned}$$

Hence $\quad C_p - C_v = R.$

We have already had occasion to point out that the gas constant, R, may be expressed in the form of any energy units desired. Since in measurements involving heat interchanges the usual unit is the calorie, it is necessary to convert R to calories. It has been shown previously that $R = 83.1 \times 10^6$ ergs. So that:

$$R = \frac{83.1 \times 10^6}{4.2 \times 10^7} \text{ calories}$$

$$= 1.99 \text{ calories.}$$

Hence $\quad C_p - C_v = 1.99$ calories, and the relationship found experimentally follows logically from energy considerations. This regularity is illustrated by the results given in the following table:

THE MOLECULAR HEATS OF GASES AT 15° C.

Gas	C_p	C_v	$C_p - C_v$	Gas	C_p	C_v	$C_p - C_v$
A	5 00	3.00	2.00	NO	6.99	4.99	2.00
Hg	4.96	2 98	1.98	CH_4	8.47	6.47	2.00
H_2	6 83	4.84	1.99	H_2S	8.63	6.54	2.09
O_2	6.97	4.98	1.99	CO_2	8.75	6.71	2.04
CO	6.94	4.94	2.00				

In the above table the data have been grouped so as to bring out certain fairly obvious regularities. It will be seen that gases which have only one atom to the molecule have exactly the same molecular heats. Those containing two atoms to the molecule have a higher value which varies to a certain extent. Those gases whose molecule contains more than two atoms have by far the largest molecular heats.

Suppose that we consider these results from the point of view of the molecular theory. According to this the energy content of a single molecule is $\frac{1}{2}mx^2$, and the total energy of all the molecules in a gram-molecule is $\frac{1}{2}mnx^2$. Now

$$pv = \tfrac{1}{3}mnx^2 = RT.$$

Hence if E_T is the energy content of one gram-molecule of gas at a temperature T, we have

$$E_T = \tfrac{1}{2}mnx^2 = \tfrac{3}{2}RT.$$

If we add an amount of heat C_v to the gas its temperature will rise to $(T+1)°$. The energy content, E_{T+1}, at this temperature will be

$$\tfrac{3}{2}R(T+1).$$

Now

$$E_{T+1} = E_T + C_v,$$

$$\tfrac{3}{2}R(T+1) = \tfrac{3}{2}RT + C_v.$$

Hence
$$C_v = \tfrac{3}{2}R$$
$$= 2.98 \text{ calories.}$$

The molecular theory, therefore, predicts the correct results for the specific heats in the case of monoatomic gases. For other gases the experimental values are all much higher. From this it is concluded that for these gases a rise in temperature means the acquisition of energy in some other way than that considered in the molecular theory, i.e., energy other than kinetic energy of translation. Inspection of the data shows that this additional energy increases with increasing complexity of the molecule. We therefore must look more closely into the assumptions regarding the structure of the molecule. It was assumed that molecules were perfectly elastic and symmetrical. The fact that monoatomic gases give such excellent agreement with the predictions of the theory justifies the assumptions in their case. If the assumptions regarding symmetry hold for single atoms, then they are obviously unsound when the molecule under consideration is composed of two such atoms. Such a molecule cannot be perfectly symmetrical in all directions. The simplest analogical representation of such a molecule would be a dumb-bell. Obviously a molecule of this form, on colliding with the wall of the vessel or with some other molecule, will acquire rotation unless by chance the collision was "head-on." After the collision the molecule will have energy of rotation as well as energy of translation. Consequently its energy of translation will be decreased and therefore its temperature will be lowered. It will thus require an additional input of energy to bring its kinetic energy of translation up to that of a monoatomic gas, the molecules of which suffer no loss of translational energy by conversion into rotational. Hence, if the molecules of a gas are not symmetrical, translational and rotational energy are both present and are interconvertible. Consequently the energy that is required to raise the temperature of such a gas one degree is greater than that required for a monoatomic gas. The experimental results on the specific heats of gases therefore lend additional support to the molecular theory, since it is only reasonable to suppose that polyatomic gases possess unsymmetrical molecules.

It is beyond the scope of this book to consider the quantitative relationships between specific heats and rotational energy, or the question of energy of vibration between the individual atoms composing a molecule.

The values obtained for the specific heats of gases are of practical use in distinguishing between mono-, di-, and polyatomic molecules. Where only minute amounts of gas are available it is possible to use Kundt's method, and to determine the ratio C_p/C_v. Then since $C_p - C_v = R$, we can calculate C_v. If the value found is 2.98 calories it is definitely proved that the gas is monoatomic, if it is about 4.97 there are 2 atoms to the molecule, and if it is 5.97 or greater then the gas is polyatomic. This method has been of special value with the inert gases which form no chemical compounds. Their atomic weights must therefore be calculated from their molecular weights, and specific heat measurements furnish a method of determining the number of atoms to the molecule.

Apparent Exceptions to the Gas Laws.—There was a time during the development of the molecular theory when grave doubts were expressed as to its validity. Certain cases were known in which the gas laws did not hold even approximately. It was some time before it was realized that this was due to a variation in the molecular weight of the gas with temperature, owing to an association or dissociation of molecules. Ammonium chloride and sulphur vapours are typical examples of this sort.

The gas laws lead to the equation

$$d = \frac{PM}{1000RT}.$$

Hence, if we know the density of a gas, we can calculate its molecular weight. In the case of ammonium chloride vapour this gives a value for the molecular weight of about 27. This is obviously an impossible value since analysis leads to the formula NH_4Cl with a molecular weight of at least 53.5, and possibly 107, 160.5, etc., if the molecule were to be $(NH_4Cl)_2$ or $(NH_4Cl)_3$. In order to explain this result the suggestion was made that the ammonium chloride might dissociate on vaporization, thus

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

If this is true we would now have 1 molecule of ammonia and 1 of hydrogen chloride for each NH_4Cl molecule initially present. Hence, in the gram-molecular volume, instead of having 22.4 litres of NH_4Cl vapour, we have 11.2 litres of ammonia with a molecular weight of 17 and 11.2 litres of hydrogen chloride with a molecular weight of 36.5. This gives a mixture of gases having an average molecular weight of $\frac{36.5 + 17}{2} = 26.75$, which agrees with the value found by experiment.

The truth of this explanation has been proved by means of diffusion experiments. If ammonium chloride vapour is allowed to diffuse out of a vessel through fine capillary tubes, it is found that the gas coming through at first is richer in ammonia than would correspond to the formula NH_4Cl; the gas remaining behind is richer in hydrogen chloride. This shows that dissociation into ammonia and hydrogen chloride must have taken place, and hence explains the discrepancy between the observed and calculated values for the molecular weight of ammonium chloride vapour.

Another apparent aberration of the same type is observed with sulphur vapour. The atomic weight of sulphur is 32. The molecular weight calculated from the vapour density is not a whole-number multiple of 32, and in addition it varies largely with the temperature. The extreme values for this variation are from 32 to about 256. It has been shown that this is due to a change in the molecular complexity and that we probably have

$$24S \rightleftarrows 12S_2 \rightleftarrows 4S_6 \rightleftarrows 3S_8.$$

The relative quantities of the four forms vary with the temperature. At temperatures in the neighbourhood of the boiling point most of the vapour consists of S_8, and the molecular weight therefore approaches 256. At very high temperatures the vapour is completely dissociated into single atoms with a molecular weight of 32.

The Limitations of the Ideal Gas Law.—As we have seen, the apparent discrepancies of large magnitude in the gas law can be satisfactorily explained. The next question to be answered is the limit of accuracy to which the gas law holds. Apart from any other considerations, it is obvious that molecules must possess volume as well as shape. Consequently the simple gas law cannot hold rigorously, since a gas cannot be compressed to zero volume. We would thus expect discrepancies at high pressures. These discrepancies become apparent only when gases are examined under extreme conditions of temperature or pressure, or under ordinary conditions with very great accuracy.

One experimental method which is capable of very great accuracy is called the condensation method. A sketch of the apparatus is given in Fig. 14. It consists of a large bulb, *A*, whose volume is accurately known, a manometer *B*, and a small bulb *C*. The bulb *A* is immersed in a bath at a known constant temperature. Gas is admitted to the apparatus and the pressure is read on the manometer. The bulb *C* is then immersed in liquid air, or some other cooling mixture, all the gas in the large volume *A* condenses in the bulb *C*, and this is sealed off at the constriction. The bulb *C* is then allowed to warm up and is weighed. It is then cooled again and the tip is broken off, the gas escapes, and the empty bulb is again weighed. We thus know the volume, pressure, and weight of the gas at the known temperature, and the density can be calculated. The great advantage of the method lies in the fact that the weight of the gas in the small bulb is of the same order of magnitude as the weight of the bulb. The weight of the gas can thus be determined very exactly on an ordinary balance. The method is accurate to about one part in 10,000.

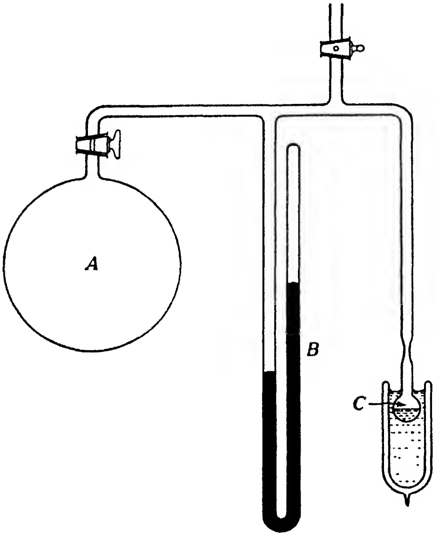

Fig. 14.

Having determined the density of the gas, we can calculate its molecular weight from the expression

$$d = \frac{PM}{1000RT}.$$

In Fig. 15 the molecular weight of carbon dioxide is plotted against the pressure of the gas during the experiment. If the simple gas law holds, M should be independent of the pressure and we would obtain a horizontal straight line parallel to the pressure axis. As can be seen from the diagram, however, there is a divergence from this relationship, and the molecular weight shows an apparent increase as the pressure increases.

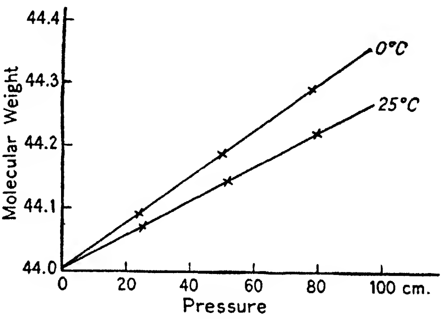

FIG. 15.

The molecular weight calculated in the above manner will be called the apparent molecular weight, as opposed to the theoretical molecular weight, which is given by the sum of the atomic weights of the atoms composing the molecule. The atomic weights of the commoner elements have been determined with an accuracy of at least one part in 5000. Consequently the theoretical molecular weights of the commoner gases are also known with this accuracy. Very accurate measurements of the pressure-volume-temperature relationships of gases have been made recently. The most striking result of these measurements is that the apparent molecular weight approaches the theoretical value with decrease in pressure, and that the extrapolated value coincides with the theoretical molecular weight at zero pressure within the accuracy of the most refined measurements. This has been found to be true for all the gases and vapours investigated at all temperatures, provided that no chemical change occurs. Hence we may say that the gas law is rigorously true at very low pressures.

The extent of the aberration from the gas law at a given pressure is greater at low temperatures than at high. Although the gas law is independent of the nature of the gas under consideration, the extent of the aberration from it varies from gas to gas, i. e., is specific and depends on the nature of the gas. As a rule, the aberration at a given temperature is greater the more easily condensible the gas.

The gas law, which has now been shown to be true only under certain definite conditions, is known as the "ideal gas law." An "ideal gas" is that imaginary one upon which the previous derivation of the ideal gas law was based, i.e., it is an imaginary gas for which the equation $PV = \frac{w}{M} RT$ would be rigorously accurate under all conditions.

It is now time to consider whether erroneous assumptions were made in the previous derivation of the ideal gas law, and to modify this derivation so as to take into account certain additional properties of the molecules. In the previous derivation of the expression

$$PV = \tfrac{1}{3}mnx^2 = RT,$$

two tacit assumptions were made which are reasonable only as approximations. The conclusions which were drawn therefore will hold only for an "ideal gas" which possesses the imaginary structure assigned to it. The two assumptions referred to are that the molecules have a negligible volume, and that they have no influence on one another.

In the derivation of the gas law on page 18, the number of hits made by a molecule in unit time, when moving in a box of length l, with a velocity u parallel to one pair of sides, is given by u/l. If the molecule has an appreciable volume, say it is a sphere of diameter d, the number of hits made in unit time will now be $\frac{u}{l - d}$, since a hit will be recorded when the centre of of the molecule comes within a distance $d/2$ of the wall.

The second tacit assumption in the previous derivation was that the molecules have no influence upon one another. It is well known, however, that all matter influences other portions of matter (i.e., gravitation). It is certain, therefore, that molecules have at least this gravitational attraction for one another. It is obvious that an attraction of this kind will decrease rapidly as the distance between the attracting objects increases. This attraction will influence the movement of the molecules of the gas, and since the pressure is due to molecular motion, it follows that molecular attraction will have an effect on the pressure of the gas. It thus causes an aberration from the ideal gas law. This aberration, however, will be insignificant at low pressures when the molecules are widely separated in the gas.

Having seen that a modification of the ideal gas law is necessary, it remains to formulate this in such a way as to give a satisfactory mathematical expression connecting the pressure, volume, and temperature of a gas. Many attempts at this have been made. That of van der Waals is one of the most successful, and it will be considered here in a more or less qualitative manner.

Van der Waals' Equation.—Van der Waals attempted to obtain a more correct expression by introducing into the simple gas law corrections to take care of the errors due to the volume of the molecules, and to molecular attraction.

In the derivation of the simple gas law, $PV = RT$, it was assumed that the molecules had no volume. If the molecules have a finite volume, then the space available for molecular motion is not the volume of the container V, but is the free space $V - b$, where b is proportional to the volume of the molecules themselves. As the pressure increases, the volume of the molecules becomes greater and greater compared with the free space available for molecular motion. Consequently the error due to neglecting the volume of the molecules becomes greater as the pressure is increased. Van der Waals therefore writes the gas law in the form

$$P(V - b) = RT,$$

where b is a constant for any particular gas and is proportional to the volume of the molecules.

The correction for molecular attraction is not quite as obvious. We will consider it here only in a qualitative manner. It may be remarked that molecular forces of attraction are actually much larger than gravitational attraction at short distances, but decrease at a much greater rate as the distance between the attracting molecules increases. The pressure which is recorded on a manometer, and which is dealt with in the gas law equation, is due to the impacts of moving molecules. It is thus dependent on the average kinetic energy of the molecules. It can be shown that, if molecular attraction exists, the molecules impinging on the manometer surface have a velocity at that moment which is less than the average velocity. As two molecules separate after a collision their velocities will be somewhat diminished by the attractive forces between them. A molecule which strikes the manometer must have come from some other molecule in the body of the gas against which it had collided. Consequently, during its movement away from this last collision it must have suffered some diminution in its velocity. Or, from another point of view, we may consider that a molecule in the body of the gas is attracted equally in all directions by its neighbours; as a result the net force acting on the molecule will be zero. A molecule colliding with the manometer, however, is *ipso facto* one on the surface of the gas body. It is therefore subjected to a resultant inward force, and consequently, on moving outwards towards the manometer, it must have its velocity diminished. The pressure recorded on the manometer is therefore due to the impacts of molecules with a kinetic energy less than the average kinetic energy of all the molecules in the gas.*

It follows that the actual pressure due to molecular movement in the body of the gas is greater than that recorded on the manometer. The gas law which we have derived theoretically refers, of course, to the pressure in the body of the gas. In order to correct the ideal gas law for this effect we must therefore write it in the form

$$(P+f)V = RT,$$

where f is dependent on molecular attraction and represents the difference between the true pressure and the pressure which is

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* It will perhaps occur to the reader that a complication might be introduced if the material of the manometer possesses an attraction for the gas molecules. It may, however, be demonstrated that the resultant effect of such an attraction is exactly balanced during the movement of the molecule *up to* and *away from* the manometer surface. Consequently the pressure recorded is entirely independent of the material from which the manometer is constructed.

recorded on a manometer. This factor f will vary from gas to gas, since each molecule has a specific attraction for those of its own kind.

It is apparent that the correction will depend upon the amount of gas in the system. In the first place, the effect occurs at every collision of a molecule with the manometer, and the correction is therefore proportional to the number of collisions. Secondly, the magnitude of the correction will depend on the strength of the attractive forces influencing the molecule at the moment it impinges on the manometer. This will depend on the number of molecules per unit volume in the body of the gas behind the impinging molecule. Hence we have

$$f \propto \text{(number of collisions per second)(number of molecules per unit volume)}.$$

But the number of collisions per second is also proportional to the number of molecules per unit volume, hence

$$\begin{aligned} f &\propto \text{(number of molecules per unit volume)}^2 \\ &\propto \text{(density of the gas)}^2 \\ &\propto \frac{1}{V^2}, \end{aligned}$$

or

$$f = \frac{a}{V^2},$$

where a is a constant for any particular gas and V is the volume of the system.

The combination of the corrections for molecular attraction and for the volume of the molecules gives

$$(P + a/V^2)(V - b) = RT.$$

This is called van der Waals' equation after its originator.

Since the formulation of the effects of molecular attraction and volume is by no means exact, as given above, it follows that van der Waals' equation cannot be expected to hold rigorously. We have seen above that the ideal gas law holds exactly at infinitely low pressures. Any corrected form of the equation must therefore satisfy this condition. Van der Waals' equation does this, since both a and b are small and become negligible when V is large. The equation thus reduces to the ideal gas law at very low pressures, as required by the experimental facts. In addition to this it represents the pressure-volume-temperature relationships of gases up to a pressure of one atmosphere with an accuracy equal to that of the most refined experiments. Thus in the case of carbon dioxide, cited previously, for one fixed value of a and one of b, the value of M, the molecular weight, is found to be constant and independent of the pressure up to a pressure of about one atmosphere.

Collisions between Molecules.—The previous section has brought out the necessity of assigning a finite volume to the molecule of a gas. It follows as a necessary consequence that molecules must collide with one another in the course of their motion in the containing vessel. The distance which molecules travel, on the average, between collisions, their actual volume, and the number of collisions which they make in unit time, can all be related to the viscosity and the heat conductivity of the gas. These will now be considered very briefly and in an entirely qualitative way.

The viscosity of a gas is the property which governs the rate of flow of the gas through tubes, and which tends to stop the relative motion of one part of the gas body with respect to another. It may thus be looked upon as the internal friction existing in the gas. From the magnitude of the viscosity, and its variation with temperature and pressure, it is possible to draw certain conclusions from the laws of dynamics regarding molecular collisions. It may be shown in this way that a hydrogen molecule, in hydrogen at one atmosphere pressure, travels on the average only about 10^{-5} cm. between successive collisions with its neighbours. This is about 1000 times the diameter of the molecule.

The above calculations have been verified by measurements of the heat conductivity of gases. This is dependent on the same factors as the viscosity. The transfer of heat through a gas occurs by means of the motion of molecules from one part of the system to another.

It is thus apparent that once we assume a finite size for the molecule, we are obliged to consider the effect of its collisions with its neighbours. This in turn leads to another important consideration, namely, Have all the molecules of a gas the same velocity? Or is it possible that some of the molecules may have velocities considerably different from the average velocity?

In calculating the velocity of a gas molecule from the temperature it was tacitly assumed that all the molecules of the gas had the same velocity. We have seen, however, that molecules must be assumed to have a finite size. If two such molecules having the same velocity collide with one another, then, even if they are perfect spheres, the chance of their having equal velocities after collision is extremely small. Although the individual velocities of the molecules have thus been altered by collision, the sum of the kinetic energies of the two molecules has remained constant. It is therefore necessary to assume that the molecules of a gas have different and varying velocities. The total kinetic energy of the molecules of the gas, however, remains constant (at constant temperature). The *average* kinetic energy of a single molecule therefore remains constant also. The average velocity of the molecules of the gas is therefore constant at any particular temperature. As a result all the deductions which have been made involving molecular velocities still remain valid, but it must be remembered that the results refer to average velocities and not to the actual velocity of any particular molecule chosen at random. It is fairly obvious that molecules whose velocity is considerably below the average will soon regain velocity by collisions; similarly molecules whose velocity is considerably above the average will have their velocity reduced. The velocities of the molecules of a gas are thus distributed as follows: A large number of molecules have a velocity which is not greatly removed from the average velocity, calculable from the temperature. A relatively small number of molecules have velocities much smaller or much larger than the average velocity. The greater the difference between a velocity and the average, the smaller will be the number of molecules having such a velocity.

Owing to the fact that we are dealing with an enormous number of molecules, the distribution of molecular velocities in any gas may be regarded as being governed solely by chance, and there will always be a definite fraction of the total number of molecules with velocities of any particular magnitude. If the distribution of velocities is disturbed in any way, say by the removal of the fast-moving molecules, an immediate redistribution of velocities will take place. The average kinetic energy of the remaining molecules will be lowered by the loss of the fast-moving ones, and hence the temperature will also be lowered. The number of molecules with any assigned velocity will differ from the former number, since the temperature is different. The redistribution of molecular velocities after a disturbance is, for all practical purposes, an instantaneous process.

Summary of Molecular Magnitudes.—By the mathematical treatment of the molecular theory, it is possible to make many calculations regarding the size of molecules, the frequency with which they collide, etc. A summary is given below of some of the more important molecular quantities deduced in this way.

Number of molecules in the gram-molecular weight of a gas...	6.062×10^{23}
Number of molecules per cubic centimetre at N.T.P..........	2.705×10^{19}
Mass of the hydrogen atom..............................	1.663×10^{-24} gram
Average velocity of the hydrogen molecule at 25° C..........	1.769×10^{5} cm./sec.
Average distance travelled between collisions by a hydrogen molecule at 25° C. and a pressure of one atmosphere.......	1.89×10^{-5} cm.
Diameter of the hydrogen molecule........................	2.4×10^{-8} cm.

QUESTIONS AND PROBLEMS

1. Calculate the molecular weight of a gas, 1 gram of which occupies 1.5 litres at a pressure of 700 mm. of mercury and a temperature of 20° C. *Ans.* 17.41.

2. Calculate the density at N.T.P. of hydrogen, oxygen, and argon.
Ans. 8.98×10^{-5}; 1.43×10^{-3}; 1.78×10^{-3}.

3. A determination of the density of a gas is made by the Dumas method. The following observations are made:

weight of bulb + air = 50.274 grams
weight of bulb + vapour = 50.436 grams
weight of bulb + water = 261.3 grams
room temperature = 20.5° C.
barometric pressure = 753 mm.
bulb sealed off at 100° C.

Given that the density of air at N.T.P. is 0.001293, calculate the density at 100° C. and the molecular weight of the gas. *Ans.* 0.00196; 60.6.

4. The following observations were made in a Victor Meyer determination:

weight of liquid used = 0.0572 gram
volume of air displaced = 15.30 c.c.
room temperature = 23.5° C.
barometric pressure = 763.2 mm.

Calculate the molecular weight and density at N.T.P. of the vapour.
Ans. 90.6; 0.00403.

5. Explain in detail why it is not necessary to determine the temperature of the bulb in the experiment given in question 4.

6. Calculate the average kinetic energy of a molecule of carbon dioxide at 288° Abs. What is its velocity?
Ans. 5.92×10^{-14} erg; 403.9 metres per sec.

7. Calculate the temperature at which the average velocity of an oxygen molecule is the same as the average velocity of a hydrogen molecule at 0° C.
Ans. 4368° Abs.

8. Calculate the average kinetic energy of a nitrogen molecule at 50° C. How fast would a one-gram weight have to move in order to have the same kinetic energy? *Ans.* 6.6×10^{-14} erg; 11.5 cm. per year.

9. A 4 to 1 mixture by volume of helium and argon is allowed to diffuse through capillary tubes into an evacuated space. What is the composition of the gas which first passes through? *Ans.* He : Ar :: 12.64 : 1.

10. In question 9, what effect would a variation in temperature or pressure have on the composition of the gas emerging into the evacuated space?

11. The following observations were made in the determination of the specific heat of nitrogen by the Regnault method:

volume of gas reservoir = 10.0 litres
initial gas pressure in reservoir = 20.0 atmospheres
final gas pressure in reservoir = 10.0 atmospheres
room temperature = 20.0° C.
temperature of heating bath = 100° C.
initial temperature of calorimeter = 20.000° C.
final temperature of calorimeter = 20.872° C.
water equivalent of calorimeter = 2625 grams.

Calculate the specific heat of nitrogen at constant pressure.
Ans. 0.2471 cal. per gram.

12. Calculate the specific heat of a gas from the following observations obtained by the Joly constant volume method:

weight of gas = 2.870 grams
initial temperature = 20.0° C.
excess water condensed = 0.172 gram
barometric pressure = 760 mm.
latent heat of evaporation of water = 538 cal. per gram.
Ans. 0.403 cal. per gram.

13. A Kundt's tube was calibrated with air, for which the ratio of the two specific heats is 1.40. With air the wave length was found to be 7.2 cm. With helium the wave length was 21.0 cm. The experiments were carried out at 20° C. and 760 mm. pressure. Calculate the ratio of the two specific heats for helium. *Ans.* 1.67.

14. From the information given in question 13 calculate C_p and C_v for both air and helium, given $R = 1.987$ cal.
Ans. Air, 6.93 and 4.95 cal.; He, 4.95 and 2.97 cal.

15. The density of gaseous carbon dioxide at 0° C. and 760 mm. pressure is 0.00197650. The density at 0° C. and 380 mm. is 0.00098488. Calculate the true molecular weight, i.e., that at very low pressures, given $R = 0.082046$ litre-atmosphere, 0° C. = 273.18° Abs. *Ans.* 44.00.

16. The van der Waals' constants, a and b, for carbon dioxide are $a = 7.06$ and $b = 0.166$, respectively, when the volume is measured in litres, the pressure in atmospheres, and the temperature in degrees absolute. By means of van der Waals' equation, calculate the volume occupied by 1 gram molecule of carbon dioxide at 0° C. and a pressure of 1 atmosphere. Use the values of R and 0° C. given in question 15. *Ans.* 22.266 litres.

17. Calculate the volume occupied by 1 gram molecule of carbon dioxide at 0° C. and a pressure of 1 atmosphere by means of the ideal gas law. Compare the result with that obtained in question 16. *Ans.* 22.413 litres.

18. Deduce the relationship between the density of a gas and its pressure, molecular weight, and temperature.

19. Describe the direct weight method of determining the densities of gases.

20. Describe the Dumas method of determining gas densities.

21. Describe the Victor Meyer method of determining gas densities.

22. Discuss the relative merits of the various methods used to measure gas densities.

23. Show how the velocity of a gas molecule may be calculated, and express R in its proper units for this purpose.

24. Explain how diffusion through capillary tubes may be used to measure the relative velocities of different species of gas molecules.

25. Discuss the temperature changes which take place when a gas expands (*a*) into an evacuated space, (*b*) by forcing a piston out of a heat-insulated cylinder. Show that the kinetic theory offers an explanation of these changes.

26. Describe experimental methods of measuring (*a*) the specific heat of a gas at constant pressure, (*b*) the specific heat of a gas at constant volume, (*c*) the ratio of the two specific heats of a gas.

27. Calculate the value of the gas constant, R, in ergs and in calories per mole.

28. Prove that $C_p - C_v = R$ cal.

29. Show that the specific heat at constant volume of a monoatomic gas is equal to $3R/2M$.

30. Explain why the molecular heats of polyatomic gases are greater than $3R/2$.

31. Discuss apparent exceptions to the gas laws.

32. Discuss the variation of the apparent molecular weight of a gas with pressure and temperature, and describe the experimental evidence for the infallibility of the ideal gas law at zero pressure.

33. Discuss aberrations from the ideal gas law, and show how van der Waals' equation may be derived.

CHAPTER IV

THE TRANSITION FROM THE GASEOUS TO THE LIQUID STATE

It has been realized for centuries that certain vapours may be condensed to form liquids. The first factor which was found to influence this phenomenon was the temperature; later it was realized that the pressure to which the system was subjected was also of importance. Once the importance of the pressure had been realized, it was found to be possible to liquefy many substances which had previously been known only in the gaseous state. By lowering the temperature and raising the pressure, every known substance has now been condensed. In this chapter the changes which occur during such a process will be examined with the molecular-kinetic theory as a guide. It is known, of course, that atoms are the basic components of all substances. In the gaseous state the molecule, however, is the fundamental unit of structure. The first question which arises in connection with liquids is whether the molecule still exists when a gas is condensed, or whether there is some fundamental alteration in the manner in which the atoms are aggregated. These questions will be approached by first considering the effect of very high pressures on substances in the gaseous state.

Gases at High Pressures.—As we have seen above, even at pressures below one atmosphere aberrations from the ideal gas law appear. In this pressure range, however, van der Waals' equation expresses the experimental results with satisfactory accuracy. If we carry out measurements at higher pressures, say up to 50 atmospheres or more, it is found that larger and larger aberrations from the ideal gas law occur, and that even van der Waals' equation begins to show discrepancies.

At a constant temperature the ideal gas law reduces to $PV = K$, and hence the product PV is constant and independent of the pressure. It is convenient to use the difference between this constant value of PV and the experimentally determined value as a criterion of the aberration from the gas law. In Fig. 16 the product PV is plotted against the corresponding pressure for ethylene. The horizontal line represents the ideal gas law, $PV = K$, the magnitude of the ordinate being calculated from the theoretical molecular weight of the gas, i.e., the sum of the atomic weights. The curve shows that the difference between the experimental and ideal values of the product PV is over 100 per cent at certain pressures. If we take two sets of experimentally determined values for P and V, we can calculate the values of a and b in van der Waals' equation for the gas in question. We can then use the values of a and b to calculate the value of the product PV at various pressures. In practice the values of a and b are chosen so that any error which exists is distributed as evenly as possible over the entire experimental pressure range. In consequence the agreement between the observed and calculated values at the higher pressures is not as striking as it would appear to be. The results obtained in this way are given in the table below. It will be seen that van der Waals' equation gives very much better agreement than the ideal gas law, although even it shows discrepancies. These discrepancies are much greater in the case of some gases than in that of ethylene.

Pressure-Volume Relationships for Ethylene at 20° C.

Pressure, Atmospheres	PV Calculated from Ideal Gas Law	PV Observed	PV Calculated from van der Waals' Equation
1	1.000	1.000	1.000
50	1.000	0.750	0.751
100	1.000	0.422	0.415
150	1.000	0.571	0.568
200	1.000	0.712	0.713
250	1.000	0.856	0.856
300	1.000	0.992	0.993
350	1.000	1.125	1.127
400	1.000	1.250	1.256

Van der Waals' equation can thus be applied with a certain degree of precision even to gases at very high pressures, where the ideal law is entirely inapplicable. As we have seen, the ideal gas law can be derived theoretically on the basis of certain assumptions. These assumptions were found to be inadequate and in need of modification. The modified assumptions led to van der Waals' equation which proved entirely satisfactory at low pressures. We now find that these modified assumptions are no longer justified when the molecules of a gas are brought very close to one another, i.e., at very high pressures. Under these conditions the actual volume of the molecules may be altered by compression, and the laws of force governing molecular attraction may be altered when the molecules are in very close proximity. These effects are of small importance and may often be neglected up to pressures of 50 or 100 atmospheres. Eventually, however, they make themselves felt, and at very high pressures van der Waals' equation becomes invalid. The actual pressure at which van der Waals' equation begins to show serious discrepancies depends on the degree of complexity of the molecule. In general, the more complicated the molecule the lower the pressure at which aberrations occur.

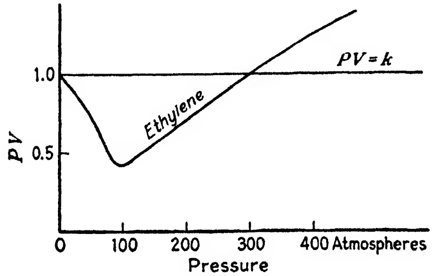

FIG. 16.

Another factor of importance is the effect of temperature on the form of the $PV - P$ curve. The general effect of temperature is the same with all gases, and a typical set of curves is given in Fig. 17. The values of PV as given by the ideal gas law are, of course, proportional to the absolute temperature. Suppose that T_1 represents a temperature which is not far removed from the normal boiling point of the particular substance, T_3 represents a very much higher temperature, and T_2 an intermediate temperature. The three horizontal lines in the diagram show the behaviour of an ideal gas at these temperatures. At the lowest temperature (curve 1) the experimentally determined value of PV decreases rapidly as the pressure increases, passes through a minimum, and then increases again. At a somewhat higher temperature (curve 2) the minimum is much closer to the line representing the behaviour of an ideal gas. Eventually a temperature is reached (curve 3) at which there is no minimum, and PV always increases with rise in pressure.

The Joule-Thomson Effect.—The above curves can also be conveniently correlated with a phenomenon known as the Joule-Thomson effect. In a previous chapter it was shown that an ideal gas suffers no temperature change when allowed to expand by diffusion, i.e., in such a manner that no external work is performed. This fact has been thoroughly confirmed for the expansion of real gases at low pressures. In an ideal gas there is no change in internal energy during the expansion, the value of the product PV being the same before the expansion as after. It can therefore be predicted that at high pressures, where ideal conditions no longer hold, and the product PV varies with the pressure, a temperature change must take place when a gas is expanded.

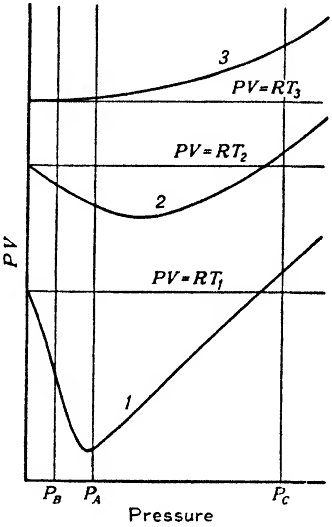

FIG. 17.

This can be tested experimentally by the apparatus shown in Fig. 18. Two chambers are separated by a diaphragm. One of the chambers contains a gas at a high pressure; the other is evacuated. The whole apparatus is brought to a constant temperature, and the diaphragm is ruptured. It will be found that the gas, which now fills both compartments, has undergone a temperature change during the expansion. Depending on the gas used, the temperature may have either increased or decreased.

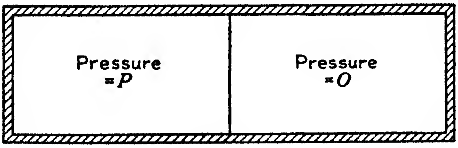

FIG. 18.

A more practical form of apparatus is shown in Fig. 19. The two portions of a long pipe are separated by a nozzle. The pressure in the left-hand section of the pipe is maintained at a high value, P, by means of a compressor. The gas flows through the nozzle and expands to some lower pressure, p. If the gas in the high-pressure section of the pipe is maintained at a fixed temperature, it is found that its temperature is altered on expanding through the nozzle.

Experiments of this kind showed that with hydrogen or helium, initially at room temperature, the temperature of the gas increased on expansion, while almost all other gases showed a cooling effect. It is worth emphasizing once more that this effect is in no way connected with the temperature change which takes place when a gas expands adiabatically with the performance of *external work.* This type of expansion with the performance of work is, moreover, always accompanied by a cooling effect.

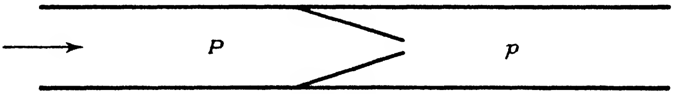

Fig. 19.

It has been found experimentally, and can be justified theoretically, that the difference between the values of PV before and after expansion is a measure of the magnitude of the temperature change which occurs. Thus in curve 1, Fig. 17, if the gas is allowed to expand from the pressure A to the pressure B a cooling effect takes place. In the case represented by curve 2 the cooling effect is smaller, since there is less difference between the values of PV before and after the expansion. In the case of curve 3 the product PV is greater before expansion than after, and hence there is a heating effect instead of a cooling on expansion. If we use a still higher pressure, say that represented by C the value of PV is in every case greater before expansion than after, and hence there is always a warming effect when a gas expands from very high pressures in this way. Most gases at room temperature are in a condition corresponding to curves 1 and 2. Hence they show a cooling effect if expanded, without doing work, from moderately high pressures. Hydrogen and helium, however, are far removed from their condensation points at room temperature and hence correspond to curve 3. They therefore show a heating effect when expanded at room temperature. If, however, they are cooled to a low temperature and then expanded, their behaviour is like that represented by curve 1, and they are cooled still further on expansion. Similarly if we heat a gas such as carbon dioxide to a high temperature, it is now in the region where its PV curve is similar to curve 3, and it shows a heating instead of a cooling effect on expansion.

The foregoing discussion of the behaviour of gases at high pressures furnishes a good illustration of the necessity of knowing how relationships are derived, and on what assumptions they are based, in order to make practical use of them for purposes of calculation. In many cases where, say, the pressure of a gas is to be calculated, knowing its weight, volume, and temperature, we can make use of the ideal gas law,

$$PV = \frac{w}{M}RT.$$

This is by far the most convenient equation, and it involves no constants which are specific for the gas in question. Where the gas is highly compressed, or where high precision is necessary, van der Waals' equation must be used. Even this, however, is inadequate for high precision at intermediate pressures, or even as an approximation in the region of 1000 atmospheres. At such high pressures use would have to be made of some empirical equation, containing five or six constants which differ from gas to gas. Such an equation, like van der Waals' equation, can be applied only when experimental data are available to evaluate the constants.* Which type of equation is to be used for any calculation depends on the judgment of the individual, and obviously this necessitates an understanding of the fundamental principles involved.

The Transition from Gas to Liquid.—We can best approach the transition from gas to liquid by describing the experimental results obtained when a vapour is compressed isothermally (i.e., at a constant temperature). Consider a cylinder filled

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* It should be pointed out that if we have x experimental observations, we can always obtain an equation with x constants which will fit the results with absolute accuracy. Such an equation is, of course, so cumbersome that it has practically no value.

with carbon dioxide at 20° C., and fitted with a piston and a device for measuring the pressure of the gas. As the piston is forced in the pressure rises, and the relation between the pressure and the volume is given by curve *AB* in Fig. 20. In this particular instance the phenomenon we are concerned with takes place when the pressure reaches 73 atmospheres. At this stage liquid begins to form and, as the piston is pushed in, there is a steady decrease in volume without any change in pressure. The amount of gas present decreases steadily, and that of the liquid increases, until the point is reached where there is nothing but liquid left (*C*). From here on a very large increase in pressure is required to effect a small volume change in the liquid (*CD*). The curve *ABCD*, shown in the figure, is called an isotherm. This curve is reproduced exactly during the reverse process of expansion. If we start at *D* and release the pressure, we obtain a slight expansion of the liquid. At *C* vapour again appears, and the pressure remains constant until all the liquid has disappeared and the point *B* is reached. After this the pressure-volume curve for the vapour (*BA*) is reproduced in the reverse direction. The constant pressure which exists when liquid and vapour are coexistent (*BC*) is known as the vapour pressure of the liquid. This pressure depends on the temperature, but is independent of the relative amounts of liquid and vapour present. It should be noted that at the vapour pressure both liquid and vapour exist, above this pressure only liquid can exist, and below it there is only vapour.

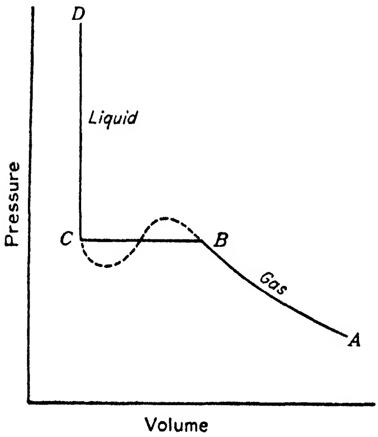

FIG. 20.

It is now of interest to see whether we can obtain any information regarding the above curve from van der Waals' equation. At first sight all that we would expect would be an expression for the gaseous part of the curve (*AB*). Since even for the gaseous state deviations from van der Waals' equation occur at high pressures, we would expect that the equation would be entirely inapplicable to the portion of the isothermal where liquid exists. It is found, however, that the equation represents the portion of the curve *CD* for the liquid just as accurately as it represents *AB* for the gas. In other words the same equation represents the pressure-volume-temperature relationships of both gas and liquid. The portion of the isothermal *BC* where the gas and liquid are coexistent is not represented by van der Waals' equation. The theoretical curve here is shown by a dotted line in Fig. 20. It should be noticed that this line is continuous with the other portions of the curve and hence van der Waals' equation does not indicate the exact point at which liquefaction takes place. Since van der Waals' equation represents the behaviour of substances in both the gaseous and liquid states, it is called an "equation of state." The fact that such an equation exists shows that there must be considerable similarity between the fundamental structure of a gas and that of a liquid. Later it will be shown that we may derive much useful information regarding the constitution of liquids from the known facts concerning the structure of gases.

The Liquefaction of Gases.—Faraday was probably the first to realize the possibility of liquefying all gases. He discovered means of obtaining low temperatures and high pressures, which he recognized as the essential factors in the process. As a means of obtaining high pressures, he generated gases from chemical reactions in a confined space and thus reached pressures which were limited only by the mechanical strength of the apparatus. To obtain a low temperature, he made use of an ice-salt mixture in his first experiments with chlorine. In these experiments he used an apparatus such as that represented in Fig. 21. A small amount of solid chlorine hydrate ($Cl_2 \cdot 8H_2O$) was placed in one arm of an inverted U-tube. The other arm was immersed in the ice-salt cooling mixture. The chlorine hydrate was then heated, gaseous chlorine was given off, and the high pressure thus produced was sufficient to cause liquefaction of the gas in the cold arm of the tube. In this way Faraday succeeded in obtaining moderate amounts of liquid chlorine. In a similar way, several other gaseous substances were obtained in liquid form.

As a further means of obtaining a low temperature Faraday made use of the cooling effect which is produced when a liquid is boiled under reduced pressure. By this means all known gases were liquefied with the exception of hydrogen, air, oxygen, and three or four other gases. These gases resisted all the attempts at liquefaction by Faraday and his contemporaries and were designated the " permanent " gases.

About this time great advances took place in the mechanical means of obtaining high pressures. Natterer, for example, succeeded in subjecting gases to pressures up to 3000 atmospheres, but was unable to liquefy any of the permanent gases. Such experiments threw all the emphasis on the pressure, and caused the necessity of a low temperature in the liquefaction of gases to be overlooked. An accidental discovery on the part of Cailletet drew attention to this. He compressed oxygen in the capillary of a thick-walled glass tube to about 300 atmospheres. A valve connected to the apparatus broke, and the gas expanded suddenly against the pressure of the atmosphere. The gas was cooled in consequence of this expansion, and a mist was formed consisting of minute drops of liquid oxygen. The important deduction was made from this experiment that the gas could be liquefied at a comparatively small pressure, provided that a low enough temperature was used.

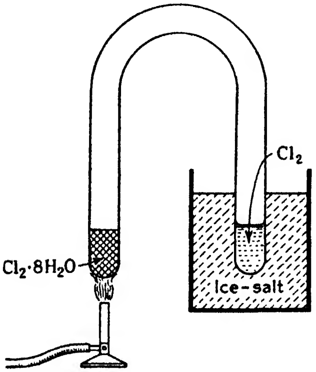

FIG. 21.

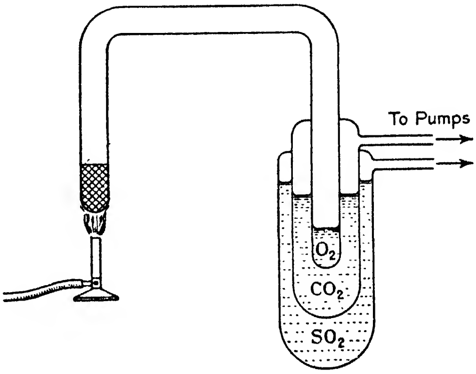

FIG. 22.

Shortly afterwards, Pictet succeeded in liquefying oxygen in somewhat larger amounts by means of the technique developed by Faraday. He used a triple-walled vessel, shown in Fig. 22. Liquid sulphur dioxide was boiled under reduced pressure in the outer vessel. This cooled the liquid carbon dioxide in the middle vessel. The liquid carbon dioxide was then boiled under reduced pressure and a temperature of about −140° C. was produced. The inner vessel was connected to an iron retort in which oxygen was generated by heating potassium chlorate. The reaction furnished the necessary pressure, and a considerable quantity of liquid oxygen was condensed in the inner vessel. A few years later Wroblewski and Olszewski succeeded in liquefying a very small amount of hydrogen by means of Cailletet's method.

All the above methods, however, give only very small quantities of liquid, and are incapable of being used in the form of a continuous process. With the realization that a low temperature is essential, another method of cooling gases has been resorted to. It has been shown previously that a non-ideal gas is usually cooled on expansion. This cooling effect becomes greater and greater as the initial temperature of the gas is reduced. By means of the apparatus illustrated in Fig. 23, this cooling effect can be employed in a continuous manner. The gas to be liquefied is compressed by a mechanical compressor and enters the apparatus at *A*. It passes through a long copper spiral, and on escaping through a small orifice at *B* is slightly cooled. The cooled gas flows up around the copper spiral, passes out at *C*, and returns to the compressor. The incoming gas is cooled by this expanded gas, and on itself expanding is cooled still further. A cumulative cooling effect is thus obtained, the temperature of the gas falling continuously until liquefaction takes place. In this way Linde and Dewar succeeded in producing liquid air in large quantities. The method is now being used commercially, the liquid air being fractionally distilled as a means of obtaining oxygen.

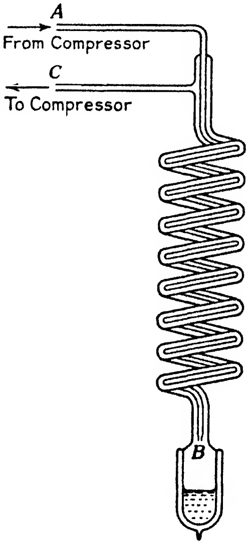

FIG. 23.

The above method can be used with all gases. It is only necessary to start the expansion from a temperature which is low enough to give a further cooling on expansion, i.e., where the $PV - P$ curve has the form shown in curves 1 and 2, Fig. 17. The initial pressure is chosen so that it corresponds to the point P_A in the above curves. For air, room temperature is sufficiently low. In the case of hydrogen, however, it is necessary to pre-cool the gas by means of liquid air, boiling under reduced pressure. For helium, the most difficult gas to liquefy, a similar pre-cooling with liquid hydrogen is necessary. In this way the gas was first liquefied by Kammerlingh Onnes. By boiling the liquid under reduced pressure, he succeeded in obtaining temperatures within 0.5° C. of the absolute zero. In recent years temperatures below 0.01° Abs. have been reached.

All known gases have now been liquefied. It should therefore be emphasized that all substances may exist in any of the three states of aggregation. Whether a substance in its common state is solid, liquid, or gaseous is merely an accidental circumstance which depends on the pressure and temperature conditions which happen to prevail in our environment.

As a matter of interest the boiling points of a number of liquefied gases are given in the following table.

Substance	B. P., °C.	B. P., °A.	Substance	B. P., °C.	B. P., °A.
Chlorine........	− 33.6	239.4	Nitrogen.......	−195.7	77.3
Sulphur dioxide..	− 10.1	262.9	Air............	−193.1	79.9
Ammonia.......	− 33.5	239.5	Argon..........	−185.7	87.3
Ethylene.......	−103.8	169.2	Hydrogen......	−252.7	20.3
Oxygen........	−182.9	90.1	Helium.........	−268.9	4.1

The Continuity of State.—In the previous sections we have been leading up to the question of the nature of the liquid state. Perhaps the best way to approach the question is to consider a series of isothermal curves giving the pressure-volume relationships for a substance over a large range of pressures and temperatures. Experimental data of this kind are available for carbon dioxide, through the investigations of Andrews, and are given in Fig. 24. The meaning of an isothermal curve of this kind, and the manner in which it may be obtained experimentally, have been dealt with previously. In Fig. 24 it should be specially noted that the volume change taking place during the condensation of the gas decreases as the temperature rises, and eventually disappears completely. In an experiment, what is actually seen during condensation is the formation of a meniscus, or line of demarcation between the gas and the liquid. In the higher temperature isothermals this appearance of discontinuity is not met with.

Consider the 35.5° isotherm. As the gas is compressed the volume at first decreases rapidly, then more slowly, and finally at high pressures only a small volume change takes place for a great increase in pressure. At no pressure does a meniscus appear, and it is concluded that the formation of a liquid at this temperature is impossible, no matter how high the pressure may be. In the 21.5° isothermal the compression of the vapour causes a relatively small decrease in volume until a pressure of about 56.5 atmospheres is reached. At this point condensation commences, and the pressure remains constant until liquefaction is complete. After this the curve shows the small volume change characteristic of the compression of a liquid. By trial Andrews obtained two curves, at 31.1° and at 31.2°. The one at the lower temperature gave a liquid-vapour equilibrium, although the region in which the two states coexisted was barely discernible. There was, however, definite visual evidence of the formation of a meniscus. In the curve for 31.2°, however, there was no evidence of liquid formation at any pressure, although this curve shows a discontinuity very similar to that in the 31.1° curve and is almost exactly the same shape throughout its entire course.

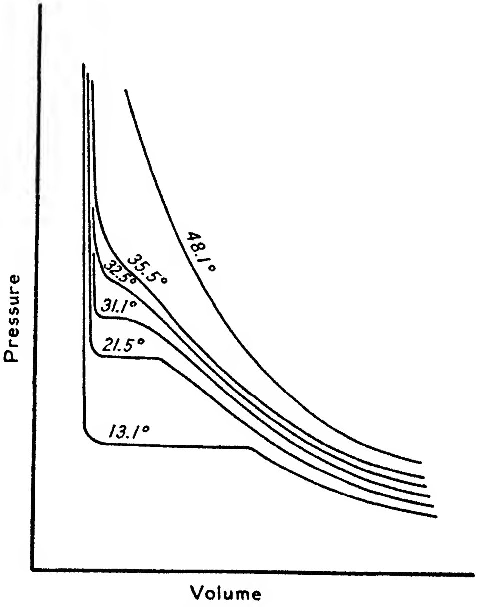

FIG. 24.

From the above, and from similar experiments with other substances, it is concluded that a temperature exists for any gas above which it cannot be liquefied. This temperature is called the critical temperature. In the discussion of the isothermal curve in Fig. 20, it has already been pointed out that van der Waals' equation holds for both the liquid and gaseous states, although somewhat inexactly for both states. This leads to the conclusion that there must be great similarity between the structure of a liquid and that of a highly compressed gas. Van der Waals' equation does not permit us to test this conclusion rigorously, since the equation is only approximate. We can, however, compare the behaviour of the two states graphically by means of experimental data such as those of Andrews. We may construct the pressure-volume isothermals at two temperatures, one slightly above and the other slightly below the critical temperature. Part of the second curve therefore represents the liquid state, whereas the first curve deals entirely with a gas. By making the temperature interval between the two curves smaller and smaller, we can make them virtually coincide over the whole range of pressure. Hence any equation which represents the pressure-volume relationship of the compressed gas must also represent that of the liquid. This state of affairs has therefore been termed the "continuity of state," and its importance is that it means that the structure of a highly compressed gas is identically the same as that of a liquid. Hence a liquid is presumably composed of molecules similar to those which compose the gas. These molecules are free to move about and to rotate, and their kinetic energy of translation constitutes the temperature of the liquid. There still remains unanswered, however, the question of the nature of the meniscus which separates the gaseous and liquid states. This will be considered in connection with the liquid state of aggregation.

The Experimental Investigation of the Critical Temperature.—When a gas, above its critical temperature, is compressed to a high pressure, and then allowed to cool to a temperature below the critical temperature, liquefaction takes place. If the pressure was sufficiently high, liquid alone will be present after the cooling. Under these circumstances nothing definite can be learned regarding the process of liquefaction. This can best be approached in a somewhat different manner. Suppose that a thick-walled tube is partially filled with liquid. The liquid is boiled to expel all air and the tube is sealed off. It is then about $\frac{2}{3}$ filled with liquid and $\frac{1}{3}$ with vapour. The tube is immersed in a bath and heated slowly. As the temperature rises the liquid expands, but this increase in volume is offset by the evaporation of the liquid to give an increased vapour pressure. Consequently the volume occupied by the liquid does not change to any great extent. When the critical temperature is reached, the meniscus separating the gas and the liquid disappears suddenly. On lowering the temperature again, a cloud forms, the drops of which coalesce to form liquid and again give a meniscus. The critical temperature is found to be sharply defined for pure substances, a tenth of a degree or less determining the formation of liquid or its disappearance. The pressure which exists in such a tube at the critical temperature is called the critical pressure. This method cannot be used in determining the critical temperatures of all substances, since it involves the use of a transparent material which will not stand the high temperatures and pressures which are sometimes necessary.

Other methods of measurement have been devised, however, which depend on the following considerations: The density of a liquid decreases with rise in temperature. The density of the vapour in equilibrium with it increases because of the rise in vapour pressure as the temperature increases. The density of the liquid and that of the vapour must therefore approach one another as the temperature rises, and it has been found that at the critical temperature the two are equal. This density is called the critical density. Its value may be obtained by plotting the average density of liquid and vapour in Fig. 24, and extrapolating the straight line thus obtained until it cuts the curve at the critical temperature. (Cailletet and Mathias' rule.) This is illustrated for carbon dioxide by Fig. 25. If, therefore, the density of the liquid and that of the vapour in equilibrium with it are measured over a range of temperature, then the critical temperature may be estimated by extrapolating the two curves to their point of junction. Another method of measuring the critical temperature is based on the fact that at temperatures above it the density of the substance is uniform throughout the whole container. This method possesses the great advantage that an opaque metal tube may be used. It is thus convenient at high temperatures and pressures. This tube is about half filled with liquid, the remainder of the space containing the vapour. The tube is pivoted on an axle which runs through its centre of gravity. When partly filled with liquid it therefore takes up a vertical position to which it will return if displaced. The tube is heated in an air bath and tipped from time to time. At and above the critical temperature the tube will remain in any position to which it is tilted, since the liquid has now disappeared and the tube is filled with a medium of uniform density.

It is now convenient to describe another illustration of the continuity of state. It is possible to change any gas (provided it is below the critical temperature) into a liquid at the same temperature without the appearance of a meniscus or discontinuity at any stage of the process. In other words, the change can be carried out without any visual evidence of liquid formation. As an example, suppose that carbon dioxide is placed in a glass tube which is connected, by means of mercury, to a pressure pump. Suppose that the carbon dioxide is at a temperature of 20° C. and a pressure of 20 atmospheres. It is a gas under these conditions. If it is now heated to 35° C., it is above the critical temperature and hence it cannot be condensed even if the pressure is raised to 100 atmospheres. If we now cool the system to 20° again, the liquid is obtained. No meniscus will be formed, however, since the pressure is far above the vapour pressure of the liquid at 20° C. Throughout the entire process, therefore, the tube is always filled with a homogeneous, transparent medium. It is thus by no means easy to distinguish between a gas and a liquid in the absence of a meniscus. One means of distinguishing between the two would be to release the pressure, and allow expansion to occur at constant temperature. In the case of the carbon dioxide at 20 atmospheres pressure there will be no meniscus formation, no matter to what

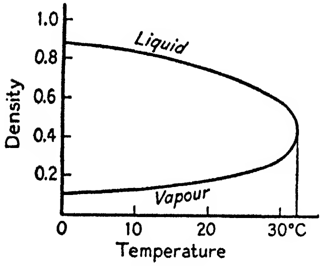

FIG. 25.

extent the pressure is released and expansion allowed to occur. It is therefore a gas. With the carbon dioxide at 100 atmospheres pressure, a meniscus will appear when the pressure has been reduced to 56.5 atmospheres. It was therefore liquid at the higher pressure. It follows that we cannot distinguish between a gas and a liquid unless both are present.

QUESTIONS

1. Show how the *PV–P* relationships of gases vary with the temperature.
2. Describe the Joule-Thomson effect, and show how it can be investigated.
3. Show how the direction and magnitude of the Joule-Thomson effect can be inferred from *PV–P* curves.
4. Discuss the transition from the gaseous to the liquid state.
5. Describe the methods used in liquefying gases.
6. Discuss the "continuity of state." Describe the experimental evidence on which it is based.
7. Discuss critical temperatures and their measurement.
8. Discuss the structure of liquids.
9. Describe the experimental methods of distinguishing between a liquid and a gas.

CHAPTER V

THE LIQUID STATE OF AGGREGATION

SINCE it is possible for substances to pass continuously from the gaseous to the liquid state, and *vice versa,* without any abrupt change in properties, it follows that there cannot be any very great difference between the ultimate composition of a liquid and that of a gas at high pressure. The differences in the constitution of substances in the two states of aggregation are differences in degree rather than differences in kind. Since a liquid is very much denser than a gas at atmospheric pressure, and yet is composed of the same sort of molecules, it is obvious that in the liquid these molecules must be much closer together. The proximity of the molecules has an important bearing on the effect produced by their volume and their attraction for one another. This influence is appreciable in gases at low pressures, becomes marked at high pressures, and must therefore be still further accentuated in the case of liquids. In other words, the factors which are symbolized by a and b in van der Waals' equation are no longer mere correction terms, but become of major importance. Of these two influences, molecular attraction plays a more apparent part and is of greater importance in governing the properties of liquids. The molecular attraction has reached such a large value in the case of liquids that the forces between the molecules which tend to hold them together are strong enough to overcome the kinetic energy of the molecules. The molecules, therefore, are no longer able to escape from one another, and liquids thus have a definite volume. The meaning of this is made apparent by the following analogy.

Suppose that two molecules (or in general any two bodies) attract one another with a force which falls off very rapidly as the distance between their centres increases. Then, if they move towards one another, collide, and move away again, what ultimately happens will depend on the following considerations.

If the force of attraction falls off very rapidly, then there must be a certain distance between the molecules beyond which the attractive force will have a negligible influence on any motion that the two molecules may have. In moving out through the field of attractive force immediately after collision, the velocity of the molecules will be reduced. If the kinetic energy immediately after collision is less than the work which must be done in order to move outside the sphere of influence of the attractive force, the molecules will be unable to separate and will return to one another again. Since perfect elasticity of the two is assumed, the molecules will oscillate to and fro interminably.

If, however, the kinetic energy after collision is greater than the work which must be done in order to escape from the field of molecular attraction, then the molecules will separate and will continue to move apart with a constant velocity, but one which is less than that at the moment of collision. If, after being reflected from some inert body, the two molecules chance again to collide, the same sequence of events will occur and they will again separate.

The first case mentioned above, in which the molecules are unable to separate after collision, corresponds to the liquid state of aggregation. The second case, in which they can separate, corresponds to the gaseous state. In the first case the molecules are free to move, but cannot escape from one another's field of attraction. Their maximum distance apart is therefore independent of the size of the containing vessel, and a liquid thus possesses a definite volume. In the second case the molecules are free to separate, and hence a gas will fill the entire container in which it is placed. The governing factor is the kinetic energy at the moment of collision. This, of course, depends on the average kinetic energy of the molecules. The average kinetic energy of the molecules is a measure of the temperature. Hence there is a certain temperature below which the molecules are unable to escape from one another, whereas above it they can escape. This is the critical temperature of the system. In a real system there are a large number of molecules all of which are attracting one another, and are moving with different and varying velocities. The conditions which govern the ability of a molecule, moving with a velocity equal to that of the average molecule, to escape are therefore much more complex. The same general principle will hold, however. The system will be gaseous if the average kinetic energy of a molecule is great enough to enable it to escape from the combined attractive forces of its neighbours. Such an average kinetic energy corresponds to a temperature which is above the critical temperature.

From this point of view, the governing factor in the process of liquefaction is the relation between the molecular force of attraction and the kinetic energy of the molecules. This is brought out to better advantage in the following section, by considering these influences from the point of view of the physical properties of liquids.

The Physical Properties of Liquids.—In a liquid a discontinuity arises, owing to the fact that the liquid possesses a surface other than that which is due to the walls of the containing vessel. This discontinuity gives rise to certain distinctive physical properties which are characteristic of the liquid state. Among such properties are included vapour pressure, surface tension, and latent heat of evaporation. The mechanism of these phenomena will be found to be in complete harmony with the previously indicated ideas of the constitution of the liquid state.

In discussing the physical properties of liquids, the first consideration will be given to a comparison between the state of a molecule in the body of the liquid and that of one which is at the surface. It has been assumed that the force of molecular attraction falls off very rapidly with distance. Consequently a molecule, such as that represented at *a* in Fig. 26, may be regarded as being attracted equally in all directions, the circle around it indicating the sphere of influence of the attractive force, i.e., the boundary beyond which molecular attraction may be regarded as negligible. This molecule will move about and will thus possess kinetic energy just as with gas molecules. Since the attractive force to which this molecule is subjected is equal in all directions, its motion will not, on the average, be affected in any way. This is not true, however, for a molecule such as *b*, which is so near the surface of the liquid that there are more molecules within its sphere of attraction below it than there are above. The velocity components of such a molecule in a direction parallel to the surface will not be influenced by molecular attraction. In a direction normal to the surface, however, movement upwards will be diminished and movement downwards enhanced. As pointed out previously, the necessary condition in order that a liquid may exist is that the average kinetic energy of a molecule is less than the work required to move it out through the field of attraction which exists at the surface. All the molecules in the surface of the liquid are under a differential force downwards due to molecular attraction. As a result they give rise to an effect similar to that which would be produced by an elastic membrane, confining the molecules below and tending to compress the volume in which they move to the smallest possible size. The differential forces at the surface thus give rise to the property of the liquid known as the surface tension.

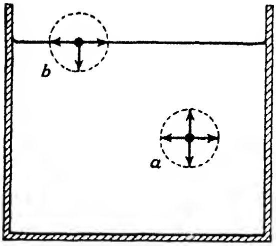

FIG. 26.

In a sense, the molecules in the surface layer constitute the wall of a containing vessel for the molecules below. This does not mean that the surface molecules are stationary, or are intrinsically different from the molecules inside, but merely that their motion away from the main body of the liquid is brought to a stop before they escape from the influence of the attractive forces.

At first sight this view of the constitution of a liquid does not appear to offer an explanation of the fact that a liquid possesses a definite vapour pressure. The existence of a vapour in equilibrium with a liquid is readily explained if we assume that there is a distribution of velocities in the case of the molecules of a liquid, just as there is in a gas, the average velocity having a definite value which depends on the temperature. The condition which prevents the escape of a molecule moving in a direction perpendicular to the surface is that its kinetic energy is less than the work which must be done in order to pull it out of the region of attractive forces. In the case of a gas there are a few molecules whose velocity is much above the average. If this is also true in the case of a liquid, then such molecules may have a velocity sufficient to take them through the surface, and quite outside the influence of the attractive forces of the molecules in the liquid. If the velocities of the molecules are distributed about an average velocity according to the laws of probability, then at any temperature there will always be a definite fraction of the molecules of the liquid with a kinetic energy great enough to enable them to escape.

Consider a liquid placed in a closed container which it partly fills, the remainder of the space being evacuated. The average molecule which chances to move in the direction of the surface will be slowed up by the attractive forces, and will return to the body of the liquid without reaching the surface. There will be a certain definite velocity which will carry a molecule just to the edge of the sphere of influence of the attractive forces, from which position it will return to the body of the liquid. Any molecule with a velocity greater than this will be enabled to escape.

As time goes on, more and more molecules will escape in the manner indicated above. The vapour pressure, i.e., the pressure in the space above the liquid, will thus increase. As a result, molecules from the space above will begin to find their way back again into the liquid whenever a favourable series of collisions sends them in that direction. The number of molecules that leave the liquid is, as we have seen, limited to a small fraction which possess high velocities. The number of molecules that return is proportional to the number in the space above. Eventually, therefore, a state will be reached in which the number of molecules leaving the liquid in unit time is equal to the number of molecules returning to it from the vapour. An equilibrium pressure will thus be reached, and a liquid has a definite constant vapour pressure at a given temperature. Since the number of molecules that can escape is proportional to the area of the free surface of the liquid, and since the number that return from the vapour is proportional to this same free area, the vapour pressure is independent of the relative amounts of liquid and vapour.

Although the vapour pressure measured by a manometer is a steady static pressure, it depends on the continual interchange of molecules between the vapour and the liquid. Such an interchange, which leads to an apparently stationary state, is called a dynamic equilibrium. The existence of this is made obvious when the vapour above the liquid is compressed. No increase in pressure results, since the vapour pressure depends solely on the existence of an interface. The compression of the vapour increases the chance of return of vapour molecules to the liquid, and therefore momentarily upsets the equilibrium between molecules leaving and returning. More molecules return than leave therefore, until equilibrium is once more established.

When the space above a liquid is connected to a vacuum pump, so that the vapour in equilibrium with the liquid is removed, the equilibrium is upset and more molecules leave the liquid than return. Only molecules with a velocity above the critical velocity can escape. This critical velocity is above the average velocity, and hence the relatively fast-moving molecules are the ones which leave the liquid. The average velocity of the molecules left in the liquid is therefore reduced. Consequently the temperature of the liquid is lowered when evaporation takes place. If the evaporation is to be conducted isothermally, heat must be allowed to enter the liquid to overcome this cooling effect. This heat, which enters the liquid without producing an accompanying rise in temperature, is known as the latent heat of evaporation. This is one of the important physical constants of a liquid, and is measured in terms of the number of calories required for the isothermal evaporation of one gram of liquid.

An apparent incongruity arises at this point. It might be thought that since the fast-moving molecules are the ones which escape, the vapour would therefore be at a higher temperature than the liquid in equilibrium with it. This, however, is not true. Suppose that we have a liquid in contact with its vapour, the system being heat-insulated from the surroundings, and that at the start the liquid and the vapour are at the same temperature. This means that the average kinetic energy of the molecules in the liquid is the same as that of the molecules in the gas. Only fast-moving molecules can leave the liquid, but these are slowed up by the attractive forces at the surface, and their kinetic energy is reduced to an average value. The liquid is not cooled, however, since the molecules which return to it from the vapour are speeded up by the forces at the surface, and thus arrive in the liquid with a kinetic energy above the average. The liquid is cooled only when the vapour above it is removed, and the dynamical equilibrium is thus upset. Similarly, if the vapour above the liquid is compressed, more molecules with a high velocity are added to the liquid, and the temperature of the liquid thus rises.

Recapitulation.—The *surface tension* of a liquid is caused by the fact that the molecules in the neighbourhood of the surface are under the influence of an unbalanced molecular force of attraction. This is somewhat equivalent to the action of an elastic membrane holding in the molecules of the liquid. The thermal agitation, or molecular motion, is not sufficient to disperse the molecules, provided that the average kinetic energy is less than the work required to move a molecule from the liquid into the vapour. Molecules having a sufficiently high velocity can escape, and if this takes place into a confined space a definite dynamic equilibrium results. This constitutes the *vapour pressure* of the liquid. When the vapour molecules are allowed to escape, more molecules evaporate, and the liquid is cooled down. The heat required to prevent this cooling constitutes the *latent heat of evaporation.* The importance of the magnitude of the forces of molecular attraction in governing these properties is at once apparent. The greater the molecular attraction, the greater the surface tension, the greater the difficulty a molecule has in escaping, and hence the lower the vapour pressure. Similarly, the greater the attraction the greater the latent heat of evaporation, since with large attractive forces only very fast molecules can escape, and the average energy of the remaining molecules is lowered to a greater extent for each molecule lost.

The Influence of Temperature on Surface Tension, Vapour Pressure, and Latent Heat of Evaporation.—Suppose that the temperature of a liquid in equilibrium with its vapour is raised by the entry of heat from outside the system. The average kinetic energy of all the molecules has been increased. The effect on the molecules in the liquid is twofold. In the first place, an increase in the average velocity means an increase also in the number of molecules whose velocity is in excess of the critical velocity. As a result, more molecules can escape and accumulate in the vapour, and the vapour pressure increases. At the same time the increased kinetic energy of the molecules drives them farther apart, against the force of molecular attraction, and the liquid expands. The force with which the surface molecules are attracted inwards depends on the number of molecules per unit volume attracting them. This is decreased by the expansion of the liquid, and hence the force with which the surface molecules are pulled inwards is decreased. The surface tension therefore decreases, and in consequence the critical velocity necessary to enable a molecule to get through the surface decreases. The vapour pressure therefore increases rapidly as the temperature rises.

This rise in vapour pressure tends to decrease further the surface tension. The molecules in the surface are under a differential force due to the molecules below. At low vapour pressures the effect of the upward attraction due to vapour molecules is negligible. As the vapour pressure increases, however, this factor will make itself felt to a greater and greater extent. The rise in the vapour pressure thus tends to lower the surface tension. As we have seen, the lowering of the surface tension tends to increase the vapour pressure. There is therefore a cumulative effect, and the very rapid increase in vapour pressure as the temperature rises is not surprising.

For the same reasons the latent heat of evaporation decreases with rise in temperature. A decrease in the surface tension means that molecules with a smaller kinetic energy can escape. The average energy of the liquid molecules is therefore not so greatly decreased per escaping molecule.

It is possible now to predict the existence of the critical temperature from the above considerations dealing with the liquid state. As the temperature increases, the density of the liquid decreases. Owing to the rise in vapour pressure, the density of the vapour increases. The two densities must eventually become equal at some temperature. The differential force at the surface depends on the difference between the number of molecules per unit volume in the liquid and in the vapour. When the densities of the liquid and the vapour become equal, the differential force at the surface disappears. The reason for the existence of the surface disappears, all the molecules are in the same state, and the meniscus vanishes. Similarly, as the temperature rises, the latent heat of evaporation decreases and must obviously vanish at the critical temperature.

Surface Tension.—There are a few facts regarding surface tension which require further elaboration.

The most apparent evidence for the existence of surface tension is the similarity between the surface of a liquid and a stretched membrane. This results in a tendency on the part of the liquid to contract its surface area as much as possible. Thus if a drop of liquid is removed from the influence of gravity, by being suspended in a liquid of equal density, it forms a sphere, since this is the configuration of smallest surface area for a given volume. The ordinary flattened form of a drop of liquid on a plane surface is a compromise between the effects of surface tension and gravity. The membrane effect can be simply demonstrated by gently lowering a small steel pin on to the surface of water. Provided that the pin is very slightly greasy, so that it is not wetted by the water, it can be supported by the surface, a distinct depression being caused by its weight. Although the density of the pin is far greater than that of water, it can thus be " floated " on the surface.

It is not at once apparent how a lateral tension existing in the surface of a liquid can be due to the action of molecular forces of attraction in a direction normal to the surface. This can, however, be demonstrated by a consideration of the apparatus shown in Fig. 27. A film of liquid is held in a U-shaped wire on which is laid a movable cross-piece. Even if this film is very thin (say 1/100 mm.) it must be remembered that it is still millions of molecules thick. The tensile membrane effect tends to decrease the area of the liquid surface, and hence tends to contract the film and pull in the movable rod. Suppose that a force is applied to the movable rod and it is pulled out, increasing the surface area of the film. In order to create the new surface, molecules have to be brought to the surface from the body of the liquid against the forces of molecular attraction. The downwards pull on the surface thus makes itself felt in a lateral manner. The molecules in the surface film are pulled inwards and thus tend to move into the body of the liquid. The number of molecules in the surface, however, cannot be decreased unless the surface area is decreased. There is thus a lateral force tending to reduce the area of the surface to the smallest possible value.

This lateral force existing in the surface film furnishes the most convenient way of measuring the magnitude of the surface tension of a liquid. For example, the arrangement shown in Fig. 27 could theoretically be employed for this purpose, by measuring the force required to hold the movable rod in a stationary position. Actually, however, this arrangement is impractical on account of friction. In practice other methods are used, such as the measurement of the force required to pull a wire ring away from the surface, or the measurement of the height to which a liquid rises in a capillary tube. All such methods depend fundamentally on the lateral force existing in the surface film of a liquid, and tending to contract the surface.

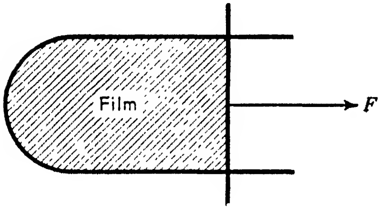

Fig. 27.

It has been remarked previously that the forces of molecular attraction can be active only over very small distances. Measurements of surface tension have given a striking confirmation of this fact. The pull exerted on the movable rod in the above apparatus is due to the attraction of the surface molecules in each face of the film towards the main body of the liquid in the film. For a given mass of liquid, the thickness of the film decreases as the rod is pulled out. The number of molecules in the main body of the liquid below the surface therefore decreases. The force on the rod due to surface tension, however, is found to remain undiminished until the thickness of the film has been decreased to about 10^{-6} cm. The range of molecular forces of attraction must therefore be of this order. Another illustration of this small range is furnished by measurements of the surface tension of sea water. It is found that the value obtained on the surface of the ocean, when the depth of the water is about one mile, is precisely the same as the value obtained with the same water in a shallow vessel. Below the surface at a distance of about 10^{-6} cm. or more, we can therefore regard the molecules as being attracted equally in all directions, and hence without influence on what is taking place at the surface.

Vapour Pressure.—The vapour pressure of a liquid has been shown to be due to a dynamic equilibrium between the molecules of the liquid and those of the vapour. The measurement of this pressure can be carried out, therefore, only if both states of aggregation are coexistent. The most obvious method of measurement is by means of an apparatus similar to that represented in Fig. 28. The liquid under investigation is contained in a bulb, which is immersed in a thermostat, and is connected to a manometer. The tubing between the bath and the manometer is wound with a heating element, and is maintained at a temperature higher than that of the bath in order to prevent condensation. Care must be taken that there is no foreign gas mixed with the vapour in the bulb.

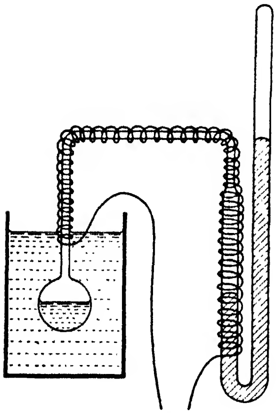

FIG. 28.

The vapour pressures of all liquids increase very rapidly with rise in temperature, as predicted previously. This is exemplified by Fig. 30, which gives the vapour pressure of water from 0° C. to the critical temperature. In this temperature range the vapour pressure increases from 4 mm. to about 165,000 mm.

It is found that the variation of the vapour pressure with temperature can be approximately represented by the equation

$$\log p = -\frac{A}{T} + B,$$

where p is the vapour pressure and A and B are constants. It follows that if the logarithm of the vapour pressure is plotted against the reciprocal of the absolute temperature a straight line is obtained. This is illustrated by Fig. 29.

The temperature at which the vapour pressure is 76 cm. is known as the normal boiling point of the liquid, i.e., it is the temperature above which vapour can be expelled into the atmosphere when normal pressure prevails. In general, the boiling point of a liquid may be defined as the temperature at which the vapour pressure is just equal to the gas pressure of the environment.

The basis of Faraday's method of obtaining low temperatures by boiling liquids under reduced pressure is now apparent.

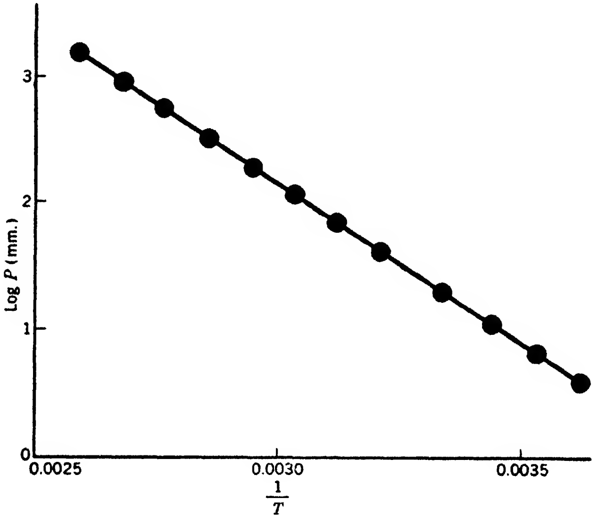

Fig. 29.

Ether, for example, has a normal boiling point of 35° C. Its vapour pressure at room temperature is about 44 cm. Suppose that a flask containing ether is connected to a vacuum pump which will maintain the pressure below 44 cm. Under these circumstances the ether will boil, and will therefore be cooled on account of the necessity of furnishing the latent heat of evaporation. The extent of the cooling produced will depend on the rate at which heat is conducted to the ether from the surroundings, and on the efficiency of the vacuum pump in handling large volumes of vapour. The ether can thus be used as a refrigerant. Some substances, for example water, can be cooled in this way to such an extent that they freeze.

Incidentally, by heat-insulating a liquid and maintaining the vapour at various constant pressures by means of a pump, we can determine the boiling temperatures corresponding to various pressures. The variation of the vapour pressure with temperature can thus be experimentally determined. This is called the dynamic method of measuring vapour pressures.

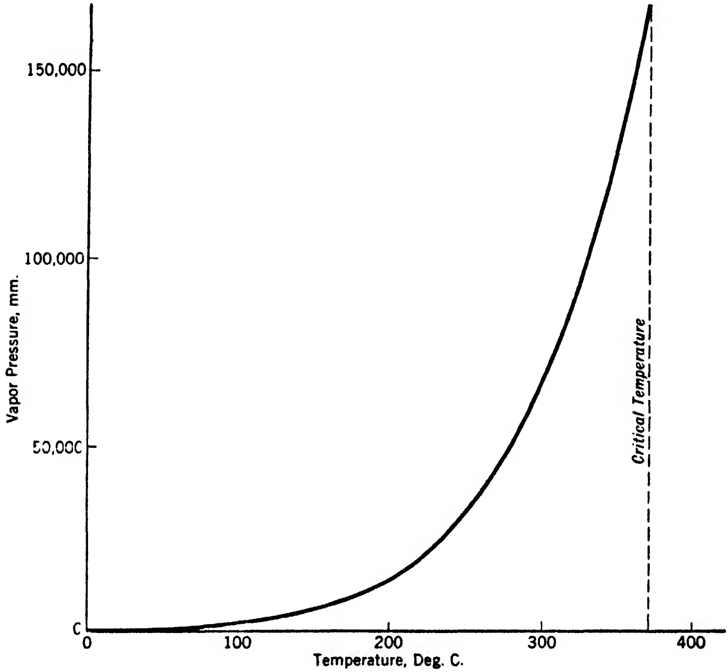

FIG. 30.—The Vapour Pressure of Water.

The Tensile Strength of Liquids.—Suppose that a liquid completely fills the containing vessel, the vapour phase being absent. Such a liquid will not necessarily register a pressure corresponding to the vapour pressure of the liquid. It is even possible to obtain "negative pressures" under these circumstances. To carry out such an experiment, a carefully purified liquid is placed in a bulb which it fills almost completely. All air is expelled from the bulb by boiling the liquid, and the bulb is sealed off. On heating the bulb, the liquid expands, and if the proper amount of liquid is present all the vapour will be condensed, and the bulb will be completely filled with liquid alone. If the apparatus is now cooled slowly, the liquid does not contract, as might be expected, but continues to occupy the whole volume. If an immersion manometer of the aneroid type, i.e., one similar to an aneroid barometer, is contained in the bulb it will register a "negative pressure" which may amount to about twenty atmospheres. This so-called negative pressure merely means that the liquid is under the action of a tension. If the cooling of the liquid is continued, the negative pressure or tension will increase steadily. Finally there will be a sharp detonation and the liquid will break away from the wall, and will no longer fill the entire volume, but will assume its normal volume corresponding to the temperature. The remaining volume of the bulb will now be filled with vapour. It should be noticed that this experiment proves that liquids not only adhere to themselves, i.e., possess tensile strength, but also adhere firmly to the glass walls of the tube.

A liquid thus possesses tensile strength and can hold together by means of cohesive forces due to molecular attraction. The molecules in the body of the liquid are attracted equally in all directions by their neighbours. Suppose that we attempt to separate two layers of liquid bounded by a hypothetical surface in the liquid. The moment that the two layers are separated to an infinitesimal extent, the forces of molecular attraction between the molecules in the two layers come into play and oppose any further separation. The use of the experimental method described above is necessitated by the fact that, on account of the mobility of liquids, it is very difficult to obtain a grip on a liquid in order to subject it to tension. It is therefore impossible to measure the tensile strengths of liquids directly, and all that can be done is to obtain very rough estimates of this by means of the apparatus described above. Such estimates, however, show that the tensile strengths of liquids are extremely high.

It follows that, in the absence of the vapour phase, a liquid will not necessarily register a hydrostatic pressure equal to the vapour pressure which would exist if the vapour phase were present. This is commonly observed when a liquid which is particularly free from dissolved gases is heated at a point some distance below its surface (for example a liquid in a tall beaker which is heated from below). A thermometer immersed in the liquid will often indicate a temperature considerably above the normal boiling point, without there being any signs of ebullition. When boiling finally does start, a sudden evolution of vapour takes place. The latent heat of evaporation is obtained at the expense of the temperature, and the liquid cools until its normal boiling point is reached. This phenomenon is known as "bumping." It is highly undesirable on account of the danger of spilling considerable quantities of the liquid. In order to prevent it, small pieces of pumice are often immersed in the liquid. These absorb small bubbles of vapour and thus bring the vapour phase into contact with the liquid near the point at which heat is being applied. True vapour pressure equilibrium is thus established, and the "superheating" of the liquid is prevented.

The Density of Liquids.—The pressure-volume-temperature relationships of a liquid may be given by an equation of state, such as that of van der Waals, provided that the constants can be evaluated experimentally. There is, however, a very serious complication owing to the tendency for the molecules of liquids to polymerize, or associate. Water is a common example of such an associated liquid. In liquid water, two or three steam molecules aggregate to form a larger complex. Thus we have

$$6H_2O \rightleftarrows 3(H_2O)_2 \rightleftarrows 2(H_2O)_3.$$

This equilibrium is largely influenced by changes in temperature, a low temperature favouring the formation of the larger complexes. As the temperature changes, the actual composition of the liquid changes, and hence the pressure-volume-temperature relationships are greatly complicated. The density of liquids, therefore, can usually be represented only by an empirical equation, which varies from liquid to liquid, and must be determined experimentally in every case.

In the previous section it was pointed out that molecular attraction causes a cohesive force in liquids. This force often runs into thousands of atmospheres. The outer layer of molecules is therefore pressing in on the body of the liquid with a pressure of this magnitude. It can therefore be readily understood that an additional applied pressure of a few atmospheres will have little influence on the volume of the liquid. The compressibility of a liquid, i.e., the effect of pressure on its volume, is therefore very small.

The experimental investigation of the densities of liquids presents little difficulty. On account of the comparatively high density of liquids, the weight of liquid occupying a definite volume is very simply determined.

The Viscosity of Liquids.—On account of the proximity of the molecules, and of the large effect of molecular attraction, there is a much greater resistance to flow with liquids than with gases. Liquids therefore possess much higher viscosities. As the temperature of a liquid is raised, the liquid expands, and the molecules are driven farther apart. The effect of molecular attraction is therefore diminished, and consequently the viscosity of a liquid decreases rapidly as the temperature increases.

The Specific Heats of Liquids.—The high density of a liquid renders the experimental determination of its specific heat comparatively simple, and the ordinary methods of calorimetry can be applied.

The molecular heats of gases give rise to certain regularities, which can be summed up concisely and interpreted theoretically on the basis of the structure of gases. Such regularities, however, are not observed with the molecular heats of liquids. In general the molecular heat of a liquid is high and it increases considerably with rise in temperature. Thus with ethylene dichloride, we have

Temperature, °C.	Molecular Heat, Calories
20	29.6
30	30.4
50	31.0
60	31.5

The large values of the molecular heats of liquids are due to the numerous and complex ways in which energy is taken up when a liquid is heated. In the first place, as with gases, energy is required to increase the translation and rotation of the molecules. Again, since it is impossible to measure C_v because of the very small compressibility of liquids, energy is required for the work done against molecular attraction when the liquid expands on heating. Finally, energy is required to provide for the vibration of the atoms in molecules, and for the dissociation of molecular complexes in the case of associated liquids. These diverse and complicated factors vary from liquid to liquid, and it has not yet been possible to effect a proper relative evaluation of their importance. The only deduction that can be made is the qualitative prediction that the molecular heats of liquids will be large and will vary greatly from liquid to liquid.

QUESTIONS AND PROBLEMS

1. The vapour pressure of benzene at 10° C. is 45.4 mm. At 40° C. it is 181.1 mm. Find graphically the vapour pressure at 20° C. by the method shown in Fig. 29. *Ans.* 74.3 mm.

2. To what is the surface tension of a liquid due?

3. To what is the latent heat of evaporation of a liquid due?

4. To what is the vapour pressure of a liquid due?

5. Discuss the influence of temperature on vapour pressure, surface tension, and latent heat of evaporation.

6. Discuss the measurement of vapour pressures.

7. Describe an experiment which proves the existence of tensile strength in a liquid.

CHAPTER VI

THE SOLID STATE OF AGGREGATION

The Transition from the Liquid to the Solid State.—When a normal * liquid cools a contraction occurs, since the forces of molecular attraction predominate more and more as the kinetic energy of the molecules decreases.

A temperature must therefore be reached where the free motion of the molecule in all directions ceases. This is a definite temperature for every substance, and is known as the freezing point of the substance concerned.

Consider two neighbouring molecules in the body of a liquid. Suppose that on cooling the liquid these molecules are brought together by its contraction, and take up a position in which their forces of attraction for one another are most pronounced. Their power of relative motion and rotation will cease, and if the energy which they formerly possessed due to such motion is abstracted they will be left in a permanent fixed position relative to one another. It is therefore found that, when the temperature has reached this point (the freezing point), energy must be abstracted from the liquid, without a change in temperature, in order to bring about solidification. This energy is therefore latent, and is called the latent heat of solidification (or of fusion). It is observed that liquids freeze at a sharply defined temperature. This is due to the fact that there is a definite degree of proximity necessary to cause the adhesion of neighbouring molecules. Once solidification starts, other molecules will add on to any group already formed, provided that their surplus energy of translation and rotation is abstracted. It was pointed out above that this aggregation of

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* A "normal liquid" is one which is not associated. With normal liquids the density invariably diminishes as the temperature increases. With associated liquids, such as water, there is sometimes an increase in density with increasing temperature. Water, for example, contracts when heated from 0° C. to 4° C.

molecules takes place when they are in such a position that the forces of molecular attraction have the greatest play. This position of maximum attractive force will presumably be located at the extremities of some definite axis through the molecules. They will therefore add on to one another in a definitely arranged, i.e., oriented, manner. This internally oriented arrangement is outwardly manifested by the crystalline form of the substance.

The molecules, which are thus anchored to their neighbours in the solid state, have lost the freedom of motion and rotation which they formerly possessed. They are left only with the energy due to the vibration of their atoms relative to one another. As we have seen previously, such vibration also comes into play in the case of liquids and of gases. The difference between the three states of aggregation lies mainly in the relative magnitudes of the kinetic energy of the molecules and the molecular attraction. In the gaseous state, the motion of the molecules is the most important feature, the effect of molecular attraction being comparatively unimportant. In the liquid state, molecular motion and molecular attraction are competing with one another on more or less equal terms. In the solid state, molecular attraction has become so strong that the free motion of the molecules is altogether prevented. The only motion that a molecule or atom can now undergo is that of oscillation about a mean position. It cannot change its position relative to its neighbours.

The Equilibrium between the Solid and the Liquid States.—When a solid is in contact with its own liquid at the freezing point, and the system is heat-insulated from the surroundings, no resultant change in the relative amounts of solid and liquid takes place. This is due to the energy change which is involved when the solid melts or the liquid freezes. The liquid molecules can enter the solid state only if part of their energy is absorbed; the solid molecules can enter the liquid state only if the necessary energy is supplied to them. This argument undoubtedly applies when we are considering *all* the molecules present. It is not true, however, when an individual molecule is considered. As pointed out before, there is a distribution of velocities amongst the molecules of a liquid. In consequence there are some molecules in the liquid which have an amount of energy below the average and hence may be in the proper condition to enter the solid state. The energy possessed by the solid exists in the form of vibration between atoms. This energy will be distributed among the atoms in much the same way as energy is distributed among the molecules in gases or liquids. It follows that at some point on the surface of the solid an aggregation of atoms may have an unusually high energy content, which will enable them to break away from the solid and become a liquid molecule. There is thus a continual interchange of molecules between the solid and the liquid states. This gives rise to a dynamic equilibrium, similar to that which exists when a liquid is in equilibrium with its vapour. In both cases the condition that the average energy of all the molecules must remain constant prevents a change in the relative amounts of the two phases present. It follows that the freezing point of a liquid is uninfluenced by the relative amounts of solid and liquid present, since the surface ratio of liquid to solid is unaltered.

Suppose now that heat energy is allowed to enter the system. This energy will be available for the liquefaction of some of the solid. The relative amounts of the two phases will therefore change, but the temperature will remain constant. In the same way, the absorption of heat energy from the system will lead to the freezing of some of the liquid.

It is thus apparent that the evaporation of a liquid and the melting of a solid are processes of a very similar nature, both of which depend upon the existence of a dynamic equilibrium.

The Transition from the Solid to the Gaseous State.—At the melting point, a solid and a liquid are in equilibrium with one another. The liquid will also be in equilibrium with its vapour at this temperature. In order that true equilibrium may result, the solid must also be in equilibrium with the vapour. Every solid must therefore have a vapour pressure. This is often overlooked because at low temperatures the vapour pressures of many solids are immeasurably small.

The existence of an equilibrium between a solid and its vapour can be predicted by a consideration of the conditions which prevail at the surface of the solid. The aggregates of atoms, which constituted the molecules of the gas or liquid, are now held in fixed positions by the neighbouring aggregates, by means of forces of attraction which are utilized in the most advantageous way. If, therefore, a chance distribution of vibrational energy causes a number of atoms to have an amount of energy considerably above the average, this amount of energy may be sufficient to enable the aggregate to leave the solid surface and become a gas molecule.

It follows that the mechanism underlying the evaporation of a solid is very similar to that underlying the evaporation of a liquid. The atoms in the surface of a solid, like those in the surface of a liquid, are under the action of a differential force inwards. A solid therefore possesses energy in virtue of its surface. The change from solid to vapour therefore requires the acquisition of energy, and the reverse change requires the absorption of energy. There is therefore a latent heat, which is analogous to the latent heat of evaporation. The direct change from the solid to the gaseous state is called sublimation, and hence the accompanying energy change is referred to as the latent heat of sublimation. The effect of temperature on the above properties of solids is the same as that which occurs with liquids.

At a given temperature, the vapour pressure varies from solid to solid, depending principally upon the magnitude of the forces coming into play. Carbon dioxide is a notable example of a solid in which these forces are unusually small. Its vapour pressure is so large that it reaches atmospheric pressure before the solid melts, and amounts to 5.1 atmospheres at the melting point. Such a substance can therefore be distilled, or "sublimed," in an open vessel without melting. It should be remembered that any solid can be sublimed by the use of a sufficiently low pressure. Thus iodine can be sublimed at its normal melting point if the pressure is below 90 mm.

The Specific Heats of Solids.—Regularities in the values of the specific heats of solids were first observed when the atomic theory was in its infancy, long before any such regularities had been observed with the specific heats of gases. It was found by Dulong and Petit that the atomic heats * of the solid elements all have the same constant value.

Later work showed that there were a few apparent exceptions to this law.

In addition to Dulong and Petit's law, another generalization called Neumann's law was discovered. This is of much greater importance from the point of view of the constitution of solids. According to this generalization the atomic heat of an element in the solid state is unaltered when the element forms part of a solid compound. The specific and atomic heats of a number of solid elements are given in the following table.

Element	Specific Heat	Atomic Heat	Element	Specific Heat	Atomic Heat
Lithium........	0.9408	6.5	Silver..........	0.0559	6.0
Carbon.........	0.0635	0.76	Antimony.....	0.0508	6.2
Sodium........	0.283	6.5	Iodine........	0.0541	**6.9**
Aluminium.....	0.2356	6.4	Tungsten.......	0.0336	6.2
Potassium......	0.1662	6.5	Gold..........	0.0316	6.2
Platinum.......	0.0323	6.3	Lead...........	0.0310	6.4
Copper.........	0.0936	6.0	Rhodium.......	0.0580	6.0
Zinc...........	0.0935	6.1	Sulphur......	0.1764	5.7
Silicon.........	0.1360	**3.8**	Iron...........	0.1162	6.5

The following example will illustrate the application of Neumann's law.

Ferrous Sulphide

Observed molecular heat = 12.1 calories
Atomic heat of iron = 6.5
Atomic heat of sulphur = 5.7
Sum of atomic heats = 12.2.

The above example is admittedly a favourable case, and there are many substances for which the agreement is by no means close. However, there is unquestionably an additive character to the atomic heats. This is quantitative as long as

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* The atomic heat of an element is the product of its atomic weight and its specific heat. In other words, it is the heat capacity of a gram-atomic weight of the element.

we are dealing with the same type of compound. Thus chlorine contributes a definite invariable amount to the molecular heats of all monovalent chlorides, a slightly different but invariable amount in divalent chlorides, etc.

There are a few elements which show a wide divergence from Dulong and Petit's law. These are usually elements of small atomic weight, carbon being the most notable example. When the atomic heat of carbon is measured at higher temperatures, however, the value rises and becomes asymptotic to a value similar to that of the majority of the elements. This is shown by the curve for carbon in Fig. 31. In the table of atomic heats given above, it will be noticed that lead has the normal value. When its atomic heat is measured at low temperatures, however, it is found to fall and to give an atomic heat-temperature curve very similar to that of carbon. The same behaviour is exhibited by other elements, and hence the behaviour of carbon cannot be looked upon as exceptional. Instead, it is necessary to restate Dulong and Petit's law, viz.: " The atomic heats of the elements have a constant value, which is the same for all of them when the measurements are made at temperatures which are not far removed from their melting points. Those elements having high atomic weights reach this constant value sooner than those which have low atomic weights." The theoretical interpretation of the decrease in atomic heats at low temperatures is a subject of great complexity, and cannot be discussed here.

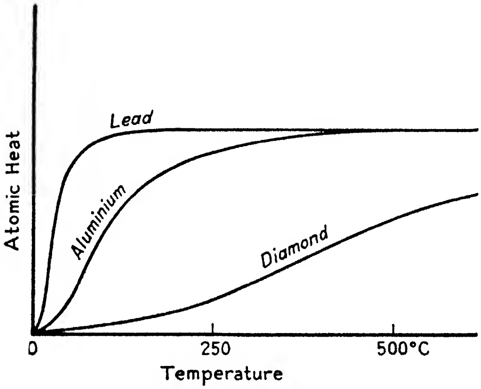

FIG. 31.

It will be noticed from the above table that the extreme values for the atomic heats of the elements at high temperatures are not quite identical. This divergence is not due to experimental error, since it is possible to measure the specific heats of solids with great accuracy. The measurements, however, are all made at constant pressure and not at constant volume. Although solids expand only slightly with rise in temperature, these expansions are sufficient to account for the small differences in the values given in the table. When corrections are applied for the work done during expansion, it is found that the atomic heats of all elements are very nearly equal to 6 calories. This value is independent of the compound of which the element happens to form a part, provided that the measurements are made at sufficiently high temperatures.

The Structure of Solids.—The change from liquid to solid at the melting point is accompanied by only a small change in volume, and yet a large amount of energy is liberated (the latent heat of fusion). It has already been pointed out that this is due to the fact that the molecule loses freedom of motion and rotation when it enters the solid state. When a molecule first becomes attached to the surface of the solid, its atoms are brought into close contact with the atoms of other molecules which had previously entered the solid state, and all the atoms in the neighbourhood have a pronounced influence upon one another. In this sense the identity of the molecule is lost, and all the atoms in the solid may be looked upon as belonging to, and being attached to, one another, inasmuch as it is impossible to move one atom through space without moving all the other atoms composing the solid.

There is a considerable body of other evidence to support such a postulate. It has been mentioned that molecules will tend to add on to a solid in such a way that there is the most effective neutralization of the forces of attraction. This necessitates a definite orderly arrangement of atoms in a solid, just as there is a definite arrangement of atoms in a complex gas molecule. By orderly arrangement is meant that the atoms of the various elements follow a definite sequence which is unaltered throughout the crystal. Evidence of such an orderly internal arrangement is furnished by the orderly external form possessed by crystals, since a structure made up of an orderly arrangement of unit parts would be expected to exhibit a symmetrical external form.*

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* It should be pointed out that *all* solid substances are crystalline. So-called amorphous solids are merely composed of exceedingly small crystals.

The specific heats of solids furnish the most striking evidence in favour of a structure in which the atoms are linked together like the atoms of a gas molecule, and are unable to change their relative positions. Specific heat measurements have shown that the variation of the energy content of a solid with the temperature depends primarily on the number of atoms involved, and is virtually independent of their nature and of the manner in which they are linked to their neighbours. This can be explained only on the assumption that the atoms possess kinetic energy of vibration about a mean position. In that case the energy content of the solid would be independent of everything except the number of atoms undergoing such a vibration. In recent years a method known as X-ray analysis has made it possible to determine the relative positions of the atoms of a solid. The results of such investigations have confirmed in a striking way the brilliant conceptions of the earlier workers, on the basis of specific heat measurements alone.

The molecules of a gas are free to move about unhindered except by chance collisions. Their motion is chaotic, and they are not subject to the action of any restoring force which would tend to make them oscillate about some assigned position. The atoms of a solid, however, are anchored to definite positions relative to one another. As they move away from their mean position, they are subjected to restoring forces which cause them to return, and to continue oscillating about a definite point. Any moving body under the action of such a restoring force must possess potential energy. As an analogous case, we may consider the action of a pendulum. All the energy of a pendulum is stored up as potential energy at the end of its swing. At the bottom of its swing all its energy is kinetic. Consequently, over a long period of time, its energy is on the average half kinetic and half potential. In a similar way, the vibrating atoms in a solid must be regarded as having both kinetic and potential energy, which on the average are equal in quantity. Consequently, in order that one form of energy may be increased, the other must be increased to an equal extent. It has been shown that the molecular heat of a monatomic gas is equal to $\frac{3}{2}R$. The atomic heat of such a gas is therefore also $\frac{3}{2}R$, or approximately 3 calories. The atoms of a solid, like the atoms of a monatomic gas, are kinetically independent. In consequence, they also will require 3 calories to increase their kinetic energy to such an extent that the temperature rises one degree. This kinetic energy increase will necessitate a potential energy increase of the same amount. Six calories will therefore be required to cause a temperature increase of one degree. The deductions regarding the structure of solids, which were made above, are therefore in quantitative agreement with the experimental facts, as summed up in Dulong and Petit's law.

Allotropy.—It has been found that a large number of solids are capable of existing in more than one crystalline form. This is called allotropy, and the different crystalline modifications are known as allotropic forms.

This phenomenon is not surprising from the point of view of the theory of the solid state developed above. In a liquid at the freezing point there may be several different ways in which the molecules can orient themselves, so as to produce effective neutralization of the forces of molecular attraction. The resulting crystals may therefore be formed from nuclei of different shapes, and will continue to grow in different crystalline forms. One of these forms must have the most effective possible neutralization of the forces of attraction, and hence there will always be one crystalline modification which is more stable than the others. Since the attractive forces are affected by the temperature, the form which is the most stable at one temperature is not necessarily so at another.

The Molecule and the States of Aggregation.—A molecule is composed of atoms, and the most fundamental problem in this connection is the determination of the number of atoms which belong to each individual molecule. The object of this section is to give the criteria by means of which this number may be ascertained, and then to discuss the condition of the molecule in the gaseous, liquid, and solid states.

In a given molecule, at constant temperature, each atom must on the average maintain the same position in space relative to the position of all the other atoms in the same molecule. The number of atoms which maintain this constancy of relative position are the number which compose the molecule. The following conditions must therefore be fulfilled by a molecule:

If one of the atoms of a molecule is displaced in space, all the other atoms in it must suffer a corresponding displacement, so as to maintain their relative positions unchanged. The molecule as a whole can thus move about, or rotate. It will be impossible, however, for two atoms of such a molecule to rotate about an axis chosen at random without a corresponding rotation of the remaining atoms. Similarly, any permanent displacement of one atom necessitates a similar displacement of all the others.*

In the gaseous state the size of the molecule is given by the expression

$$M = \frac{wRT}{PV},$$

this size, or " molecular weight," being referred to the hydrogen atom as unity. From this molecular weight the number of atoms composing the molecule may be deduced. The size of the molecule is thus based upon the gas laws, and the molecule is to be regarded as the unit particle which registers a pressure by hitting the walls of the container. In a gas the discontinuity of matter is most marked, i.e., the distances between the entities composing the gas are large compared to their size. These entities are therefore easy to distinguish. The atoms of a molecule form a small cluster, which moves through space as a unit, and is quite distinct from similar clusters. The molecule of a gas is therefore a very definite entity, and there is little difficulty in determining its size.

On compressing a gas, the molecules are brought closer and closer together and, if the temperature is sufficiently low, the forces of molecular attraction cause liquefaction. The molecules of the liquid still maintain their individual characteristics, inasmuch as they are free to move through space and to rotate. They are now so close together, however, that specific atoms in one molecule begin to influence specific atoms in another. It is

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* The atoms of a molecule may vibrate, however. Such movement is of an ordered nature, and the atoms move to and fro in a cyclic manner about some mean position. There is thus a definite fixed position to which the atom returns at regular intervals in the course of its vibratory movement. Such a definite position may be regarded as the permanent location of the atom for the purpose of this discussion.

therefore more difficult to determine the exact size of the molecule in the liquid state.

As the temperature is lowered still further the effect of the attractive forces becomes more and more marked, and finally solidification occurs as a result of the specific attraction of atoms in neighbouring molecules for one another. Each molecule loses its individuality as it joins on to the crystal, since all the atoms of the solid are fixed in place and cannot be displaced relative to their neighbours. Since each atom in the solid is fixed to its neighbours, and these in turn to other atoms, the whole structure is definitely fixed and no atom can be displaced without the displacement of the complete crystal. The whole crystal, therefore, must be regarded as a single enormous molecule.

Some confusion has arisen on account of the fact that, in ignorance of the true significance of the term, the " molecular weight " of solid substances is often referred to. The molecular weight of a solid, in the proper sense of the term, is merely the weight of the whole crystal divided by the weight of a hydrogen atom. The stoichiometric proportions of the various elements composing the solid are, of course, independent of the size of the crystal. In the case of a solid substance a formula is assigned which gives these stoichiometric proportions. This is often the same as that which represents the molecule of the substance in the vapour state. Thus the formula $NaCl$ represents the molecule of sodium chloride vapour. In the case of solid sodium chloride, however, all that it means is that sodium and chlorine are combined in the ratio of 23 to 35.5 by weight. No information is given by such a formula concerning the structural unit in the solid state.

Confusion is also caused by the fact that the formula is sometimes arranged so as to give the smallest size to which a crystal may be subdivided without altering its crystalline form. Thus it is sometimes loosely stated that the molecule of water is represented by $(H_2O)_4$ in the solid state. What really should be said, in this case, is that the unit crystal cell contains 8 hydrogen and 4 oxygen atoms. In all cases, whether a solid can be vaporized without decomposition or not, the size of this unit crystal cell, and the relative positions of the atoms, are all the information that can be obtained regarding the structure of the solid. This may have no connection whatsoever with the real or hypothetical molecule of the vapour. The "molecular weight" of a substance in the solid state cannot be determined, because it does not exist.

Association.—Although the molecule has a definite existence in both the gaseous and the liquid states, it does not necessarily follow that the size of the molecule will remain unaltered when a gas is condensed. We have already referred to association in liquids, and it will be of interest to follow through the three states of aggregation a definite example of a substance that gives an associated liquid. The best-known substance of this kind is water. In the gaseous state the molecular weight of water is 18, corresponding to the H_2O molecule. In the liquid state the pressure-volume-temperature relationships cannot be formulated with very great precision, on account of the large effects due to molecular attraction and to the volume of the molecules. In consequence the molecular weight cannot be determined with the same ease and accuracy as in gases. However, where there are great abnormalities in the pressure-volume-temperature relationships, it is possible to estimate roughly the degree of association, or molecular weight. It is also possible to estimate the molecular weight roughly from measurements of the surface tension and latent heat of evaporation. In the case of water, the data indicate that the molecules in the liquid state are partly $(H_2O)_2$ and partly $(H_2O)_3$. These are referred to as dihydrol and trihydrol, respectively. In the case of the latter, for example, there are 9 atoms in the molecule. These move about as a separate and distinct unit. None of them can be displaced without the displacement of the remainder in such a way as to preserve their relative positions. Liquid water is thus a mixture of different molecules, and all we can do is to assign to it an average molecular weight.

In the solid state the molecular weight will be the weight of any particular crystal of ice, divided by the weight of an atom of hydrogen, and will therefore have a variable value. As we have mentioned, the unit crystal cell contains 8 hydrogen and 4 oxygen atoms. The groups of 4 (H_2O)'s represent merely the way in which the atoms in the crystal are arranged. They are not molecules in any sense, since they have no power of independent motion.

It is evident that the conception of the molecule is one of great simplicity in the gaseous state. It is virtually meaningless in the solid state. In the liquid state complications may arise when association occurs, and the size of the molecule may vary with pressure and temperature. This leads to great complications in the treatment of the physical properties of associated liquids.

QUESTIONS AND PROBLEMS

1. From the data given in the table on page 105 calculate the specific heats of solid lithium iodide and copper sulphide. *Ans.* LiI—0.100 cal. per gram.
CuS—0.1223 cal. per gram.

2. Discuss the transition from the liquid to the solid state, and the equilibrium between solid and liquid at the freezing point.

3. State Dulong and Petit's law and its limitations.

4. State Neumann's law and discuss its limitations.

5. Discuss the structure of solids, and show how specific heat measurements have contributed to our knowledge of the structure of the solid state.

6. Define the term *molecule*. Discuss its applicability to the three states of aggregation.

CHAPTER VII

ATOMIC STRUCTURE

We have already discussed the experimental evidence which led to the modern conception of the discontinuous structure of matter. In the present chapter we will go further to examine the question of the structure of the atom itself. The original conception of atoms was that they were indivisible and were the "ultimate" constituents of matter. Evidence soon accumulated from various sources, however, which indicated that there were definite regularities in the properties of the various atoms, and thus suggested the possibility that all atoms were built up from common constituents. The first evidence of this kind was of a chemical nature. In 1815 Prout pointed out that a very large number of atomic weights are integral, or nearly so, and he suggested that all atoms were really composed of an aggregation of hydrogen atoms. Further, and more accurate, atomic weight determinations, however, showed that the integral nature of most atomic weights was only approximate, and Prout's hypothesis fell into disrepute.

The Classification of the Elements.—The next significant advances centred around attempts to classify the elements on the basis of their chemical properties. The first attempt in this direction was that of Döbereiner who pointed out that there were a number of "triads," or groups of three elements, which showed a striking gradation in properties. Thus, consider the group lithium, sodium, potassium. These show a marked gradation in chemical properties, and at the same time their atomic weights constitute a rather accurate arithmetic progression, viz.,

	Li		Na		K
atomic weight.......	6.94		23.00		39.10
difference...........		16.06		16.10	

A further attempt at classification was that of Newlands, who showed that by arranging the elements in groups of eight

The Periodic Table

Period	Group 0	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
1	He 2 4.00	H 1 1.008 Li 3 6.94	Be 4 9.02	B 5 10.82	C 6 12.01	N 7 14.01	O 8 16.00	F 9 19.00	
2	Ne 10 20.18	Na 11 23.00	Mg 12 24.32	Al 13 26.97	Si 14 28.06	P 15 31.02	S 16 32.06	Cl 17 35.46	
3	A 18 39.94	K 19 39.10	Ca 20 40.08	Sc 21 45.10	Ti 22 47.90	V 23 50.95	Cr 24 52.01	Mn 25 54.93	Fe 26 55.84 Co 27 58.94 Ni 28 58.69
		Cu 29 63.57	Zn 30 65.38	Ga 31 69.72	Ge 32 72.60	As 33 74.91	Se 34 78.96	Br 35 79.92	
4	Kr 36 83.7	Rb 37 85.48	Sr 38 87.63	Y 39 88.92	Zr 40 91.22	Cb 41 92.91	Mo 42 95.95	Ma 43 —	Ru 44 101.7 Rh 45 102.91 Pd 46 106.7
		Ag 47 107.88	Cd 48 112.41	In 49 114.76	Sn 50 118.70	Sb 51 121.76	Te 52 127.61	I 53 126.92	
5	Xe 54 131.3	Cs 55 132.91	Ba 56 137.36	La 57 138.92	Rare Earths 58–72	Ta 73 180.88	W 74 183.92	Re 75 186.31	Os 76 190.2 Ir 77 193.1 Pt 78 195.23
		Au 79 197.2	Hg 80 200.61	Tl 81 204.39	Pb 82 207.21	Bi 83 209.00	Po 84 —	— 85	
6	Rn 86 222	87 —	Ra 88 226.05	Ac 89 —	Th 90 232.12	Ux_2 91 —	U 92 238.07		

there was a periodic repetition of properties. Thus, if the elements are arranged in the order of their atomic weights, the eighth element after lithium is sodium, the eighth after sodium is potassium, etc.

Finally, through the work of Mendeléef and of Meyer, the periodic system of classification in its modern form was developed. The periodic table of the elements is reproduced below, and it will be assumed that the reader is already familiar with it. For our present purpose the most important aspect of this system is the *periodic law*, viz., the properties of the elements are periodic functions of their atomic weights. In other words, the mass of an atom is definitely connected with its other properties. This fact alone virtually forces us to the assumption that the atoms of the various elements must be in some way built up from more fundamental constituents.

The periodic classification of the elements has also been of the greatest practical utility in helping to classify the chemical and physical properties of the elements, as a mnemonic guide, in the prediction of the existence and properties of hitherto undiscovered elements, and as a check on the accuracy of atomic weight determinations. It has, however, two very serious defects:

a. A number of pairs of elements have to be placed in the inverted order of their atomic weights in the table, in order to bring them into the correct groups from the point of view of their chemical properties. The elements which are thus misplaced are tellurium (127.61) and iodine (126.92), cobalt (58.94) and nickel (58.69), and argon (39.94) and potassium (39.10).

b. The rare earth elements are very difficult to fit into the table.

These defects indicate that the periodic law is an approximation. The reason for this will be shown in the subsequent discussion.

Atomic Structure.—Modern knowledge of the structure of the atom comes from three main sources, the investigation of electrical phenomena in gases, radioactivity, and phenomena connected with the emission and absorption of radiation. These subjects will therefore be discussed in some detail in the following sections.

Electrical Phenomena in Gases.—When a current from a high potential source is passed through a gas in a tube (a discharge tube) light is emitted by the residual gas in the body of the tube. This was discovered by Julius Plücker. The effects produced are complicated and depend on a number of factors, the chief of which is the gas pressure. At very low pressures the emission of light ceases entirely, and there is merely a phosphorescent glow on the wall at one end of the tube. One type of apparatus which may be used to illustrate this phenomenon is shown in Fig. 32 (*a*). Two metallic electrodes, *A* and *C*, are sealed into a glass tube. The tube is evacuated to less than 0.001 mm. pressure, and *A* and *C* are attached to a high voltage source, *A* being positive and *C* negative. Under these circumstances a greenish phosphorescent glow appears on the end of the tube opposite the negative terminal, or cathode. If solid objects are interposed in the tube between the cathode and the end *B*, it is found that they cast a shadow at *B*, i.e., part of the tube end no longer phosphoresces. From this fact it is concluded that whatever is coming from the cathode and causing the phosphorescence is being propagated rectilinearly. The "rays" are therefore called *cathode rays*.

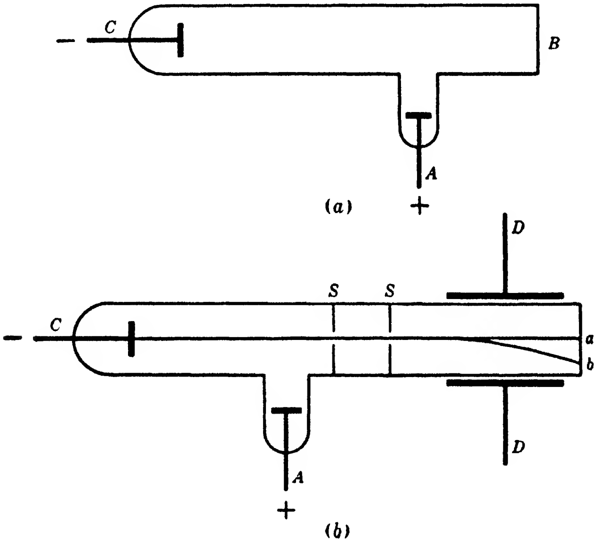


FIG. 32.

It is further found that if a small wheel with vanes is placed in their path it is caused to rotate, and we may thus infer that the cathode rays are really composed of a stream of particles shot out from the cathode. If the apparatus illustrated in Fig. 32 (*b*) is employed, the slits, *S*, will cut out all except the central rays, and a well-defined beam of cathode rays is thus obtained. The fluorescence at the end of the tube will then be confined to a small spot, *a*, opposite the slits. If now an electric or magnetic field is placed at *D*, the phosphorescent spot is found to be deflected to *b*. In other words, the cathode particles are deflected by an electric or a magnetic field, and they must therefore be electrically charged. The direction of the deflection indicates that their charge is negative.

The Determination of e/m for the Cathode Particles.—When a stream of cathode particles is passed through a magnetic or electric field, it is deflected as pointed out above. The extent to which any particle in the stream is deflected in a given field depends, among other things, on the charge on the particle and its mass. If the charge is great the deflection will be large; if the mass is great the deflection will be small. The two factors, charge and mass, therefore work against one another. By measuring the deflection in a field of known strength of a beam of cathode particles, it is possible to calculate the ratio of the charge on the particle, e, to the mass, m. It is found that e/m is constant and equal to 1.8×10^7 electromagnetic units, no matter what gas is used in the tube, or what material is used for the electrodes. We may therefore draw the very important conclusion that cathode particles are all the same, no matter what substance they come from, and they must therefore be a universal constituent of matter. They are now called *electrons*.

As we shall see later, it is known that ions in solution carry a definite charge, and this charge can be determined. No ion in solution ever carries a charge smaller than that on a hydrogen ion, and all hydrogen ions have the same charge. It therefore seems reasonable to assume that there is something fundamental about the magnitude of the charge on a hydrogen ion, and it is of interest to compare e/m for a hydrogen ion with that found for the electron. In electrolysis it is found that 96,500 coulombs of electricity are required to liberate 1 gram of hydrogen, i.e., that amount of electricity is required to neutralize the charge carried by 1 gram of hydrogen ions. Now 1 gram of hydrogen ions contains 6.06×10^{23} ions. Hence the charge on 1 hydrogen ion in electrolysis is

$$\frac{96{,}500}{6.06 \times 10^{23}} \text{ coulombs}$$

$$= \frac{96{,}500}{10 \times 6.06 \times 10^{23}} \text{ electromagnetic units}$$

$$= 1.6 \times 10^{-20} \text{ electromagnetic unit.}$$

The mass of a hydrogen ion is almost exactly the same as that of a hydrogen atom, viz., 1.6×10^{-24} gram. Hence

$$e/m \text{ for the hydrogen ion } = \frac{1.6 \times 10^{-20}}{1.6 \times 10^{-24}}$$

$$= 10^4,$$

as compared with 1.8×10^7 for the electron. There are obviously three possible ways in which the difference can be accounted for:

a. The electron and the hydrogen ion have the same charge, but the mass of the electron is about 1/1800 of that of the hydrogen ion.

b. The electron and the hydrogen ion have the same mass, but the electron has a charge 1800 times larger.

c. The charges and masses are both different.

The Determination of the Charge on the Electron.—In order to choose between the alternatives above, it was necessary to determine either e or m for the electron separately. The most accurate measurements are those of e by Millikan. His method made use of the fact that free electrons can be "captured" by small drops of water or oil. Millikan prepared an oil fog by the use of an atomizer, and then watched one single drop in this fog under a microscope. The drop, of course, fell under the action of gravity, but on account of its small size the rate at which it fell was comparatively slow. Electrons were then introduced into the air in which the drop was falling. If the drop captured an electron, it still continued to fall under the action of gravity. If, however, an electric field was switched on, the plate above the drop being made positive, the drop could be made to rise under the action of the field. The field could then be varied until the drop just remained stationary. Under these circumstances the force due to the field just balances that due to gravity, i.e.,

$$wg = Xe,$$

where w is the mass of the oil drop, g the gravitational constant, e the charge on the electron, and X the field strength. Hence if the mass of the drop is known, e can be determined. In practice Millikan determined w by calculation from the observed rate of fall of the drop under the action of gravity alone. His results led to the value

$$e = 1.6 \times 10^{-20} \text{ electromagnetic unit.}$$

The charge on an electron is therefore the same as the charge on a hydrogen ion in electrolysis, and hence the mass of the electron must be only 1/1800 of that of a hydrogen ion (or atom).

Millikan's work, since it involves the measurement of the charge due to single electrons, also proves that all electrons have the same charge and that the above value is not a mere average charge. The investigation of cathode rays has thus shown:

a. All matter contains electrons.

b. All electrons are the same.

c. The charge on an electron is negative, and is equal in magnitude to the charge on a hydrogen ion in electrolysis.

d. The mass of an electron is approximately 1/1800 the mass of a hydrogen atom.

Canal Rays.—Since all atoms contain electrons, and yet are electrically neutral, there must be positive electricity in the atom. If the current is merely reversed in a cathode ray tube, there is no detectable positive ray. Definite results, however, have been obtained with an apparatus of the type shown in Fig. 33. In this apparatus the cathode is constructed with a channel, or canal, through it. In this way positive particles travelling toward the cathode can pass through the electrode and appear on the far side where their properties may be investigated. With this apparatus a relatively weak positive radiation is detectable. In the presence of an electric or magnetic field the particles making up the ray are found to be deflected in a direction opposite to that with cathode rays, and hence they must be positively charged. The ratio e/m is found to be of the same order of magnitude as that for the hydrogen ion, and *to vary with the residual gas in the tube.* If it is assumed that e is the same as the charge on the electron, m is found to be equal to the atomic weight of the gas in the tube. It follows that positive rays consist merely of positively charged atoms (or sometimes molecules). The mass of the atom is thus associated with the positively charged particle.

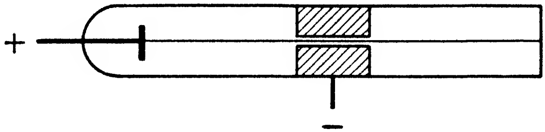


FIG. 33.

It has thus been concluded from the study of electrical phenomena in gases that the atom is constructed from particles of two kinds, electrons and a positive residue with which the mass of the atom is associated. More detailed information about these particles is obtainable from the study of radioactivity, which will be discussed in the next section.

Apart from their bearing on the problem of atomic structure, the above experiments offer an explanation of the conduction of electricity by gases. When a high voltage is applied to a gas, electrons are stripped off some of the atoms. The residue of the atom is thus positively charged. Thus with helium we get He^+ and He^{++} when 1 and 2 electrons, respectively, are lost by an atom. These positively charged atoms, or ions, are then attracted to the negative electrode and thus carry current through the gas. In addition current is carried by free electrons, and by atoms which have captured electrons and have thus acquired a negative charge.

Radioactivity.—In 1896 Becquerel, while engaged in an investigation of phosphorescence, discovered that uranium minerals send out radiation continuously, and will thus affect a photographic plate in the dark. Coupled with this emission of radiation are other properties, such as the bestowing on gases of the power to conduct electricity. This latter property is of very great practical importance in the further investigation of the phenomenon. Since gases are made electrically conducting when exposed to these radiations, it follows that the gases will be able to discharge an electroscope. This is a very sensitive instrument, and it can thus be employed as a delicate test for the presence or absence of the phenomenon of "radioactivity."

A simple form of electroscope is shown in Fig. 34. A wire *B* passes through an insulating block *C* into the interior of a vessel *D*, made of glass, or of metal with glass windows. Attached to the wire at one end is a very thin strip of gold foil *A*. If now a rod of wax is rubbed with fur and touched to *E*, a static charge will be imparted to the wire and foil. Since these acquire a charge of the same sign, they will repel each other, and the free end of the foil will move away from the wire as shown in the diagram. If nothing is done to remove the charge it will persist for a long time, and will only very slowly "leak" away. As the charge disappears the gold foil, *A*, will creep in, and eventually when there is no charge left it will coincide with *B*. If the air in *D* is made conducting, say by blowing air over a spark and then through *D*, the charge will rapidly disappear. It is found that the introduction of a piece of a uranium mineral into *D* will similarly cause the rapid discharge of the electroscope, since the radiations from the uranium ionize the air and make it electrically conducting.

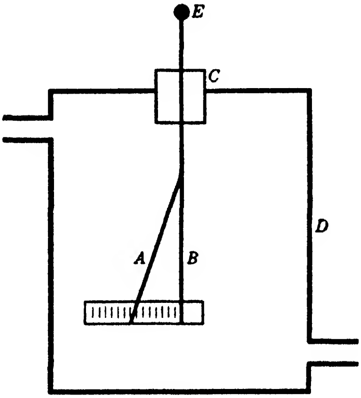


FIG. 34.—A Simple Electroscope.

It was found by the Curies that certain uranium minerals are more radioactive than others. They concluded therefore that these minerals must contain some impurity which was more radioactive than uranium itself, and they set out to search for this substance. In this search they used more or less conventional analytical technique for the separation of the different groups of elements, and after each precipitation they examined the precipitate and the filtrate with an electroscope to determine which contained the active material. In this way they were able to follow the active material in spite of its small amount. They were finally successful in isolating a new element, radium, belonging to the calcium, strontium, barium group, which possessed an intense radioactivity.

This new element was at first a source of great interest and bewilderment. Chemically it behaved normally in every respect. Nevertheless it gave off radiation continually, and also emitted much heat. The fact that an element could give off energy continually without being visibly changed in the process constituted an apparent exception to the law of the conservation of energy, and led to much speculation.

Radiations from Radioactive Substances.—Soon after the discovery of radium, Rutherford commenced an intensive investigation of the radiations from radioactive substances. The active rays were found to be of three distinct types, so-called α-, β-, and γ-rays. Deflection experiments with magnetic and electric fields showed that β-rays are negatively charged and have the same e/m as cathode rays. They are therefore merely electrons. Their velocity is much higher than that of electrons in discharge tubes, however, and they consequently have a high penetrating power, and can pass through considerable thicknesses of metal foil, etc.

γ-rays cannot be deflected by a magnetic field, and hence cannot consist of charged particles. They have a very high penetrating power. They are now known to be merely light waves of very short wave length.

α-rays may be shown by deflection experiments to carry a positive charge. They have a much smaller penetrating power than β- and γ-rays. The value of e/m for them is found to be one-half that for the hydrogen ion, H^+. It therefore appears that they are either H_2^+ or He^{++}. The question was settled by Rutherford who proved spectroscopically that helium is slowly formed when radium disintegrates. The α-particle is therefore a doubly charged helium atom.

Radioactive Disintegration.—The activity of radium chloride solutions was investigated by bubbling air through a solution of radium chloride, and then passing it into an electroscope. The activity of the air was then followed over a period of several days. It was found that the activity of the air from the radium chloride solution fell off slowly in accordance with the equation for a unimolecular reaction (see Chapter XV), i.e.,

$$\log \frac{I_0}{I} = Kt,$$

where I_0 is the initial activity, I is the activity after t seconds, and K is a constant. It was concluded that radium disintegrates to give an α-particle and a new substance which is itself radioactive. This substance is called radon, and given the symbol Rn. In other words, the first step in the disintegration of radium is

$$\text{Ra} \rightarrow \text{Rn} + \text{He}^{++}.$$

Radon is obviously a gas, since it is carried over with the air. By interposing cold traps between the electroscope and the radium chloride solution it was shown that radon can be condensed out with liquid air. Ramsay succeeded in collecting sufficient radon to enable a density determination, and thus found the atomic (or molecular) weight of the gas to be 222. Hence we have

$$\underset{\text{atomic weight } 226}{\text{Ra}} \rightarrow \underset{222}{\text{Rn}} + \underset{4}{\text{He}}.$$

Radon was found to be inert chemically, and to resemble in every way the rare gases in group 0 of the periodic table.

Since the activity of radon falls off with time according to the equation for a unimolecular reaction, the next step presumably is

$$\text{Rn} \rightarrow \text{other products}.$$

Investigations were made of the chemical properties and radioactivity of these products, and it was concluded that from radon a whole series of other new elements is obtained by successive disintegrations. In some of these disintegrations

α-particles are given off, in others β-particles accompanied by γ-radiation. The main course of events is

		Atomic Weight
$\alpha \swarrow$	Ra $\downarrow$	226
$\alpha \swarrow$	Rn $\downarrow$	222
$\alpha \swarrow$	Ra A $\downarrow$	218
$\beta \swarrow$	Ra B $\downarrow$	214
$\beta \swarrow$	Ra C $\downarrow$	214
$\alpha \swarrow$	Ra C_1 $\downarrow$	214
$\beta \swarrow$	Ra D $\downarrow$	210
$\beta \swarrow$	Ra E $\downarrow$	210
$\alpha \swarrow$	Ra F (Polonium) $\downarrow$	210
	End Product	206

When an alpha particle is emitted, the new element formed must have an atomic weight 4 less than its parent. Since a β-particle has a negligible mass, its emission results in practically no change in the atomic weight.

At first this disintegration hypothesis met with considerable opposition, since the idea of atoms splitting up into other atoms was repugnant to the classical chemist. The whole scheme outlined above, however, has now been established with certainty. Chemical investigation has shown that radium A, radium B, etc., have definite and distinct chemical properties which are entirely different from those of the substances from which they came. At first, however, there appeared to be certain fundamental difficulties in the above scheme. These were:

a. Ra B, Ra C, and Ra C_1 have properties which are quite different from a chemical point of view, and which suggest that the three substances belong to different groups in the periodic table. Thus Ra B exhibits the properties of an element of group 4, Ra C those of group 5, and Ra C_1 those of group 6. In spite of these chemical differences, however, all these elements are postulated to have the same atomic weight of 214. This is obviously inconsistent with the classical idea that the atomic weight is the fundamental chemical property.

b. Ra B and Ra D are found to have quite different "radioactive" properties, and to disintegrate at quite different rates. Their chemical properties, however, are identical, and if they are mixed they cannot be separated by chemical means. We thus appear to have two substances with the same chemical properties but different atomic weights (214 and 210).

c. The final product of the disintegration series is no longer radioactive. Since it does not disintegrate, it should accumulate with time and be present in amounts large enough to detect by ordinary chemical methods. Lead is present in all uranium ores; but the atomic weight of lead is 207.2, whereas the end product, since it is formed from Ra F which has an atomic weight of 210 by the loss of an α-particle, must have an atomic weight of 206.

We shall show later how these difficulties have been overcome.

The Rate of Radioactive Disintegration.—It has been mentioned above that the rate of radioactive disintegration obeys a unimolecular equation. It is found that this rate is entirely independent of the temperature, pressure, or state of chemical combination of the radioactive element. Each element thus disintegrates at a characteristic rate independent of all external factors. The most convenient measure of this disintegration rate is the time required for one-half of the original amount of material to disappear, or half-period. As we shall see in Chapter XV, this time is independent of the amount of material started with.

Some radioactive substances disintegrate at a conveniently measurable rate, and their half-period can thus be directly determined. Radon, for example, has a half-period of about 5 days, whereas radium B is much less stable and has a half-period of about 27 minutes. In a number of cases, however, the rates are so slow or so fast that they are not conveniently susceptible to direct measurement; thus radium itself has a half-period of the order of 1800 years, whereas that of radium C_1 is about 10^{-6} second. In cases of this kind the half-period can be conveniently estimated by an indirect method. The basis of this method can best be explained by the following analogy.

Consider a set of funnels with different-sized orifices, as shown in Fig. 35. Suppose that water flows into *A* from some outside source at a constant rate. The rate of flow out of *A* will depend on the hydrostatic head of water in *A*. Hence water will bank up until eventually the head in *A* is such that water flows out of the vessel at the same rate that it flows in. A steady state is then reached and the level will remain constant thereafter. In the same way the water levels in *B*, *C*, and *D* will adjust themselves until finally a steady state is reached throughout, and the heads of water in the four vessels are *a*, *b*, *c*, and *d*, respectively. It will be noted that at the steady state, the larger the orifice the smaller the head. Also, if we consider a given water molecule, it will remain longest in the vessel with the greatest head of water. Hence, if the average time spent by a water molecule in one of the containers is *L*, we have

$$\frac{L_a}{a} = \frac{L_b}{b} = \frac{L_c}{c} = \frac{L_d}{d}.$$

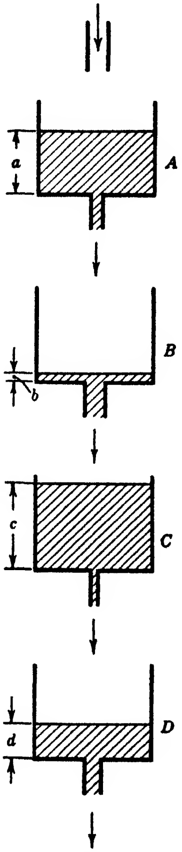


FIG. 35.

Similarly, in the case of the radioactive disintegration series, considerable material will accumulate when an element has a long life. If, however, it has a short life, it will disintegrate rapidly and very little of it will accumulate. Hence, suppose that we start with a certain amount of radium and wait until equilibrium is established and every element in the series is disintegrating as rapidly as it is being formed, then we shall have

$$\frac{L_A}{W_A} = \frac{L_B}{W_B} = \frac{L_C}{W_C} = \ldots,$$

where L_A, L_B, and L_C represent the average lives, and W_A, W_B, and W_C the amounts present at equilibrium. Hence by analysing the mixture of products at equilibrium (i.e., determining W_A, W_B, etc.) we can calculate the relative lives of the elements. Then, knowing the actual life of one of the members of the series, say radon, we can calculate the lives of the others. From the average lives the half-periods may be simply calculated. For the radium disintegration series the following half-periods have been found:

Element	Half-period, Minutes
Ra	9.4×10^8
Rn	5.5×10^3
Ra A	0.31
Ra B	27
Ra C	20
Ra C_1	1×10^{-8}
Ra D	8.4×10^6
Ra E	7.0×10^3
Ra F	1.9×10^5
End product	∞

The Disintegration of Uranium.—Radium has been found to be itself a product of the slow disintegration of uranium. The disintegration of uranium like that of radium proceeds through a series of intermediate radioactive elements, viz.,

$$\begin{tikzcd}
{} & U_1 \arrow[dl, "\alpha"] \arrow[d] & \text{at. wt.} = 238 \\
{} & U_{x1} \arrow[dl, "\beta"] \arrow[d] & 234 \\
{} & U_{x2} \arrow[dl, "\alpha"] \arrow[d] & 234 \\
{} & U_2 \arrow[dl, "\beta"] \arrow[d] & 230 \\
{} & \text{Ionium} \arrow[dl, "\alpha"] \arrow[d] & 230 \\
{} & \text{Ra} & 226
\end{tikzcd}$$

Two other elements, actinium and thorium, are also radioactive and disintegrate in a manner similar to the disintegration of uranium.

The Rutherford Nuclear Atom.—A large number of experiments have been made on the so-called scattering of α-particles. These show that α-particles can travel surprisingly long distances through metal foil, etc., before being deflected from their path by collision with an atom. This suggests that the atom is mainly "empty space." As we have seen, the atom is composed of two fundamental constituents, electrons, and a positive residue with which is associated the mass of the atom. In order to account for the results of α-particle scattering experiments, Rutherford suggested the *nuclear atom.* He assumed that the mass and positive charge are concentrated in a very small central nucleus, which is surrounded by electrons in a manner somewhat resembling the solar system. (See Fig. 36.) This theory has been exceedingly fruitful in the explanation of atomic phenomena.

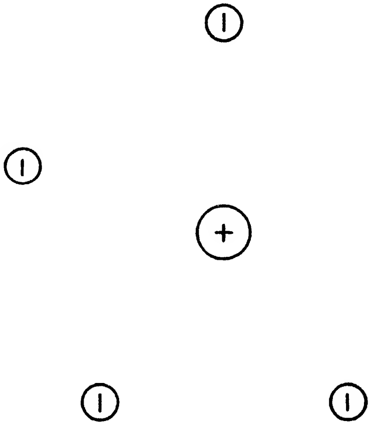


FIG. 36.

On this basis, atoms of different substances will differ from one another in the mass of the central nucleus and its charge, and in the number of external electrons. The central positive charge must obviously be equal to the total negative charge carried by the external electrons, since the atom as a whole is electrically neutral. The evidence from α-particle scattering indicates definitely that the number of charges on the nucleus, and hence the number of extranuclear electrons, increases steadily with increasing atomic weight of the atom. However, it remained to determine accurately the magnitude of the charge on the nucleus and the exact number of extranuclear electrons.

The quantitative determination of these factors was made by Moseley. If a target of some solid material is introduced into the path of a beam of electrons in a cathode-ray tube, it is found that light waves of very short wave length and high penetrating power are given off. These are called X-rays, and they have many practical applications. When such an X-ray tube is operated at high voltages, it is found that a large fraction of the emitted X-rays have wave lengths which are characteristic of the target used in the tube. For each substance used as a target a series of X-rays of different wave length are obtained. There are for each substance a number of groups of lines, those of shortest wave length being called the K series, those of next longer wave length the L series, etc. Moseley investigated the wave lengths of the lines in the K and L series for a large number of elements. He found that the wave length of any given line in the K or L series decreased steadily with increasing atomic weight, with one or two exceptions. These exceptions were found to be just those elements which have to be "misplaced" in the periodic classification of the elements in order to bring their chemical properties into line. If, instead of using the atomic weight as a criterion, we merely use the position of the elements in the periodic table, it is found that there is now a steady decrease in the wave length of the X-rays as we ascend the periodic table. Further, if we define the *atomic number* of an element as the ordinal number of its place in the periodic table, i.e., H = 1, He = 2, Li = 3, etc., Moseley found that the wave lengths for all elements were accurately given by

$$\sqrt{\nu} = a(N - N_0),$$

where ν is the frequency of the X-rays, a and N_0 are constants, and N is the atomic number.

The significant thing about this expression is that all the "exceptions" to the periodic law disappear when we substitute atomic number for atomic weight. Hence it appears that the atomic number, and not the atomic weight, is the fundamental property of an atom. It is now known that the atomic number is merely a measure of the charge on the nucleus. Hence, on the basis of the Rutherford atom, the following state of affairs exists.

The atomic number tells us the magnitude of the central positive charge and the number of extranuclear electrons. Thus consider a carbon atom. Carbon has an atomic number of 6. Hence its central positive nucleus must have a charge of 6, and there must be 6 extranuclear electrons. Now since the mass is associated with the positive charge, it is natural to consider the positive nucleus as being built up of single positive charges, each associated with a certain amount of mass. All evidence points to these charges being equal in magnitude and having associated with them equal amounts of mass. This fundamental positive charge with its associated mass is called a *proton*. Since the hydrogen nucleus contains only one positive charge, it is identical with the proton. We therefore have for the carbon atom a nucleus consisting of 6 protons, surrounded by 6 extranuclear electrons. This, however, would give carbon an atomic weight of 6, whereas in fact its atomic weight is 12. We must therefore assume that, although the *net* positive charge, or atomic number, is 6, the total positive charge on the nucleus is 12; but 6 of these are balanced by the presence of 6 electrons *in the nucleus*, in addition to the 6 extranuclear electrons. We thus obtain the structure for the carbon atom illustrated in Fig. 37.

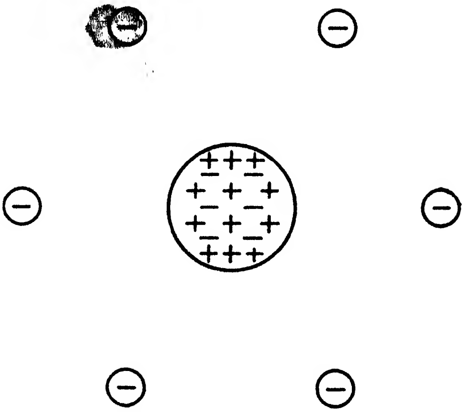


FIG. 37.—The Carbon Atom.

Protons in Nucleus = 12 = Atomic Weight
Electrons in Nucleus = 6
Net Positive Charge on Nucleus
= Number of Extranuclear Electrons
= Atomic Number
= 6

It will be seen that the atomic weight is a property of only secondary importance, being merely the total number of protons in the nucleus. The important quantity is the atomic number, which gives a measure of the net positive charge on the nucleus and of the number of extranuclear electrons.

Isotopes.—The difficulties in the application of the disintegration hypothesis to the radium series have already been noted.

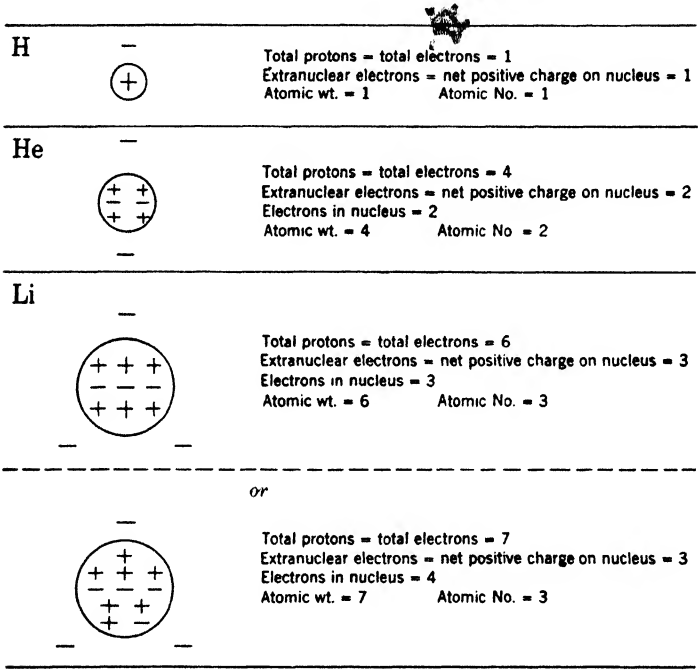


FIG. 38.

We are now in a position to explain these discrepancies. If we accept the idea that the atomic number is the fundamental property of an atom, rather than the atomic weight, then it is obviously possible for two atoms to be fundamentally the same, i.e., to have the same atomic number, although their atomic weights are different. Such substances are called isotopes. Thus consider the structure of the first few atoms in the periodic table, as illustrated by Fig. 38. In the case of lithium two isotopes exist, as shown. These have identical nuclear charges, and identical numbers of extranuclear electrons, and are therefore virtually identical in all respects except mass. Their atomic weights, however, are distinctly different, being 6 and 7, respectively. Ordinary lithium as found in nature is a mixture of these two in the proportions of approximately 1 of the isotope of mass 6 to 16 of the isotope of mass 7, giving an average atomic weight of 6.94.

The same situation holds exactly in the case of Ra B and Ra D, which are chemically identical, but have different atomic weights. Here we have

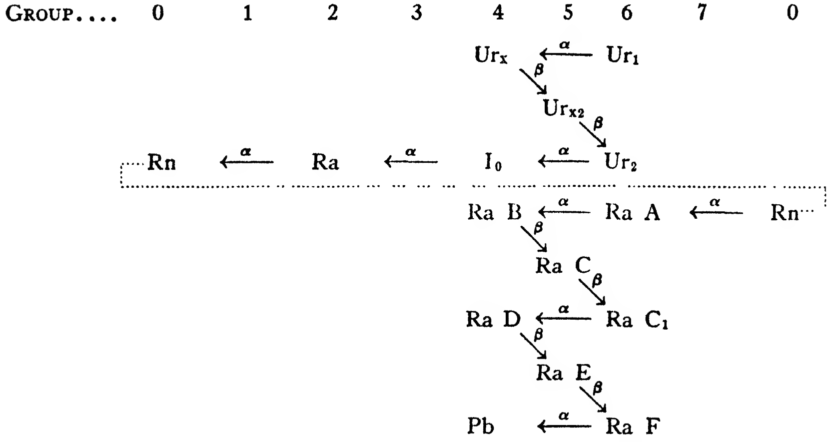
	Atomic Weight	Atomic Number	Charge on Nucleus	Protons in Nucleus	Electrons in Nucleus
Ra B......	214	82	82	214	132
Ra D......	210	82	82	210	128

Again, we saw that Ra B, Ra C, and Ra C_1 had different properties but the same atomic weight. In this case, although the atomic weights are the same, the atomic numbers are different, viz.,

	Atomic Weight	Atomic Number	Charge on Nucleus	Protons in Nucleus	Electrons in Nucleus
Ra B......	214	82	82	214	132
Ra C......	214	83	83	214	131
Ra C_1.....	214	84	84	214	130

Finally, it was mentioned that the indications were that the end product of the radium disintegration series was lead, but that its atomic weight is 206, whereas the atomic weight of ordinary lead is 207.2. It has since been shown by ordinary chemical atomic weight methods that lead derived from the disintegration of radium has an atomic weight of 206, whereas that derived from thorium has an atomic weight of 208, and ordinary lead is merely a mixture of the two isotopes. It follows therefore that the concept of the atomic number as the fundamental characteristic of an atom at once removes all the discrepancies in the radioactive disintegration hypothesis.

Radioactive Elements and the Periodic Law.—Investigation of the chemical properties of the elements involved in radioactive disintegration has shown well-marked regularities. It is found that when an element disintegrates with the loss of an α-particle, the element produced always has properties corresponding to those of a substance two groups to the left of the parent element in the periodic table. Similarly, the loss of a β-particle causes a shift one place to the right in the table. Thus with the uranium-radium disintegration series we have:



These facts find a ready explanation on the basis of the nuclear atom. Thus consider U_1. Let its atomic number be n, and let N_1 be the number of protons in its nucleus, and N_2 the number of electrons in its nucleus. Then, obviously

$$n = N_1 - N_2.$$

When U_1 disintegrates it loses an α-particle, i.e., He^{++}. The normal helium atom has an atomic number of 2 and an atomic weight of 4, i.e., it has 4 protons and 2 electrons in the nucleus, and 2 extranuclear electrons. The doubly charged helium atom has the same nucleus, but lacks the 2 extranuclear electrons. It follows that when U_1 loses an α-particle, its nucleus loses 4 protons and 2 electrons. Hence for the product of the disintegration, U_{x1}, we have

$$\begin{aligned}\text{atomic number} &= (N_1 - 4) - (N_2 - 2)\\ &= n - 2.\end{aligned}$$

Hence the atomic number of U_{x1} is two less than that of its parent, and it is therefore 2 places to the left in the periodic table.

U_{x1} in disintegrating loses a β-particle.

Hence for the product U_{x2}, we have

$$\text{atomic number} = (N_1 - 4) - (N_2 - 3)$$
$$= n - 1.$$

Hence U_{x2} is one place to the right in the table. U_{x2} also loses a β-particle to give U_2. Hence for U_2 we have

$$\text{atomic number} = (N_1 - 4) - (N_2 - 4)$$
$$= n.$$

Hence U_1 and U_2 are isotopes, and the atomic weight of U_2 is 4 less than that of U_1.

It should be noted that when an α-particle is lost by an atom there is a net loss of 2 positive charges from the nucleus. In order for the atom to be electrically neutral, 2 extranuclear electrons must also be lost. Until these are lost, the product of the disintegration is not a normal atom of the element formed, but a doubly charged negative ion. The extra electrons, however, are soon lost and the product becomes a normal atom. The electrons thus lost, however, are not shot out violently like β-particles. They merely leave with normal molecular speeds, and hence have no penetrating power, and do not exhibit the more spectacular properties of the β-particle.

The Identification and Separation of Isotopes.—It has been previously pointed out that in a cathode-ray tube the deflection of the rays in an electric or magnetic field is dependent on e/m. Similarly in the case of canal rays the deflection will be proportional to the charge and inversely proportional to the mass. Now most of the ions produced in such a tube will have only a single positive charge, so that the deflections of the particles in a mixture will be inversely proportional to their masses. With a suitable experimental arrangement a beam of such ions can thus be spread out into a mass spectrum, and the masses of all the particles present determined. Such an arrangement is called a mass spectrograph.

With the mass spectrograph investigations have been made with virtually all elements to determine whether or not the naturally occurring element is a "pure" one, or a mixture of isotopes. It has been found that a very large number of elements are composed of two or more isotopes. In particular, elements for which the atomic weight is not integral, or nearly so, are always found to be a mixture of isotopes. Thus Prout's hypothesis is finally vindicated. Typical examples are:

Element	Atomic Weight	Isotopes, in Order of Their Abundance
Lithium	6.94	7, 6
Neon	20.2	20, 22, 21
Magnesium	24.32	24, 25, 26
Chlorine	35.46	35, 37
Cadmium	112.4	114, 112, 110, 113, 111, 116
Tin	118.7	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
Mercury	200.6	202, 200, 199, 198, 201, 204

In the previous discussion isotopes were defined as identical in all respects except atomic weight. This is not quite accurate, and slight differences in other properties exist as well. In general, however, only those properties which depend on the mass of the atom are appreciably different. It has been possible in a number of cases to separate naturally occurring elements into their isotopic constituents. Various methods have been used for this purpose, the most important being:

(*a*) *Diffusion.*—Since the rate of diffusion of a gas is inversely proportional to the square root of the molecular weight, it is obvious that the separation of isotopes by this method is possible. Actually, however, it is very tedious, since the separation in each stage is very small, and a long-drawn-out series of fractional diffusions is necessary. However, it has been successfully applied in a number of cases, such as the separation of ordinary oxygen into its constituent isotopes of masses 16 and 18.

(*b*) *Separation by Chemical Reactions.*—The chemical differences between isotopes of the same element are exceedingly small, but partial separations have been effected by a laborious technique.

(*c*) *Other Physical Methods.*—Separations by fractional distillation, by the use of a mass spectrograph, and by photochemical means have also been successful to some extent.

(*d*) *Separation by Electrolysis.*—Urey and his collaborators have succeeded in separating ordinary hydrogen into two isotopes of masses 1 and 2 by the fractional electrolysis of water. The heavy hydrogen isotope (usually called deuterium, and given the symbol D) is present in ordinary hydrogen, or in the combined hydrogen of ordinary water, to the extent of about 1 part in 4500. The electrolytic process has been adapted to large-scale production, and water containing only the heavy isotope (D_2O) is now commercially available in moderately large quantities.

The hydrogen isotopes are in a class by themselves in so far as differences in properties are concerned, since in this case the percentage mass difference is much greater than in any other case. Thus the ratio of the masses of the two isotopes is here $2/1 = 2$, whereas in the case of, say, the chlorine isotopes, it is only $37/35 = 1.057$. However, even the hydrogen isotopes exhibit only comparatively small differences in properties.

In order to distinguish between the isotopes of elements, it is customary to write the chemical symbol with the atomic number as a subscript to the left, and the atomic weight as a superscript to the right. Thus the two hydrogen isotopes, instead of being designated H and D, may be written ${}_1H^1$, and ${}_1H^2$.

The Artificial Disintegration of the Elements.—In radioactive processes elements are disintegrating and new elements are being formed. The disintegration process is one which concerns the nucleus of the atom. This disintegration is spontaneous, and its rate is entirely unaffected by variations in the physical or chemical states of the substances concerned. It has, however, proved possible in a large number of cases to cause artificially the disintegration of ordinary stable atoms.

Two main methods have been used for such disintegration. In one of these, fast-moving α-particles from the radioactive disintegration of some element are allowed to collide with an atom of some other element. Provided that the collision is sufficiently violent and direct, the atom may be shattered.

The new atoms thus formed are often hitherto unknown isotopes, and are sometimes radioactive. As an example, if beryllium is bombarded with α-particles, we have

$$_{5}\mathrm{Be}^{10} + {}_{2}\mathrm{He}^{4} = {}_{6}\mathrm{C}^{13} + {}_{1}\mathrm{H}^{1},$$

i.e., a hydrogen atom is formed together with a carbon isotope of mass 13. In the other method of artificial disintegration a hydrogen or deuterium ion, H^+ or D^+, is formed, and this is then accelerated in a powerful electric field until it reaches enormous velocities. It is then used as a projectile and allowed to collide with an atom of some other element. A very large number of such transmutations have been carried out, and the subject is an exceedingly fascinating one for future investigation.

In addition to the actual transmutations, certain facts of very great importance have emerged from experiments of the type just described. It has been shown that, in addition to the electron and the proton, there are other particles which may be regarded as fundamental constituents of matter. The most important of these are the *positron*, a particle with a positive charge and a mass equal to that of the electron, and the *neutron*, which has a mass almost exactly equal to that of the proton, but no charge.

The discovery of the neutron necessitates some change in our previous discussion of the structure of the atomic nucleus. Thus for $_{3}\mathrm{Li}^{6}$ we previously had the structure

extranuclear electrons = 3
net positive charge on nucleus = 3
protons in nucleus = 6
electrons in nucleus = 3

It now appears that in place of every electron-proton pair in the nucleus we should have a neutron, viz.,

extranuclear electrons = 3
net positive charge on nucleus = 3
protons in nucleus = 3
neutrons in nucleus = 3

It will be seen that the net result is not very different from that given in the previous discussion.

The Quantum Theory.—In addition to the above lines of evidence, modern ideas of atomic structure are also largely based on information obtained from observations of the absorption and emission of radiation.

In order to explain the distribution of so-called black body radiation, Planck assumed that light energy was absorbed and emitted, not continuously, but in bundles, or quanta, of magnitude $h\nu$, where ν is the frequency of the radiation, and h is a universal constant.

Now it is found that atoms and molecules absorb and emit light of definite wave lengths only, each substance having its characteristic absorption or emission spectrum. This spectrum in the case of atoms consists of series of sharply defined lines spaced in a regular way. To explain these facts Bohr modified the Rutherford nuclear atom in such a way as to incorporate into it the quantum ideas of Planck. He assumed that the extranuclear electrons rotated in certain definite orbits around the nucleus, and that the energy of the atom depended on the orbits of the outer electrons. The absorption of a quantum of radiation by the atom was assumed to result in the transition of one of the outer electrons to an orbit further removed from the nucleus. We can thus picture the outside of the atom as consisting of a number of shells into which an electron may go, and the state of the atom will depend on which of these shells are occupied.

The quantitative application of these ideas has been of tremendous importance, and the application of the quantum theory to the problems of atomic structure has been the major theoretical advance of the present century. Recently the fundamental basis of the quantum theory has undergone modification, and the newer ideas have led to even more striking advances.

On the basis of the Bohr theory it becomes possible to calculate the orbits of the electrons, and to determine the number of electrons which can occupy each shell. Thus consider the rare gases, He, Ne, A, Kr, Xe, and Rn. These have atomic numbers of 2, 10, 18, 36, 54, 86, respectively, and these atomic numbers denote the number of extranuclear electrons which must exist in each atom. The Bohr theory indicates that these electrons are distributed in certain shells, usually designated by the letters K, L, M, etc., the K shell being the one closest to the nucleus. The distribution of the electrons for the rare gases is:

ATOM	SHELL					
	K	L	M	N	O	P
He	2					
Ne	2	8				
A	2	8	8			
Kr	2	8	18	8		
Xe	2	8	18	18	8	
Rn	2	8	18	32	18	8

Thus the structure of helium, neon, and argon is roughly that illustrated by Fig. 39. Since the chemical properties of an

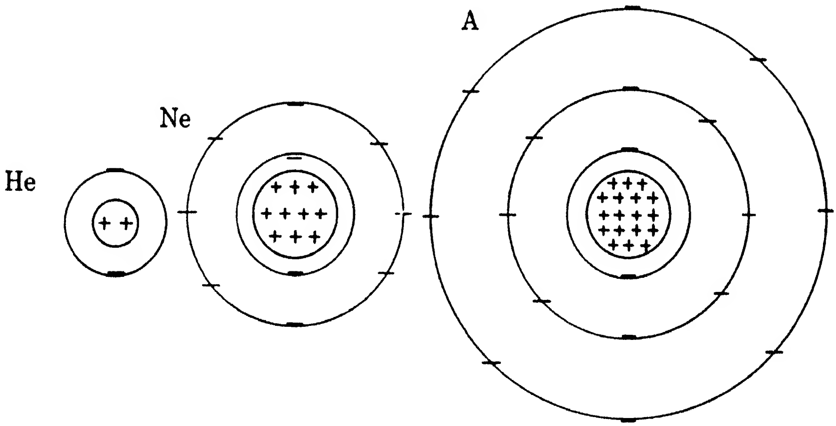


FIG. 39.

atom depend on the forces at its exterior, and the external shell is the same for all the higher members of the rare gases, the reason for the periodicity of properties is obvious.

The arrangement of the electrons in shells for other elements also offers a striking explanation of periodicity. For the lighter elements, for example, we have

Arrangement of Extranuclear Electrons in the Lighter Elements

Element	Atomic Number	K Shell	L Shell	M Shell	N Shell
H	1	1			
He	2	2			
Li	3	2	1		
Be	4	2	2		
B	5	2	3		
C	6	2	4		
N	7	2	5		
O	8	2	6		
F	9	2	7		
Ne	10	2	8		
Na	11	2	8	1	
Mg	12	2	8	2	
Al	13	2	8	3	
Si	14	2	8	4	
P	15	2	8	5	
S	16	2	8	6	
Cl	17	2	8	7	
A	18	2	8	8	
K	19	2	8	8	1
Ca	20	2	8	8	2

QUESTIONS

1. Describe the development of the classification of the elements, and state the periodic law.
2. Describe the cathode-ray tube, and the properties of electrons.
3. How may e/m for the electron be determined?
4. Discuss the relation between e/m for the electron and that for the hydrogen ion in electrolysis.
5. Calculate e/m for the hydrogen ion.
6. Describe Millikan's determination of the charge on the electron.
7. Discuss the properties of α-, β-, and γ-rays.
8. Discuss the disintegration of radium.
9. Describe the Rutherford nuclear atom.
10. Show that the atomic number is the fundamental property of an atom.
11. What are isotopes?
12. Discuss the chemical properties of the radioactive elements, and show that the hypothesis of the nuclear atom offers an explanation of the facts.
13. Discuss the identification and separation of isotopes.
14. Discuss the artificial disintegration of the elements.

CHAPTER VIII

ENERGY AND THE STRUCTURE OF MATTER

It has already been assumed in the preceding pages that the reader is familiar with the term energy, and with the law of the conservation of energy, of which use has been made on several occasions. The object of the present chapter is to consider certain forms of energy in relation to the structure of matter. The law of the conservation of energy, or first law of thermodynamics, will be discussed more thoroughly than is customary in elementary texts, and what is known as the second law of thermodynamics will be discussed in a non-mathematical way in order that deductions made from it may be used in subsequent chapters.

Energy.—There are some general concepts which are instinctively recognized by everyone, but which are very difficult to state in absolute terms on account of their fundamental nature. Since energy exists in innumerable diverse forms, this difficulty is especially pronounced in its case. For the purpose of our discussion, the most important forms of energy are kinetic energy, potential energy, and heat energy.

Energy in the science of mechanics is defined as the ability to do work, and involves the idea of a force acting through a distance, with which the reader is assumed to be familiar. The forms of energy dealt with in mechanics are kinetic energy and potential energy.

Kinetic energy is that energy which is possessed by a body in virtue of its motion, and is quantitatively represented by one-half the product of the mass and the square of the velocity. This motion may be transferred to some other body by collision, the other body thus acquiring energy.

It has been observed in certain cases that, when kinetic energy disappears, the resulting system is of such a nature that the lost kinetic energy can be regenerated. Suppose, for example, that a weight is thrown upwards from the earth's surface against gravity in an evacuated space. Its kinetic energy will decrease as it rises and will finally become equal to zero. Suppose that the body is supported at this point by resting on a ledge. If this support is removed, the body falls and retraces its former upward path in the reverse direction. Observation shows that its kinetic energy at any point will be exactly equal to that which it had during its upward motion. While the body is moving upward, therefore, and its kinetic energy is decreasing, we may say that its lost kinetic energy is being stored up, and that, under proper conditions, it may again be made available without any diminution in quantity. The body is therefore said to have transformed its kinetic energy into "potential energy," i.e., energy due not to its motion, but to its position relative to the earth's surface. We may therefore say that when kinetic energy disappears its exact equivalent in potential energy is produced. This statement is the result of a large number of experimental observations. Gravity is not the only cause of potential energy; a body possesses potential energy when it is under the action of any force which tends to cause it to move.

As indicated above, a body may possess energy in virtue of its motion or of its position. This is true not only in virtue of the motion or position of the body as a whole, i.e., "mechanical" energy, but a body may also possess energy in virtue of the motion or position of its component parts, such as molecules, atoms, etc. Energy of such a kind is usually referred to by special names such as heat energy, electrical energy, etc. The possibility of the interchange of these "forms" of energy, one into another, is of special importance in this chapter. This interchange may be illustrated as follows: Suppose that hydrogen is burnt in oxygen, as illustrated in Fig. 40, and the flame is directed against the bottom of a cylinder which contains water. The cylinder is fitted with a piston, whose weight is just balanced by the vapour pressure of the water. The heat given out by the burning hydrogen warms up the water, more water evaporates, and the piston is driven out by the increased vapour pressure. In other words, what may be called chemical energy has been transformed into heat energy, and this in turn into kinetic energy possessed by the moving piston. Although the only motion visible to the eye is that of the piston, an analysis of the phenomena which occur, from the point of view of the structure of matter, shows that throughout the whole process the energy of the system has been associated with motion. The molecules of hydrogen and oxygen before their combination possess some energy in virtue of their motion. When they combine to form water what may be called " chemical forces " come into play. Strong vibrations are set up in the resulting water molecules, and this vibration through collisions results in the increased motion of the molecules, i.e., the water molecules formed are moving more rapidly and are, in consequence, at a higher temperature. When these rapidly moving molecules (the flame) are brought into contact with the cylinder, their energy is communicated to the water, whose temperature is increased. Consequently the molecules in the liquid have their velocities increased. More molecules enter the vapour, the piston suffers an increased bombardment, and it moves out. The process may be summed up by saying that hydrogen and oxygen molecules have potential energy which results in rapid motion of the water molecules which they form. This motion is communicated through several intermediate stages to the piston itself. All the stages in the above process represent, therefore, either the motion of some material body or bodies, or else the potential ability to produce such motion.

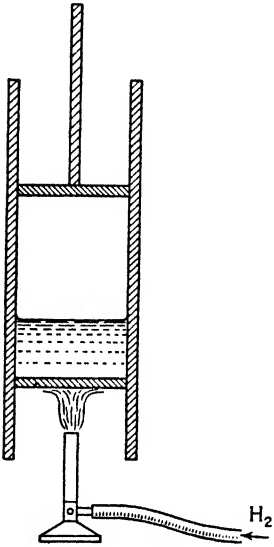


FIG. 40.

The Law of the Conservation of Energy: (The First Law of Thermodynamics).*—The next consideration is the magnitude of the energy in the various intermediate forms in which it occurs in a process such as that outlined above. In the case of

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* Thermodynamics as originally defined is the science which deals with the relation between heat and mechanical energy. The subject has since been extended to include the relation between heat and all other forms of energy.

large moving objects, the interchanges of kinetic energy which occur have been summed up in Newton's laws of motion. These are not an explanation of the mechanism of energy changes, but are an empirical summary of observed facts. In the case of interchanges of energy of different forms, another empirical law has been formulated on the basis of countless observations. This is called the first law of thermodynamics, or the law of the conservation of energy. This law has probably had a greater influence in the development of science than has any other law. Before stating the law explicitly, we will examine the question of the interchange of energy in greater detail.

The manifestations of energy have been classified, as pointed out above, into various forms, viz.: mechanical energy, heat energy, chemical energy, radiant energy, electrical energy, etc. An example has already been given of the interchangeability of certain forms of energy. Experiment has shown that when mechanical energy is transformed into heat energy a definite amount of heat energy is produced, and similarly if heat energy is changed back into mechanical energy there is again a definite amount formed. In other words, there is an exact equivalence between heat and mechanical energy. In general, it has been found that when any form of energy A is changed into a form B, if B can be changed back into A, the original amount of energy will invariably be reproduced. In other words, all observations lead to the conclusion that energy cannot be created or destroyed. This is the law of the conservation of energy, or the first law of thermodynamics.

It is beyond the scope of this book to deal with " action at a distance," or the transfer of energy through space by radiation. It may be pointed out, however, that radiation is connected with motion, and that it fits into the above scheme as a special form of energy.

Numerous attempts have been made to design a mechanism by means of which energy can be created, i.e., a " perpetual motion " machine. All such attempts have failed, and their failure constitutes an important part of the experimental evidence upon which the first law of thermodynamics is based. An alternative method of stating the law is therefore: A perpetual motion machine is impossible. Any attempt to create energy is thus frustrated by nature, but on the other hand all existing energy is indestructible.

The Second Law of Thermodynamics.—According to the first law, a perpetual motion machine is impossible, and when one form of energy is converted into another there is no loss or gain. The possibility of this conversion, however, has been found to be subject to certain limitations. As an example, consider a gas which is heat-insulated from its environment. The gas possesses energy in virtue of the motion of its molecules, i.e., heat energy. It has been found by experience that this energy cannot be continuously converted into mechanical energy by any mechanism which is not itself altered in the process. If, however, a medium at a lower temperature is available, then, and only then, can a mechanism be devised by which the heat energy of the gas can be converted into mechanical energy; and during the process there will be a flow of heat from the gas to the colder medium.

A striking illustration of this is furnished by the consideration of a vessel on an ocean at a constant temperature. The heat energy of the ocean is enormous, and there is ample energy to propel the boat back and forth across the ocean indefinitely. The heat energy taken from the ocean might be converted into mechanical energy and the boat driven by it. This mechanical energy would be converted back into heat by friction as the vessel moved, and would thus be returned to the ocean. As a result the vessel would be propelled at will without any net expenditure of energy.

All attempts to devise a process of this kind have proved futile, although such a process would in no way violate the first law of thermodynamics. Such a mechanism is called a perpetual motion machine of the second type. The impossibility of inventing such a mechanism is the practical result of what is called the second law of thermodynamics. This may be stated as follows: It is impossible by means of any mechanism to derive mechanical energy from any portion of matter by cooling it below the temperature of the coldest of surrounding objects, and heat of itself will never pass from one body to another at a higher temperature.

To revert to the previous example, a ship can be driven across an ocean only by means of energy from some source, such as the combustion of coal. This is an irreversible process, and the energy content of the system (i.e., ship plus fuel) is different at the end of the voyage from its original condition.

The second law is based upon a large amount of experimental observation. It may, however, be shown that it follows logically from the known structure of matter, and that under certain conditions it is inapplicable. The basis of what may be called the material concept of the second law is to be found in the tendency for ordered movement to become, and remain, chaotic.

The principle involved may be illustrated by the analogy of a pack of cards which have been arranged in the order of sequence of the various suits. If such a pack is shuffled, the ordered arrangement of the cards is destroyed, and the chance of its ever reappearing spontaneously with continued shuffling is extremely small. By far the most probable distribution will be one of the large number of possible random arrangements. The greater the number of objects " shuffled " the less will be the chance of their all taking up any particular orderly arrangement. In the case of a gas, in which the number of molecules is enormous, the probability of a random distribution depending on their movement, rather than any particular ordered arrangement, becomes a virtual certainty.

Suppose that we consider in more detail the specific case of the distribution of gas molecules in a confined space. Suppose that the distribution of molecules is such that there are more molecules on one side of a hypothetical plane through the centre of a given molecule than there are on the other. The chance of collision will then be greater on the one side than on the other, and the molecule will be apt to be deflected back into the region containing the smaller number of molecules. There will therefore be a tendency to maintain a uniform concentration of molecules in the gas. The larger the number of molecules considered, the smaller will be the chance of an appreciable variation in their concentration, i.e., in the density of the gas. Since even a cubic millimetre of gas at N–T–P. contains about 10^{16} molecules, the probability that there will be a uniform density becomes a virtual certainty, and every cubic millimetre of space in the gas will contain the same number of molecules within the accuracy of the most refined measurements. The probability that any measurable difference in the number of molecules in such a space will ever be detected is so small that it is a practical impossibility.

Since the gas molecules considered above are in violent motion, it follows that the sum of the velocity components of all the molecules in any direction must be equal to that in any other direction; otherwise, there would be a tendency for the molecules to accumulate in the direction of the larger velocity components. The tendency for the uniform concentration of gas molecules therefore implies a random directional distribution of molecular velocities when a system is in equilibrium. The chance is vanishingly small that any ordered directional motion of the molecules of a gas will arise spontaneously in a closed system.

Suppose that some regional ordered motion of molecules is started in a gas by an artificial means, and that there is thus a stream of molecules moving in a certain direction through the gas. The molecules in the van of such a stream will be subjected to more collisions from ahead than from behind. Their ordered motion will therefore be destroyed and the system will eventually revert to random movement.

The change of the heat energy of a gas into mechanical energy is due to the impacts of the gas molecules on some surface, such as that of a piston, which is free to move. If a solid disc is placed in a gas, the impacts of the molecules on either side of it will exactly balance each other, provided that the disc is large compared to the average distance between molecules. The energy inherent in the gas molecules cannot, therefore, be used to give kinetic energy to a uniform disc, i.e., heat energy cannot be transformed into mechanical energy in such a system. If an ordered motion of the gas molecules is artificially set up, then a disc placed in their path will receive more impacts on one side than on the other. Kinetic energy is therefore imparted to the disc, which thus acquires mechanical energy at the expense of the motion, i.e., the heat energy, of the gas molecules. An ordered motion of gas molecules can therefore be made to furnish mechanical energy. Such an ordered flow of molecules is said to possess " available " energy, i.e., the ability to perform work. It should be especially noted that such an ordered arrangement, and its concomitant available energy, cannot arise spontaneously in a gas at constant temperature.

Available Energy.—Suppose that two containers of equal volume, A and B, are filled with gas, and are separated by a common wall which can be removed at will. From the point of view of the possibility of obtaining mechanical energy from the system, we will consider four different cases. Let the pressures in the two vessels be P_A and P_B, the temperatures be T_A and T_B, and the number of molecules in each be N_A and N_B.

Case I.—Suppose that the same gas is contained in both compartments, and that $P_A = P_B$, $T_A = T_B$, and $N_A = N_B$. If the membrane is removed, the average distribution of the gas molecules in the two containers will not be altered in any way. It is true that diffusion from one compartment to the other will occur, but the number of molecules diffusing in either direction will be the same and the random distribution of molecular velocities will not be affected. There is therefore no ordered movement of molecules in any direction, and no mechanical contrivance can be devised by means of which the heat energy of the gas can be converted into work. In other words, as far as the mutual influence of the two compartments is concerned, there is no available energy in the system.

Case II.—Suppose that again there is the same gas in the two compartments. Let $T_A = T_B$, but P_A be greater than P_B, then N_A must be greater than N_B. In the chapter on gases we have already discussed such a system from the point of view of the energy changes which occur when a gas expands. When the membrane is removed there will be a directed movement of the molecules, i.e., a resultant velocity component in the direction of B which was originally at the lower pressure. This resultant motion exists until uniform distribution of the gas has taken place. Directed motion of molecules is a criterion of available energy, and there must therefore be some mechanism by means of which mechanical energy can be derived from the above system. For example, the membrane could be replaced by a piston head, and the pressure in the two compartments equalized by the motion of the piston, mechanical energy being thus obtained. It should be pointed out that in this process heat is converted into mechanical energy, i.e., the temperature of the gas as a whole falls and work is done. This is, however, not contrary to the second law of thermodynamics since the initial and final states of the gas are not the same. It can be shown that the amount of mechanical energy necessary to bring the gas back into its initial condition is exactly equal to the mechanical energy obtained in Case II.

Case III.—Again, suppose the same gas fills both compartments. Let $P_A = P_B$, but suppose that T_A is greater than T_B, then N_B must be greater than N_A. Suppose that the two containers are perfectly heat-insulated from the surroundings, and that they have no heat capacity. If the membrane is broken, temperature equalization will result, the gas in *A* being cooled and that in *B* being warmed. Since the initial pressures were equal, but the temperatures were different, the number of molecules in the cold compartment must have been greater than the number in the hot compartment. Consequently the equalization of temperature must be accompanied by a directed resultant movement of molecules from *B* to *A*. The system must therefore have possessed available energy. The following mechanism will indicate the manner in which some of this might have been obtained. Suppose that the membrane is replaced by a piston made of some heat-conducting material, and that the piston is clamped in position until temperature equilibrium is established. The pressure will fall in *A*, since the temperature falls, and will rise in *B*, since the temperature rises. The system thus reverts to Case II, and some of the heat energy possessed by the original system can be transformed into mechanical energy.

Case IV.—Suppose that $P_A = P_B$, $T_A = T_B$, and $N_A = N_B$, but that one of the compartments contains hydrogen and the other oxygen. When the membrane is removed interdiffusion of the two gases will occur. This must mean a directed motion of the molecules of each kind, and a resultant permanent alteration in the distribution of the molecules. In Case I, where *A* and *B* contained the same gas, the diffusion of molecules from *A* to *B* was exactly balanced by the diffusion of an equal number of molecules of the same kind from *B* to *A*. In the present case, however, when the membrane is first removed there is a diffusion of oxygen into hydrogen and of hydrogen into oxygen, which is not compensated. This uncompensated directed motion indicates that, with a proper contrivance, mechanical energy should be obtainable from the system. Such a contrivance may be very simply devised by means of a piston made of a "semi-permeable membrane," which will be described in a later chapter.

All the above contrivances have been described in order to show the possibility of obtaining mechanical energy from the system. It should be pointed out that the mechanisms described are not necessarily the most efficient in obtaining the largest possible amount of mechanical energy from the systems. When a mechanism is devised by means of which the available energy obtained from a system can be used to bring the system back again into its original state, such a mechanism is called a reversible one. The heat energy which is converted into mechanical energy in such a reversible process is the largest amount which could be transformed into mechanical energy by any possible device. This fact is of great value in various quantitative calculations.

Spontaneous Changes.—As we have seen, an ordered movement of molecules cannot arise spontaneously or persist in a closed system. This fact often furnishes a convenient method of demonstrating the impossibility of a supposition, by showing that if it were true it would lead to such a spontaneous continuous ordered movement.

Another important principle in this connection is that any process which occurs spontaneously always involves a loss of available energy, and hence can always be made to occur in such a way as to furnish mechanical energy. This is obvious from the molecular point of view, since ordered movement always tends to become chaotic, but there is no spontaneous tendency for chaotic movement to become ordered. We may therefore state as a general principle: The available energy of a system tends to become a minimum.

Since potential energy is always available energy, it follows that all systems tend to take up such a configuration that their potential energy is reduced to its minimum possible value.

The Principle of Le Chatelier.—It is possible to derive from the second law of thermodynamics certain quantitative relationships, which are applicable to systems in which there is a dynamic equilibrium between molecules. All these relationships can be qualitatively summed up in what is known as Le Châtelier's principle. This principle may be stated as follows: If an attempt is made to change the pressure, temperature, or concentration of a system in equilibrium, then the equilibrium will shift, if possible, in such a manner as to diminish the magnitude of the alteration in the factor which is varied.

As an example suppose we consider a cylinder, fitted with a piston, which contains a liquid and its vapour. If the piston is pushed in, an increase in pressure would naturally be expected. Condensation of vapour, however, results in a much smaller increase in pressure than would be anticipated, the only increase in pressure being due to the latent heat of condensation warming up the liquid and slightly increasing its vapour pressure. In other words, when we attempt to increase the pressure in the system, the liquid-vapour equilibrium shifts in such a way as to lessen the expected pressure change, by means of a diminution in the volume.

In general, we may say that an increase in pressure will always tend to cause an equilibrium to shift in such a direction that there is a decrease in volume. Similarly in an equilibrium which is dependent upon the temperature, the addition of heat (i.e., a rise in temperature) will always cause the equilibrium to tend to shift in such a direction that heat is absorbed.

Limitations of the Second Law of Thermodynamics.—The second law of thermodynamics may be applied rigorously, and without reservation, to almost all natural phenomena. It has, however, certain limitations which, while unimportant in themselves, are of interest because they show the necessity of taking into account the structure of matter even when dealing with energy changes.

According to the second law, the heat energy of a gas cannot be used continuously unless there is a difference in temperature between the gas and its environment. Attention has already been drawn to the fact that it is the average velocity of the molecules which determines the temperature, and that the velocities of individual molecules in a gas are subject to wide variations. It was suggested by Maxwell that, on account of the distribution of molecular velocities, processes could be imagined to occur which were contrary to the second law.

Suppose, for example, that two portions of a gas are separated by a membrane which contains a valve, the opening of which is of molecular dimensions. Suppose that the valve is operated by a thinking being ("Maxwell's demon") who can detect individual molecules. When the valve is closed, molecules will strike it on either side and will rebound into the compartment from which they came. If the demon opens the valve for fast-moving molecules coming from one compartment, and for slow-moving molecules from the other, it will be theoretically possible to separate the gas into two portions, one of which is at a higher temperature than the other. As we have seen in Case III above, the resultant system can perform useful work, the gas being cooled in the process. The gas can therefore take up heat until it is again in temperature equilibrium with its surroundings, and the above process can be repeated. In consequence it would be possible to continuously convert the heat energy of the surroundings into work, in violation of the second law of thermodynamics.

The above anomaly is due to the fact that the second law is based on experimentally observable systems, in which the average velocity of a large number of molecules is under consideration. The second law is only a statistical truth, which holds when the number of molecules concerned is large. That Maxwell's suggested mechanism is actually observable experimentally will be made evident later in connection with the Brownian movement of colloidal particles.

QUESTIONS

1. State the first law of thermodynamics and discuss its meaning.
2. State the second law of thermodynamics and discuss its meaning.
3. Discuss the second law from the point of view of ordered vs. chaotic movement of molecules.
4. Discuss the heat energy of a gas, a liquid, and a solid.
5. Discuss the application of the concept of temperature to gases, liquids, and solids.

CHAPTER IX

MIXTURES, SOLUTIONS, AND COMPOUNDS

Introduction.—In the discussion of matter in the various states of aggregation, we have so far been considering pure substances only. In the next few chapters the influence of one pure substance upon another will be discussed.

If two substances, A and B, are brought together at some definite temperature and pressure, the resulting system will fall into one of two classes. It may be either homogeneous or heterogeneous. We may distinguish between the two types by the analysis of samples taken from various parts of the system. If all the samples show absolute concordance in composition (i.e., exactly the same quantities of A and B), no matter how small the samples may be, then the system is said to be homogeneous. In a heterogeneous system, on the other hand, if sufficiently small samples are taken the analytical results begin to show wide fluctuations.

Phases.—It follows from the definition of homogeneity that if more than one state of aggregation is present the system must be heterogeneous. This will be true even if a single pure substance is under consideration. Thus a liquid in contact with its own vapour forms a heterogeneous system, because the amount of substance in unit volume of the liquid is different from that in unit volume of the vapour. Such a system, though heterogeneous considered as a whole, contains within itself two homogeneous systems, viz.: the liquid, and the vapour. Such a homogeneous system, which forms a part of a larger heterogeneous system, is called a phase.

Consider, for example, a system formed by bringing together equal amounts of water and ether in the liquid state. When equilibrium is reached, i.e., when all visible changes have come to an end, it is found that two liquid layers have been formed. Each of these layers is in itself perfectly homogeneous from the point of view of the analysis of minute samples. The composition of the upper layer, however, is quite different from that of the lower layer. The system as a whole is therefore heterogeneous, since as we pass through the liquid we encounter an interface where there is an abrupt change in properties. We thus have two homogeneous phases which are separated by an interface and which taken together compose a heterogeneous system.

Mixtures, Solutions, and Compounds.—A consideration of the foregoing definition of homogeneity will show that some ambiguity arises in connection with the size of the sample taken. In the case of a pure compound, for example, if the size of the sample were reduced until molecular dimensions were reached, various samples might by chance contain different numbers of atoms, and in consequence their composition would show large variations. Even with a somewhat larger volume, the chance distribution of molecules might lead to detectable fluctuations in the composition of a solution, or attenuated gas. On the other hand, a mechanical mixture may be so finely subdivided that the smallest samples which it is practicable to take would show perfect homogeneity. No rigorous definitions of homogeneity and heterogeneity are therefore possible. It is consequently of value to consider as many criteria as possible, by means of which a practical classification can be made of the various types of system which result when two different kinds of matter are brought into contact with one another.

Suppose that we consider three systems: sugar and sulphur; sugar and water; and copper and chlorine. These systems, when they have reached equilibrium, are usually called a mixture, a solution, and a compound, respectively. We will now discuss the various criteria by means of which such systems can be distinguished and classified.

Spontaneous Formation.—Suppose that the two ingredients in the above examples are in every case brought together and allowed to remain undisturbed. It will be found that the behaviour of the first pair is distinctly different from that of the others. Thus the sugar, without any agitation or other outside influence, disappears and spreads uniformly throughout the water. This action will occur even against the action of the force of gravity. Similarly the chlorine disappears spontaneously, reacting with the copper to form a chloride. On the other hand, if powdered sulphur is poured on top of powdered sugar no change occurs even after a long period of time. There thus seems to be no tendency to form a mixture spontaneously, and it must be prepared by mechanical means (grinding, stirring, shaking, etc.). The criterion of spontaneous formation can therefore be used to distinguish between a mixture, on the one hand, and a solution or compound on the other.

From a practical point of view this criterion possesses the one great disadvantage that it is dependent on the time which is allowed to elapse. Thus two solids, when brought into contact, will sometimes form a solid solution or a compound. These changes, however, may be so slow that they escape detection in a reasonable time. One thing is certain, however, and that is that the occurrence of a spontaneous change is definite evidence that the phase formed is not a mere mixture but is either a solution or a compound.

Homogeneity.—As previously mentioned, the homogeneity of a system furnishes a means of differentiating between mixtures and homogeneous systems (solutions and compounds). If sulphur and sugar are very finely ground and shaken up together a medium may be produced which appears to be uniform. If samples of a few tenths of a gram are taken from such a system they will show constancy of composition on being analysed. If a sample is observed by means of a microscope, however, differences become apparent, and if very small samples (0.001 gram) are submitted to micro-analysis, differences in composition may be detected. The test of homogeneity is therefore dependent upon our ability to analyse a sample so small that it is of an order of magnitude comparable to the fineness of subdivision of the two ingredients. From a practical point of view a degree of fineness can never be reached by mechanical means where such analysis is impossible. The finest particles obtained by grinding are incomparably greater than molecular dimensions, and usually contain billions of molecules.

Theoretically, of course, a distinction could also be made between solutions and compounds. In the case of solutions, samples of molecular dimensions would show differences in composition due to the chance distribution of molecules of solvent and solute. With compounds, however, the molecules are all alike, and heterogeneity could not be obtained without splitting the molecule.

The Properties of the System.—In a mixture the properties such as specific gravity, refractive index, magnetic permeability, etc., vary discontinuously throughout the system. In a solution or compound, however, no such variation is found until atomic dimensions are reached. The physical properties of a mixture are, in general, the average of the properties of the constituents. We can thus calculate the magnitude of the physical properties from the percentage composition of the mixture. In a solution the properties of the ingredients are considerably modified, but are usually readily discernible. The properties of a compound, on the other hand, are almost always quite different from those of its constituents.

The specific gravity is a property which serves as a convenient example of this behaviour. As we go through a mixture of sulphur and sugar the specific gravity varies from particle to particle; the average specific gravity, however, can be calculated exactly from the percentage composition, and the specific gravities of the constituents. In a solution of sugar in water, the specific gravity is uniform throughout the system. The specific gravity of the solution is not far from the average specific gravity of the constituents, but it cannot be calculated with any degree of exactness. The specific gravity of the compound formed from copper and chlorine is also uniform throughout. It is, however, totally different from the specific gravities of copper and chlorine, and cannot be calculated from them.

Variation in Composition.—The possibility of varying the composition of a system furnishes the most useful method of differentiating between a compound, on the one hand, and a solution or mixture, on the other. The composition of a solution or a mixture can be altered in a continuous manner; this, however, is not possible in the case of compound formation.

Thus chlorine and copper must be brought together in definite equivalent weights in order that a uniform homogeneous system may be formed whose composition is unaltered throughout. It is true that there are two such compounds which may be formed: cuprous chloride, which contains 63.3 per cent of copper; and cupric chloride, 47.0 per cent copper. No other uniform substance, however, can be formed by the combination of the two elements. The only possible variation in composition is therefore step-like in character, and the steps are few in number. On the other hand, the composition of a solution of sugar in water can be varied continuously, a uniform medium being produced no matter what the relative proportions of the two constituents may be. The only limit to such a variation in composition is the saturation concentration of the solution, which will be discussed later. Similarly, a mixture can be formed from its ingredients in any desired proportion without limit.

Mechanical Separation into the Constituents, and the Energy Changes Involved.—The means by which the constituents of a system may be separated, and the energy changes involved, furnish another important means of differentiating between the various types of system. In this connection it is often stated that the constituents of a mixture can be separated by mechanical means, whereas the constituents of a solution or compound cannot be so separated. In order to make such a statement of any value it is obviously necessary to give a precise definition of the term "mechanical means." This necessity is often avoided by merely giving examples of mechanical methods, such as hand-picking, filtering, centrifuging, etc.

The inadequacy of this method of classifying systems can be well shown by considering the example of centrifuging. When a mixture composed of two ingredients of different specific gravities is centrifuged, a separation of the constituents is brought about. This therefore constitutes mechanical separation. However, if a true solution is centrifuged a measurable change in the concentration of the constituents in different parts of the solution can be effected, provided that the speed of rotation is sufficiently great.

Again, a gas mixture, as will be seen later, is to be regarded as a type of solution. A partial separation of the constituents of such a system can be effected by diffusion through capillary tubes into an evacuated space. It is necessary to decide if such a process is to be regarded as a mechanical separation. Such uncertainties can best be avoided by rejecting the criterion of mechanical separation as such, and considering instead the energy which must be expended in order to effect the separation of the constituents.

In the case of a mixture, no energy is required to effect such a separation. In the case of a solution a measurable, perfectly defined amount of energy is necessary, the magnitude of which depends upon the concentration. With a compound a definite amount of energy is also necessary for the separation; the amount is dependent, however, solely upon chemical forces between the atoms involved. The above criterion furnishes the most fundamental method of classifying systems of this kind. It is impossible to give a completely satisfactory discussion of it in a qualitative way. The general idea, however, may be somewhat clarified by the consideration of the specific examples which follow.

It might appear at first sight that the separation of finely divided particles of, say, sugar and sulphur would require the expenditure of a certain amount of energy. Such, however, is not the case. Any particle in the mixture can be withdrawn from its neighbours without there being any tendency for it to revert to its original position. There is therefore no force coming into play during the separation, against which work must be done. In such "hand-picking," if the particle is moved upwards work is done against the force of gravity, but this work is obtained again when the particle is brought back to its original level. From the point of view of the energy involved, it is immaterial whether the particle is replaced in the mixture, or in some other container at the same level.

To remove a sugar particle from a solution of sugar in water, on the other hand, must involve a resultant energy change. It has already been noted that the sugar spreads spontaneously and uniformly throughout the water in which it is placed. In consequence its removal requires the expenditure of energy in opposing the tendency, or forces, causing this spontaneous dispersion.

It is obvious that the separation of the atoms in combination in copper chloride involves work against the forces of chemical affinity.

Suppose that we now revert to the subject of centrifuging. In the case of a mixture, if the machine is frictionless, no appreciable energy is required in the separation except that due to any movement against gravity. This energy is recoverable, and depends merely upon the levels to which the ingredients of the mixture have been moved. There is no innate tendency for the constituents to revert to their original position.

In the case of a solution, however, the separation brought about by a high-speed centrifuge requires the expenditure of a definite amount of energy. This is indicated by the fact that as soon as the centrifuge stops the solution automatically resumes its original state by diffusion. In the case of a gas mixture diffusing through capillary tubes into an evacuated space, it need only be pointed out that energy is required to create the evacuated space, which alone makes the separation by this method possible.

The fundamental ideas described above can be thoroughly understood only when the student possesses sufficient knowledge of physical chemistry to be able to undertake quantitative calculations of the energy changes involved.

All the criteria considered have been summarized in the table given below.

The Effect of Temperature and Pressure on the State of the System.—In the previous discussion, we have been tacitly dealing with systems under constant conditions of temperature and pressure. In some cases the system changes its type when these conditions are altered. The systems formed from iron and carbon furnish an excellent example of this. At low temperatures iron and carbon form a mere mechanical mixture. At higher temperatures, depending upon the conditions, either a compound Fe_3C or a solid solution of carbon in iron is formed. Steel is composed of iron and carbon, and its properties are intimately connected with the state of the system when hot, and also with the rate at which it was cooled to room temperature.

Systems Formed from Different Kinds of Matter

Method by Which System Can Be Distinguished	Heterogeneous	Homogeneous	
	Mixtures	Solutions	Compounds
Formation.	Not spontaneous.	Spontaneous.	Spontaneous.
Homogeneity.	Ceases when sample contains a large number of molecules.	Ceases when sample contains a small number of molecules.	Ceases when sample contains less than one molecule.
Physical properties of the system.	The average of those of the constituents.	Properties of constituents somewhat modified.	Properties entirely different from those of the constituents.
Variation of composition.	Continuous variation possible.	Continuous variation possible within limits.	Step-like variation only.
Mechanical separation into constituents, and energy changes involved.	No energy required for separation.	A definite amount of energy required, dependent upon the concentration.	A definite amount of energy required, not connected with relative proportions of the constituents.

QUESTIONS

1. Define phase, homogeneous system, heterogeneous sytem.
2. Illustrate by examples what is meant by a mixture, a solution, and a compound.
3. Discuss the criteria by means of which mixtures, solutions, and compounds may be distinguished from one another.
4. Discuss in detail the mechanical separation of the constituents of a system, and the energy changes involved.

CHAPTER X

SOLUTIONS

In the previous chapter we have discussed the nature of homogeneous systems, i.e., systems consisting of only one continuous phase. In the present chapter we will discuss those homogeneous systems which are composed of more than one chemical substance. Such systems are called solutions. The most common type of solution is that in which a solid is dissolved in a liquid; the word solution has, however, a much broader meaning than this. The following classification of solutions is convenient:

I. Gas dissolved in gas
II. Gas dissolved in liquid
III. Gas dissolved in solid
IV. Liquid dissolved in gas
V. Liquid dissolved in liquid
VI. Liquid dissolved in solid
VII. Solid dissolved in gas
VIII. Solid dissolved in liquid
IX. Solid dissolved in solid

In the above list the substance in the first-mentioned state of aggregation is usually called the solute, and the other substance the solvent. It is customary to consider the material present in smaller quantity to be the solute, and that present in larger quantity the solvent. Actually, however, this usage is governed by convenience. In particular, water is almost always referred to as the solvent even if it is present in small quantity. Thus we refer to a 95 per cent solution of alcohol in water, rather than a 5 per cent solution of water in alcohol.

A number of different methods are in use by means of which the concentration, i.e., the strength, of a solution may be expressed. These include:

Weight Per Cent.—This is defined as the number of grams of solute per 100 grams of solution.

Mole Fraction.—The number of gram molecules of solute divided by the total number of gram molecules of solute plus solvent.

Mole Per Cent.—This is the mole fraction multiplied by 100.

Gram Molecules Per Litre.—This is the number of gram molecules of solute contained in one litre of solution. It is the most convenient method of expressing concentrations when dealing with dilute solutions, and unless otherwise stated is the method used in this book. A solution which contains one gram molecule of solute per litre is called a molar solution. A *molal* solution is one which contains one gram molecule of solute per 1000 grams of water.

A numerical example will illustrate the above definitions. When 10 grams of sugar are dissolved in 90 grams of water a solution having a density of 1.040 is produced.

The weight per cent of sugar in the solution is obviously

$$\frac{10}{10 + 90} \times 100 = 10.$$

The mole fraction of sugar is given by:

$$\frac{\frac{10}{342}}{\frac{10}{342} + \frac{90}{18}} = 0.00581.$$

The mole per cent is this value multiplied by 100, i.e.:

$$0.00581 \times 100 = 0.581.$$

The number of gram molecules of sugar per litre may be found thus:

There is 10/342 gram molecule of sugar in 100/1.04 c.c. of solution. Therefore there is 0.304 gram molecule per litre.

We will now discuss the various types of solution in detail.

I. Gas in Gas.—According to the kinetic theory of gases, the pressure exerted by an ideal gas depends upon the number of impacts made by the molecules on the walls of the containing vessel. The pressure is therefore independent of the nature of the molecule, since at a constant temperature the kinetic energy of all gas molecules is the same. Consequently, in a gas mixture each gas will exert its pressure independently of the other gas, or gases, present. On account of the large distances between the molecules of a gas they are free to move about, and their chaotic movement will result in a uniform mixing whenever two or more gases are brought together. All gases are therefore completely miscible with (or soluble in) one another.

According to what is called Dalton's law, the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures which each would exert if separate. This law was based upon experiments in which known amounts of different gases were forced into a given volume. The total pressure was measured and compared with the sum of the pressures, calculated from the gas law, which each gas would have exerted alone.

As might be expected, more refined measurements have shown that Dalton's law holds accurately only at very low pressures. At higher pressures aberrations occur, due both to the volume of the molecules and to molecular attraction. In a mixture of two gases *A* and *B*, we have to consider not only the attraction of *A* molecules for *A* molecules, and of *B* molecules for *B* molecules, but also a new factor, viz.: the attraction of *A* molecules for *B* molecules. A few examples of aberrations from Dalton's law are given below. The experiments were performed by allowing equal volumes of gases at 25° C. to mix. The initial pressure of each gas was 760 mm.

Gas Mixture	Pressure after Mixing, Mm.
Helium-methyl ether	763.52
Helium-carbon dioxide	761.1
Hydrogen-methyl ether	763.1
Hydrogen-carbon dioxide	760.77
Sulphur dioxide-methyl ether	750.6
Carbon dioxide-methyl ether	759.9
Helium-hydrogen	760.0
Carbon dioxide-sulphur dioxide	759.17

From the above table it will be seen that the sum of the partial pressures may be either greater, or less, than the resultant pressure produced.

II. Gas in Liquid.—When a gas is brought into contact with a liquid it invariably dissolves to some extent. The actual solubility, however, may vary widely, depending on the particular gas and liquid under consideration. It is convenient to divide gas-liquid systems into two classes, those in which the solubility is small, and those in which it is large.

Gases which are slightly soluble dissolve to an extent which is proportional to the pressure of the gas in contact with the liquid. Thus if C represents the concentration of the dissolved gas in gram molecules per litre, we have

$$C = Hp,$$

where p is the pressure of the gas above the liquid, and H is a constant which varies from system to system. This relationship is known as Henry's law.

In the liquid state the molecules are still free to move about and there are spaces between them. Into these spaces the molecules of a gas may diffuse spontaneously. At first sight it might be expected that all gases would dissolve to approximately the same extent in all liquids, i.e., that H would be a universal constant. It must be remembered, however, that the molecules of a liquid are very close together. Molecular forces therefore come into play to a very large extent, and Dalton's law is not even approximately obeyed. In consequence H in Henry's law is a purely empirical constant. The value of H for a particular system remains constant only at constant temperature, and decreases rapidly with rise in temperature, i.e., the solubility of gases in liquids decreases as the temperature rises. Under high pressures Henry's law breaks down, as might be expected.

In the case of gas-liquid systems where the solubility is large, Henry's law does not hold at any pressure. Aqueous solutions of hydrogen chloride and ammonia furnish good examples of such systems. In both cases the formation of compounds between the solute and the solvent is a complicating factor, and is probably the cause of the aberrations from Henry's law. There are also intermediate cases such as the system sulphur dioxide-water. Part of the sulphur dioxide dissolves as a gas, and this part obeys Henry's law. In addition, some of the sulphur dioxide combines chemically with the water to form H_2SO_3. This part by no means obeys Henry's law.

In the following table some examples of the solubilities of gases in water are given.

SOLUBILITY OF GASES IN WATER

Gas	C.c. of Gas Dissolved by 1 c.c. of Water at 0° C., When the Pressure Is 1 Atmosphere
Oxygen	0.05
Hydrogen	0.02
Carbon dioxide	1.7
Ammonia	1299
Hydrogen chloride	506

III. Gas in Solid.—The solubility of gases in solids differs in general from that of gases in liquids in that it is a far less general phenomenon. Thus in the case of solid silver, oxygen is soluble to a moderate extent (about 0.35 c.c. of oxygen per c.c. of silver at 800° C. and a pressure of one atmosphere); hydrogen is also soluble to a very slight extent. No other gas, however, is soluble to a measurable extent. A rise in temperature causes an increase in the solubility of both oxygen and hydrogen in silver, i.e., the influence of temperature is the opposite of that in gas-liquid systems. At any given temperature the solubility of oxygen or hydrogen obeys a modified form of Henry's law, viz.:

$$C = K\sqrt{p},$$

where C is the concentration of the dissolved gas, p is the pressure of the gas in contact with the metal, and K is a constant.

The above example is typical of a large number of cases, for example: copper and hydrogen, nickel and hydrogen, iron and nitrogen, and copper and sulphur dioxide. Silica and helium obey the unmodified form of Henry's Law. It should be especially noted that the phenomenon is highly specific. A given solid will, in general, dissolve only one or two gases, all others being quite insoluble. This is quite different from the behaviour of liquids.

As with gas-liquid systems, there are also cases in which a gas is very soluble in a solid. In such cases the modified form of Henry's law is not applicable. Palladium and hydrogen furnish a good example of such a system. At 0° C. and a pressure of one atmosphere, about 980 c.c. of hydrogen are dissolved by 1 c.c. of palladium, In this case the solubility *decreases* as the temperature is increased. There is a certain amount of evidence to show that an unstable compound is formed in this case.

The Diffusion of Gases through Solids.—As a result of the specific nature of the solubility of gases in metals, it is possible to use a membrane of a metal such as palladium, which dissolves only hydrogen, for the separation of hydrogen from a gas mixture. Suppose, for example, that we have a mixture of hydrogen and nitrogen, each with a partial pressure of one atmosphere. The mixture is placed in a bulb (Fig. 41) which is separated from an evacuated manometer by means of a very thin membrane of palladium. The hydrogen is soluble in the palladium to an extent which depends on its pressure, and in virtue of this solubility it diffuses rapidly through the palladium at high temperatures in an attempt to form a homogeneous solution. Since the other side of the membrane is connected to a vacuum, hydrogen emerges from the palladium and enters the space above the manometer. This will continue until a pressure is reached such that the hydrogen on both sides is in equilibrium with the gas dissolved in the membrane. When this occurs the pressure of the hydrogen will be the same on both sides of the membrane. The pressure registered on the manometer will then be equal to the partial pressure of hydrogen in the gas mixture.

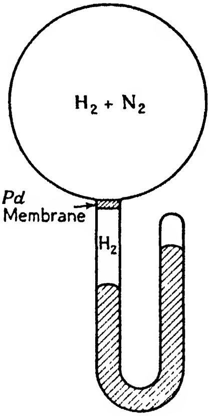

FIG. 41.

It should be noted that the above phenomenon depends upon the fact that the palladium membrane is permeable to hydrogen but not to nitrogen. Such a membrane which permits the passage by diffusion of one substance, but not that of another, is termed a "semi-permeable membrane." Such a membrane can be used for the measurement of the partial pressure of the gas to which it is permeable as shown above, or for the complete separation of such a gas from a mixture. As will be seen later, semi-permeable membranes are of great interest in connection with the constitution of solutions.

IV. Liquid in Gas.—Every liquid has a vapour pressure and will evaporate and enter the gas phase. All gases are completely miscible, and the vapour will therefore form a uniform solution with any gas which happens to be present. We may therefore say that every liquid is soluble in every gas. The concentration of vapour in equilibrium with the liquid is not the same when alone, however, as when in the presence of some other gas. In other words, the solubility of a liquid in a gas is different from what might be loosely termed its solubility in a vacuum. This difference is due to two causes. In the first place, if the gas pressure is high the liquid is appreciably compressed. This increases the vapour pressure of the liquid, since there are now more molecules per unit volume in the liquid than there are when it is not under pressure. This effect is independent of the nature of the gas above the liquid, and depends solely on its pressure. Added to this is another effect which depends upon the nature of the gas. Thus, when argon at a pressure of 100 atmospheres is brought into contact with liquid bromine, the equilibrium concentration of bromine in the gas phase is less than that in the presence of oxygen at the same pressure. In other words, bromine is more soluble in oxygen than in argon.

V. Liquid in Liquid.—Theoretically any two liquids are mutually soluble to some extent. The process of solution depends primarily upon molecular forces. These vary widely, and hence the extent to which the liquids are soluble in one another also varies over a wide range.

At this point is is necessary to discuss the terms saturation concentration and solubility. A criterion of the formation of a solution is the possibility of continuous variation in concentration, but not necessarily without limit. Starting from zero concentration, the concentration of a solution must be continuously variable, at least up to some measurable value. If such a measurable limiting value exists, it will represent the maximum possible concentration of solute. Such a concentration is referred to as the saturation concentration, or solubility of the substance in question. A solution having such a concentration is called a saturated solution.

There are thus two distinct types of liquid-liquid systems:

those in which the liquids are soluble in one another in all proportions (no saturation concentration); and those in which the liquids are not soluble in all proportions (a definite saturation concentration). Systems of the latter type will often form two liquid layers, each of which is a saturated solution of one liquid in the other.

In general, two liquids which have very similar chemical and physical properties will be soluble in one another in all proportions. Thus methyl and ethyl alcohol are miscible in all proportions with water, and with each other. Butyl alcohol, with its increased hydrocarbon chain, becomes too unlike water to be completely miscible with it; it is still completely miscible, however, with the other two alcohols.

With rise in temperature the influence of molecular attraction on the properties of liquids becomes less and less important, owing to their expansion and to increased molecular movement. The ability of two liquids to dissolve in one another therefore increases with rise in temperature. Thus secondary butyl alcohol and water become completely miscible at 114° C. Every pair of liquids which are not completely miscible at low temperatures become so at some definite temperature. Such a temperature is known as the critical solution temperature, by analogy with the critical temperature of a pure liquid, because it is the temperature at which the meniscus between the two layers disappears, and a single homogeneous phase results. In the case of two very dissimilar liquids, the critical solution temperature may be above the critical temperature of one of the substances, and consequently cannot be reached.

VI. Liquid in Solid.—Very little is known about this type of solution. The solubility of liquids in solids must not be confused with the sponge-like action by means of which some solids take up liquids. Such action merely consists of the filling up of minute interstices in the solid. Similarly, solubility must not be confused with compound formation, such as takes place when a substance like copper sulphate takes up water to form definite compounds (hydrates). Such compounds are usually known as compounds of crystallization, because they are most readily formed by crystallization on cooling a saturated solution. Thus, when a saturated solution of copper sulphate in water is cooled, the solid crystallizes out together with water of crystallization, in the stoichiometric proportions indicated by the formula $CuSO_4 \cdot 5H_2O$.

A good example of what might be termed a true solution of a liquid in a solid is furnished by the mercury-tin system. When a small amount of mercury is added to solid tin, a solid phase is formed in which the concentration of mercury can be varied continuously within limits, thus proving that a solution is formed and not a compound.

VII. Solid in Gas.—All solids possess a vapour pressure. All that has been said regarding the solubility of liquids in gases will therefore be applicable also to solids. Here also the solubility is often specific. The equilibrium concentration of iodine in the presence of oxygen is greater than that in the presence of argon at the same pressure.

VIII. Solid in Liquid.—All solids are soluble in all liquids, but the solubility, i.e., the concentration of the saturated solution formed, varies enormously from system to system. If the solubility is exceedingly small the solid is said to be " insoluble " in the liquid. Thus silica is usually said to be insoluble in water. If, however, water is boiled for a long time in a silica beaker, a measurable amount of silica is taken up by the water. The solvent often has a chemical action on the solid, and it is very difficult at times to distinguish between this action and true solubility. Thus the silica taken up by water is not dissolved as such, but is in the form of silicic acid. Perhaps the best way of distinguishing such chemical action from true solution is by attempting to reverse the process.

In the case of a true solution, a saturation concentration is reached beyond which no more of the solid will dissolve. This saturation concentration increases with rise in temperature in most cases. In the absence of the solid phase, it is possible to cool a saturated solution without the crystallization of the solid. Such a solution is known as a supersaturated solution. If a small crystal of the solid is added to such a supersaturated solution, the solid phase will crystallize out, and the concentration of the solution will diminish until a value is reached which corresponds to the saturation concentration at the temperature of the experiment. If the solid which crystallizes out under these conditions has the same composition as the solid which was originally dissolved, then it may be considered to have been in true solution.

Thus potassium chloride will dissolve in water to form a saturated solution having a composition of 26.4 per cent potassium chloride at 25.2° C. If a supersaturated solution at this temperature is brought into contact with a crystal of potassium chloride, solid will crystallize out until the solution reaches the above concentration. The solid which comes out is composed of crystals of potassium chloride, which are in every way similar to those originally dissolved. We may therefore say that potassium chloride is in true solution in water.

Very often, however, the phenomenon of solution is complicated by the formation of additive compounds between the solute and the solvent, which are themselves soluble. In this case the solubility is really that of the complex compound, and not of the original solid.

A good example of such solubility is furnished by copper sulphate and water. Anhydrous copper sulphate will dissolve in water at 25° C. to form a saturated solution having a composition of 17.4 per cent copper sulphate. From a supersaturated solution at this temperature, the solid phase crystallizing out is not $CuSO_4$ but $CuSO_4 \cdot 5H_2O$. The above solution may therefore be regarded not as a 17.4 per cent solution of $CuSO_4$ but as a 27.2 per cent solution of $CuSO_4 \cdot 5H_2O$. If a supersaturated solution of $CuSO_4 \cdot 5H_2O$ were made up and crystallized at the above temperature, the solid coming out would have the same composition as the original solid, viz.: $CuSO_4 \cdot 5H_2O$. Two separate phenomena therefore occurred when anhydrous copper sulphate was dissolved: (*a*) a chemical reaction $CuSO_4 + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O$; (*b*) the solution of $CuSO_4 \cdot 5H_2O$ in water.

The effect of temperature on the solubility of solids in liquids will be discussed later, when dealing with the theory of solutions.

IX. Solid in Solid.—Solutions of solids in solids are of great importance from a practical point of view, especially in metallurgy. The main difficulty involved in the investigation of such solutions is the fact that the criterion of spontaneity is masked by the excessively long time required for an appreciable change, when two solids are brought into contact. In consequence, such solid solutions are usually prepared by crystallizing from a liquid solution of the substances. Continuous variation in composition can be obtained by varying the composition of the liquid solution from which the solid is crystallized. If gold and silver, for example, are mixed together in various proportions, melted, and then cooled, solids are obtained which vary in composition and which are perfectly homogeneous down to atomic dimensions.

In certain cases it has been possible to investigate the spontaneous formation of solid solutions. When gold and lead are brought together, and pressure is applied to ensure good contact, it is found that gold diffuses into the lead even at room temperature. The amount of diffusion is small, but is quite definitely measurable after the lapse of a few years.

The formation of solid solutions is, of course, not limited to metals. Many organic compounds form such solutions, or " mixed crystals." A good example is furnished by naphthalene and beta-naphthol.

QUESTIONS AND PROBLEMS

1. Ten grams of benzene are added to 96 grams of toluene. The density of the resulting solution is 0.873. Calculate the concentrations of both constituents in terms of (*a*) gram molecules per litre; (*b*) weight per cent; (*c*) mole fraction; (*d*) mole per cent.

Ans.	C_6H_6	C_7H_8
(*a*)	1.055	8.59
(*b*)	9.434	90.566
(*c*)	0.1094	0.8906
(*d*)	10.94	89.06

2. One gram of oxygen and 2 grams of nitrogen are contained in a volume of 5 litres at 50° C. Calculate the pressure, assuming that Dalton's law holds.

Ans. 41.1 cm.

3. A gas dissolves in water and obeys Henry's law. At 10° C., 0.050 c.c. measured at N.T.P. are dissolved by 100 c.c. of water when the gas pressure is 50 cm. Calculate Henry's constant and the volume of gas dissolved when the pressure is 76 cm. *Ans.* 0.076 c.c.; 4.46×10^{-7} mole per litre per cm.

4. Measured at N.T.P., 0.35 c.c. of oxygen will dissolve in 1 c.c. of silver at 800° C. and a pressure of 1 atmosphere. Calculate the weight of oxygen dissolved by 1 gram of silver when the oxygen pressure is 25 cm. The density of silver is 10.5. *Ans.* 2.73×10^{-5} gram.

5. Ten grams of $BaCl_2 \cdot 2H_2O$ are dissolved in 1 litre of water. Calculate the concentration of the solute in weight per cent regarding the solute as (*a*) $BaCl_2$, (*b*) $BaCl_2 \cdot 2H_2O$. *Ans.* (*a*) 0.844 per cent, (*b*) 0.990 per cent.

6. State Dalton's law and discuss its limitations.

7. State Henry's law and discuss its limitations.

8. Discuss the solubility of gases in solids.

9. Discuss the diffusion of gases through solids

10. State the various types of solution, and give examples of each.

11. Discuss solutions of liquids in liquids, solids in liquids, and solids in solids.

CHAPTER XI

COLLOIDAL SYSTEMS

WHEN a substance which is insoluble in a liquid is suspended in it, the time required for settling will depend upon the degree of subdivision of the substance. By mechanical or other means it is possible to subdivide certain substances, such as gold or sulphur, to such an extent that the particles will remain in suspension in water indefinitely, in spite of the fact that their density is much greater than that of the liquid. Such substances are called colloids, or colloidal solutions. If their degree of subdivision is sufficiently great, they will appear to be perfectly homogeneous in any ordinary physical test. Furthermore, although most of these systems will not form spontaneously, the addition of further water to a colloid once it is formed is followed by a spontaneous spreading of the particles to form again an apparently homogeneous system. The ordinary methods of distinguishing the heterogeneity of a system fail when applied to colloids. Thus mechanical separation of the constituents by an ordinary filter is impossible. Special filters, however, with extremely fine pores can be used to separate the suspended particles from the medium in which they are dispersed. Whether a colloid can thus be mechanically separated depends upon the degree of fineness of the particles and of the pores of the filter.

The criteria given in Chapter IX to distinguish between a mixture and a solution are therefore inconclusive in the case of colloidal systems. It will be shown later that in certain cases colloids can be considered to behave as though they were solutions, whereas in other cases they apparently behave as mixtures. They are therefore to be regarded as border-line systems, which are in a sense both solutions and mixtures.

On account of the high degree of subdivision of colloids, their surface is exceedingly large. An intelligent appreciation of the properties of colloids is therefore possible only if the properties of surfaces are understood. The first section of this chapter will accordingly be devoted to a brief survey of the chemistry of macroscopic surfaces.

SURFACE CHEMISTRY

Interfaces.—An interface is the boundary between two phases. It is found that the properties of the material at an interface are often somewhat different from those of the same material in bulk. The concentration at the interface may also be different from that in either phase, and this phenomenon is called adsorption. Interfaces may be classified into six types, depending on the state of aggregation of the phases on either side of the boundary, viz., gas-gas, gas-liquid, gas-solid, liquid-liquid, liquid-solid, and solid-solid. Since all gases are completely miscible, the gas-gas interface can exist only momentarily. We have already discussed the gas-liquid interface in some detail in connection with the phenomenon of surface tension. Of the others, only the solid-gas and solid-liquid interfaces are of much importance for our present purpose. The solid-gas interface is much the simpler both theoretically and experimentally, and it will therefore be discussed first.

The Solid-Gas Interface.—It has been known for a long time that solids can take up gases. Thus if a piece of charcoal is introduced into a eudiometer containing gaseous ammonia over mercury, there is an immediate rise of the mercury in the tube owing to condensation of the gas on (or in) the charcoal. It is usual to distinguish between gas dissolved in the solid (absorption) and gas condensed on the surface of the solid (adsorption).

Practically all gases are adsorbed by all solids to an extent which can be measured under the appropriate experimental conditions. There is, however, a great variation in the quantities of various gases adsorbed by a given solid. Thus, for example, a given sample of charcoal adsorbed the following quantities of different gases (expressed as cubic centimetres of gas adsorbed by one cubic centimetre of charcoal when the pressure of the gas was one atmosphere).

Gas	Ar	O_2	CO	N_2	H_2	He
at 0° C	12	18	21	15	4	2
at −185° C.........	175	230	190	155	135	15

It will be seen that in general the more easily liquefiable gases are the more strongly adsorbed. Since adsorption is a surface effect, the amount of gas taken up will depend upon the extent of the surface. Consequently there are very large variations in the adsorptive powers of different samples of charcoal.

The effect of the pressure of the gas on the amount of adsorption is marked, as may be seen from Fig. 42. To describe the variation of adsorption with pressure, Freundlich proposed the empirical equation

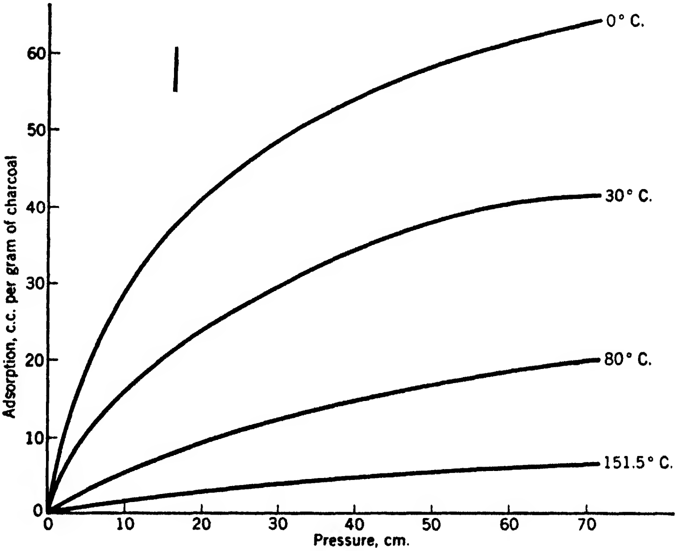

Fig. 42.—The Adsorption of Carbon Dioxide by Charcoal.

$$a = \alpha P^{1/n},$$

where a is the amount of gas adsorbed, P is the pressure, and α and n are constants for a given temperature and system. This equation fits experimental results satisfactorily except at high pressures. It follows from this equation that a plot of log a against log P gives a straight line. The equation of Freundlich would indicate that adsorption should increase indefinitely as the pressure is raised. As we shall see later, the evidence points to a saturation limit to adsorption, and hence the equation does not hold at high pressures.

Langmuir's Theory of Adsorption.—As we have seen, in a solid crystal the molecule loses its identity, and the solid is to be regarded as composed of an aggregation of atoms each of which is held to its neighbours by forces which may be regarded as "chemical" in nature. Langmuir points out that from this viewpoint the atoms on the surface of the solid are to be regarded as unsaturated. He suggests that the adsorption of a gas is really due to chemical combination with these surface atoms. Thus the adsorption of oxygen by tungsten will be as represented in Fig. 43. This, of course, is quite different from the formation of a definite oxide layer on the surface, since in the case of adsorption the oxygen atoms are to be regarded as chemically combined with the surface atoms of tungsten, *which in turn are combined with the underlying tungsten atoms.*

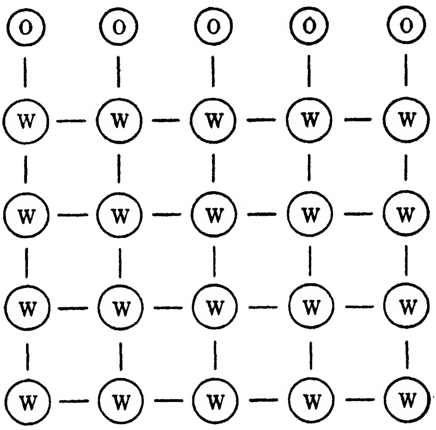

FIG. 43.—Langmuir's Representation of the Adsorption of Oxygen by Tungsten.

It is apparent that from the Langmuir point of view it is unlikely that the adsorbed layer of gas will ever be greater than one molecule thick. It is thus to be expected that as the pressure increases saturation will eventually be reached, and further increase in pressure will have no effect on the amount adsorbed. It is difficult to make accurate tests of this question, but what evidence there is seems to favour Langmuir's conception of an adsorbed layer one molecule deep.

The Solid-Liquid Interface.—From the point of view of adsorption the solid-liquid interface is very similar to the solid-gas interface. It is, however, much more difficult to deal with from an experimental point of view. It is almost impossible to investigate the adsorption of a pure liquid by a solid. We can, however, easily investigate the adsorption by a solid of a substance which is dissolved in a liquid. For example, charcoal is used as a decolorizing agent for dye solutions. The amount of a dissolved substance adsorbed is a function of the concentration, and the Freundlich equation also holds here, i.e.,

$$a = \alpha c^{1/n},$$

where c in this case represents the concentration of the dissolved substance instead of the pressure.

On account of the peculiar shape of the adsorption-concentration curve, very large amounts of material may be adsorbed at very low concentrations. This is the cause of numerous effects where a very small amount of a dissolved substance produces large changes in the properties of a system. Examples are catalytic phenomena, the action of enzymes, the effects of disinfectants and poisons, and a large number of biological phenomena. In all these cases where minute quantities of material have a pronounced effect an adsorption process of some kind is occurring, and the substance responsible for the effect exists in high concentration in the adsorbed layer in spite of its low concentration in the solution. The shape of the adsorption-concentration curve is also responsible for the fact that it is extremely difficult to wash out the last traces of an adsorbed substance. The fastness to washing of some types of dyes is due to this cause.

The mere presence of a large surface does not necessarily mean that there will be large adsorption; in fact adsorption is a highly specific phenomenon. There are, however, some rough general rules which may be given. Adsorption is usually small for all inorganic substances with the exception of the halogens. The salts of the heavy metals are adsorbed to a greater extent than those of the alkali metals. Organic substances are much more strongly adsorbed, especially aromatic compounds. In general, for all compounds, the more complicated the molecule the more strongly is the substance adsorbed.

The Adsorption of Electrolytes.—The adsorption of electrolytes follows the same general laws as that of non-electrolytes. It appears, however, that the adsorbed particle in this case is an ion, not a molecule. The ions of one sign are more or less firmly attached to the adsorbing substance. This gives the surface an electrical charge, and the electrostatic forces thus set up attract the ions of opposite sign, which form a sort of loose outer layer. Thus if sulphuric acid is adsorbed on a platinum surface, we shall have the state of affairs shown in Fig. 44.

Certain complicated effects are frequently observed on account of the ionic nature of the process. Thus suppose that manganese peroxide is prepared from potassium permanganate and sulphuric acid. The precipitated peroxide will be strongly acid, but if it is washed thoroughly a stage will be reached where it will no longer be possible to detect acid in the wash water. If, however, a neutral solution of potassium chloride is now added it will become acid. This is due to the fact that the particle was originally covered by an adsorbed layer of sulphuric acid similar to that illustrated in Fig. 44. On adding potassium chloride, however, the potassium ions largely displace the hydrogen ions from the outer layer, leaving the particle as represented in Fig. 45. The displaced hydrogen ions take the place of the potassium ions in the solution, which thus becomes acid.

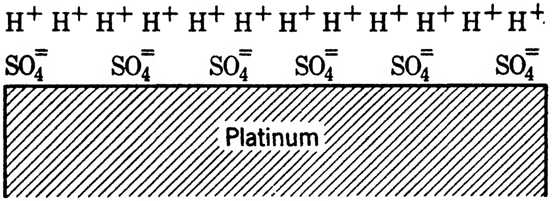

FIG. 44.

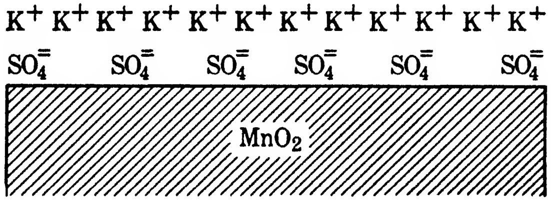

FIG. 45.

DIFFERENTIATION BETWEEN COLLOIDS AND SOLUTIONS

It is, in the first instance, obviously important to know how we can tell when a colloidal system is being dealt with. There is, of course, no hard and fast way of differentiating between colloids and true solutions. It is, however, possible to give certain general methods of testing a system to determine whether or not it is colloidal in nature. These are discussed below:

(a) **Spontaneous Formation.**—A sugar solution will form spontaneously if sugar and water are merely brought together. A colloidal solution of silver in water may be obtained by reducing an aqueous solution of silver oxide with hydrogen. If, however, we merely put a lump of silver in water, the silver will not spontaneously disperse itself throughout the water. Thus the formation of a colloidal solution of silver can be brought about only in an indirect way. In general colloidal systems cannot be formed spontaneously. It is true that if we put a lump of gelatin in water it will spontaneously disperse itself. However, in this case the "dry" gelatin is really a concentrated colloidal system of gelatin in water, and we are not observing the spontaneous *formation* of a colloid, but merely the spontaneous *dilution* of an already existing colloidal system.

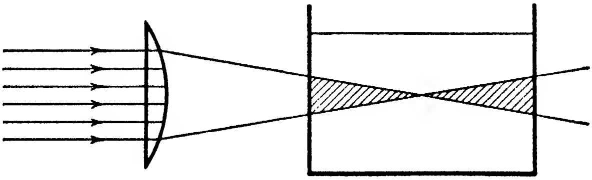

FIG. 46.—The Tyndall Effect.

(b) **The Tyndall Cone.**—If light is passed through a medium in which there are discontinuities and if the size of the discontinuities is of the same order of magnitude as the wave length of the light, then light is scattered and the path of the beam becomes visible when observed from the side. We thus get a so-called Tyndall cone (Fig. 46) with colloids but not with solutions, since the molecules in a true solution are too small to scatter an appreciable amount of light.

This phenomenon can often be observed when a beam of sunlight enters a darkened room. Owing to the presence of dispersed dust and smoke in the air the path of the sunlight is visible.

(c) **Filtration.**—Both true solutions and colloids will pass through ordinary filter paper. It is, however, possible to construct filters of unglazed porcelain (ultrafilters) which will filter out a colloidally dispersed substance.

(d) **Dialysis.**—This is somewhat similar to ultrafiltration. It is found that substances in true solution will pass through parchment, collodion, or animal membranes, but the larger particles in a colloidal system cannot do so.

(e) **Diffusion.**—True solutes will usually diffuse through a gelatin jelly, but colloidal particles will not. If the material in question is coloured the test is easy to apply.

THE CLASSIFICATION OF COLLOIDS

Sols and Gels.—A *sol* is any colloidal system which is liquid. A *gel* is a jelly-like system formed when a sol solidifies.

Disperse Phase and Dispersion Medium.—If we have a suspension of particles in a fluid, it is customary to refer to the particles as the *disperse phase,* and to the fluid as the *dispersion medium.* It is to be noted that the disperse phase is discontinuous, i.e., to get from one part of it to another the boundary into the dispersion medium must be crossed. On the other hand, the dispersion medium is continuous, and any part of it can be reached from any other part without crossing a boundary.

Types of Dispersion.—There are nine possible types of colloidal system. These are listed below, the disperse phase being named first in each case.

(1) *Gas in gas*	Does not exist since all gases are mutually miscible.
(2) *Gas in liquid*	Foam.
(3) *Gas in solid*	Occurs in certain minerals, small bubbles of gas being scattered through the mineral.
(4) *Liquid in gas*	Mist.
(5) *Liquid in liquid*	Emulsion.
(6) *Liquid in solid*	Jellies or gels.
(7) *Solid in gas*	Smoke.
(8) *Solid in liquid*	Sol, or suspension.
(9) *Solid in solid*	Coloured glass, etc.

Of these, we will confine our attention to types (6) and (8), since these are by far the most important.

Types of Sols.—There are two main types of sols:

(*a*) *Suspensoids, or Lyophobic Sols.*—In these the particles and the liquid remain distinct, and no hydration or absorption of liquid by the particles occurs.

(*b*) *Emulsoids, or Lyophilic Sols.*—In these the particles are strongly hydrated (or solvated, if the dispersion medium is a liquid other than water).

The two types of sols differ in several respects in a striking manner. Lyophobic sols are almost invariably inorganic, whereas lyophilic sols are usually organic, and are frequently of biological origin. The physical properties, such as density, freezing point, etc., of lyophobic sols are usually almost exactly the same as the corresponding properties of the dispersion medium. The physical properties of lyophilic sols, on the other hand, generally differ greatly from those of the dispersion medium. This is especially true of the viscosity. A striking difference between the two types of sols is exhibited in their behaviour towards added electrolytes. Lyophobic sols are very sensitive to, and are flocculated by, small amounts of electrolytes. On the other hand, it requires very large quantities of electrolytes to affect the stability of lyophilic sols.

It should be noted that this classification of sols is not absolutely hard and fast, and that there are cases which are intermediate between the two types.

THE SIZE OF COLLOIDAL PARTICLES

On account of the very small size of colloidal particles, special units are, for convenience, used in their description. It is customary to designate 0.001 mm. as 1μ (pronounced, and often written, mu), and 0.000001 mm., or 0.001μ, as 1 $m\mu$ (millimu). In order to enable a visualization of such quantities, it may be mentioned that the smallest object which can be seen with the naked eye under ordinary lighting conditions is about 5μ. With a microscope it is possible to distinguish objects about 100 $m\mu$ in diameter, or slightly less. The wave length of red light is about 600 $m\mu$. A hydrogen molecule has a diameter of 0.2 $m\mu$.

As we have emphasized before, it is not possible to draw hard and fast lines between solutions, colloids, and coarse suspensions or mixtures. For convenience, however, it is customary to define the colloidal range as extending roughly from diameters of 5 to 500 mμ, i.e., from about 25 times the diameter of a hydrogen molecule up to well within the limits of an ordinary microscope.

On account of the small size of colloidal particles, their surface area per unit mass is enormous, and a great many of the properties of colloidal systems are due to this extensive surface. As an illustration of the way in which the surface area increases with the degree of subdivision, suppose that we start with a 1-cm. cube of material, and repeatedly subdivide it into cubes having one-tenth the length of side. We thus obtain

Length of Side	Number of Cubes	Total Area
1 cm	1	6 cm.^{2}
0.1 cm	1000	60 cm.^{2}
0.01 cm	10^6	600 cm.^{2}
0.001 cm	10^9	6000 cm.^{2}
0.0001 cm. = 1 μ	10^{12}	6 m.^{2}
0.00001 cm. = 0.1 μ	10^{15}	60 m.^{2}
0.000001 cm. = 0.01 μ	10^{18}	600 m.^{2}
0.0000001 cm. = 1·mμ	10^{21}	6000 m.^{2}

LYOPHOBIC SOLS

In considering lyophobic sols it must be remembered that they may be regarded from two distinct points of view.

(*a*) The sol may be considered to consist of molecular-kinetic particles, i.e., to be merely a limiting case of a solution in which the molecules of the solute are very large.

(*b*) The sol may be considered to be an interfacial system with a very large total surface.

The complexity of colloid chemistry is thus entirely due to the fact that the systems are at once both homogeneous and heterogeneous.

The Preparation of Lyophobic Sols.—Since we are concerned primarily with the principles of the subject, it is not necessary for us to go into the methods of preparing colloids in any detail. We shall therefore mention merely a few of the main methods of preparation. It may be remarked that under suitable conditions virtually any substance may be dispersed in any other in which it is insoluble to form a colloid, provided, of course, that the substances do not react with one another chemically.

There are two main methods of preparing lyophobic sols, *condensation methods* in which the colloidal particles are built up from molecules and *dispersion methods* in which larger particles are broken up into smaller particles of colloidal size.

Condensation methods consist merely of the preparation of an insoluble substance by a chemical reaction between dissolved substances. At the moment of formation, of course, the insoluble material is in the form of molecules, i.e., the first step is really the preparation of an enormously supersaturated solution of an insoluble substance. The insoluble material then forms a precipitate, or a colloidal suspension, depending on the conditions. Thus colloidal silver may be prepared by the reduction of a solution of silver oxide by the reaction

$$Ag_2O + H_2 = 2Ag + H_2O.$$

Similarly colloidal sulphur may be prepared by the reaction

$$2H_2S + SO_2 = 3S + 2H_2O,$$

or colloidal ferric oxide by the hydrolysis of ferric chloride

$$2FeCl_3 + 3H_2O = Fe_2O_3 + 6HCl.$$

In dispersion methods we start with large particles of the material to be dispersed and break them up into small ones. This may be accomplished by grinding a solid under a liquid, by the addition of certain substances called peptizing agents (thus ferric oxide can be peptized to give a colloidal dispersion by adding ferric chloride), or by passing an electric arc between metal rods under water.

Lyophobic Sols from the Kinetic Viewpoint.—In 1827 Brown observed that pollen grains suspended in water were in continual irregular motion. It was shown that inanimate material behaved in the same way if sufficiently finely divided, and that the phenomenon was not connected with convection currents, chemical action, etc. The motion is now known to be due to molecular impacts. If we have a particle suspended in water it is subject to continual bombardment from the surrounding molecules. Over a long period of time the total number of impacts will be practically the same from all sides, and hence there should be no resultant motion. With short intervals of time, if the particle is small, the impacts in some one direction may predominate, and hence there will be an irregular random motion.

As we have seen, in a perfect gas the kinetic energy of all the molecules in a gram molecule is $3/2\ RT$. Hence the kinetic energy of a single molecule is $3/2\ (RT/N)$. Thus in a perfect gas the kinetic energy of a single molecule depends on the temperature and on nothing else, i.e., it is independent of the molecular weight. Hence if we have a large colloid particle in temperature equilibrium with the surrounding medium, it must have a kinetic energy due to molecular agitation which is equal to that possessed by one molecule of a gas at the same temperature.

It follows that a brick in a bucket of water will have a kinetic energy equal to that of one water molecule. The mass of the brick is enormously greater than the mass of a molecule, and hence since the kinetic energy is equal to $1/2\ mx^2$, the velocity of the brick will be immeasurably small. (A one-gram weight in equilibrium with the atmosphere at room temperature has a velocity due to molecular agitation of about 12 cm. per year. Of course, its actual path is a zigzag one, and it will not be displaced anything like this amount from its original position at the end of a year.) With small colloidal particles, however, the mass of the particle may be only a few million times the mass of a molecule, and hence its velocity will be a few thousand times less than that of a molecule. Such motion is readily observable under the microscope. An observed particle of this kind will behave kinetically like a molecule of gas or solute in every way, and it has thus been possible to obtain visual confirmation of many of the predictions of the kinetic theory of gases.

In the light of the Brownian movement we can regard sols as solutions of enormous molecules. From this point of view we can explain all the colligative properties, i.e., those properties which are dependent on the number of molecules present and not on their kind. From this standpoint all sols are extremely dilute. Metallic sols rarely contain as much as 1 gram per litre of disperse phase. One of the most concentrated lyophobic sols which has ever been prepared contained 75 grams of arsenic sulphide per litre. Let us consider a sol with this amount of disperse phase, and assume that the particles have a density of 5. Suppose that the radius of the particles is 50 $m\mu$. Then the volume of a particle is

$$4/3\pi(50)^3 \text{ cubic } m\mu,$$

or, approximately 5×10^{-16} c.c. The weight of a particle is therefore 2.5×10^{-15} gram. Hence the number of particles per litre is

$$\frac{75}{2.5 \times 10^{-15}} = 3.0 \times 10^{16}.$$

Hence, regarded as a solution, the sol has a molarity of

$$\frac{3.0 \times 10^{16}}{6.0 \times 10^{23}} = 5 \times 10^{-8}\ M.$$

It follows that, as we shall see later, the freezing point, boiling point, and vapour pressure of the sol will be indistinguishable from those of the dispersion medium. We may also, as a matter of interest, calculate the "molecular weight" of the above sol. The weight of one particle is 2.5×10^{-15} gram. Hence the weight of N particles, or the molecular weight, is

$$2.5 \times 10^{-15} \times 6.0 \times 10^{23} = 1.5 \times 10^9 \text{ grams.}$$

Lyophobic Sols Regarded as Surface Systems.—On account of the methods used in preparing sols, they almost invariably contain impurities. Thus we are by no means justified in thinking of a gold sol as being composed merely of particles of gold suspended in water. Certain impurities are bound to be present, and are indeed essential for the stability of the sol. These impurities are present mainly in the form of an adsorbed layer on the surface of the particles.

Because colloidal particles are charged (or, more accurately, are surrounded by a double layer of adsorbed ions of opposite electrical sign) they are affected by the application of an electric field. If, for example, the ions in the inner layer are positively charged, then if we put two electrodes into the sol the particles will wander towards the negative electrode. This phenomenon is known as cataphoresis. It owes its existence to the fact that the inner layer of ions is firmly attached to the particle, whereas the outer layer is only loosely attached. As a result the particle together with its inner positive layer moves to the negative electrode, continually losing some of the ions in the negative outer layer and replacing them with others.

Burton carried out measurements on the velocity of cataphoresis of a gold sol to which electrolytes had been added. With added aluminium chloride the following results were obtained.

Milligrams of Aluminium Chloride per Litre	Velocity of Cataphoresis in Millimu per Volt per Centimetre per Second	Nature of the Sol
0.00	330 (towards anode)	Indefinitely stable
0.19	171 " "	Coagulated in 4 hours
0.36	0	Coagulated immediately
0.38	17 (towards cathode)	Coagulated in 4 hours
0.63	135 " "	Stable for several days

The addition of an electrolyte apparently affects the charge on the particles. As long as there is a large charge the sol is stable, the sign of the charge being immaterial. If, however, we remove the charge, as shown by the fact that cataphoresis no longer occurs, the sol coagulates immediately. It may therefore be concluded that the stability of the sol is dependent on the magnitude of the charge which is possessed by the particles.

The explanation of this effect is that we are dealing with particles which are protected from collisions with one another by their charge. The particles, of course, tend to coagulate, since by so doing they can reduce their total surface, and thus reduce the potential energy associated with the surface. As the particles move about under molecular agitation, they would normally enter into numerous collisions with one another. On account of their like charges, however, they repel one another and merely approach and recede without coming into actual contact. As the electric charge is decreased this effect becomes less and less efficient, and finally when all the charge is removed we may assume that every collision between two particles will result in their union. Under these circumstances the sol will no longer be stable and will coagulate almost instantaneously.

The so-called *flocculation value* is often used as a semi-quantitative measure of the efficiency of electrolytes in causing flocculation. The flocculation value is defined as the quantity of electrolyte per litre which is necessary to produce complete flocculation of the sol in some arbitrarily defined time. For example, a certain negatively charged arsenic sulphide sol had the following flocculation values (in millimoles per litre):

Univalent cations............	LiCl	58
	NaCl	51
	$\frac{1}{2}K_2SO_4$	63
Divalent cations..............	$MgSO_4$	0.81
	$CaCl_2$	0.65
	$BaCl_2$	0.69
Trivalent cations.............	$AlCl_3$	0.093
	$Al(NO_3)_3$	0.095
	$Ce(NO_3)_3$	0.080

Since the sol has a negative charge, it is apparent that it is the ion of opposite sign which plays the major part in the process. The valence of this ion is obviously the main factor in determining the flocculation value, a concentration about 500 times higher being required with univalent than with trivalent ions. The same type of behaviour is found with all lyophobic sols. Freundlich has pointed out that most of the lighter inorganic ions are adsorbed to practically the same extent. As a result we can draw a common adsorption-concentration curve for all the above ions, as is done in Fig. 47.

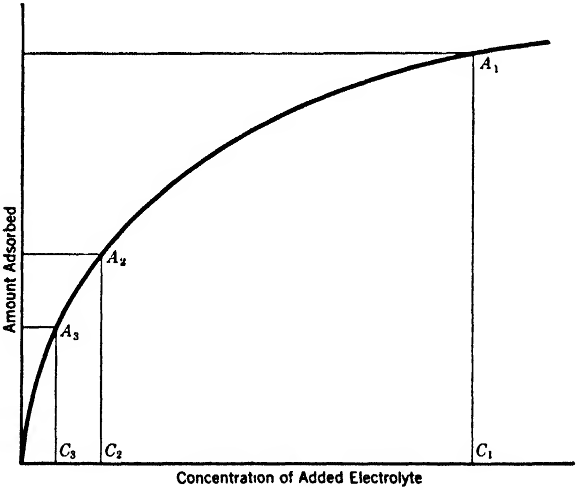

Fig. 47.

Flocculation is due to the neutralization of the charge on the sol particles by the adsorption of ions of opposite sign. It is obvious that a trivalent ion will be three times as effective as a univalent ion since it brings three times as much charge to the particle. Hence if A_1 is the amount of adsorption necessary with a univalent ion, only one-half as much of a divalent ion need be adsorbed (A_2), and only one-third as much of a trivalent ion (A_3). Hence a very much smaller concentration in the body of the solution is necessary when we have a di- or trivalent ion.

Hydrogen and most organic ions are adsorbed to a considerably greater extent than are the ions listed above. We cannot therefore include these in the common adsorption curve above, and they will cause flocculation at lower concentrations than would otherwise be expected from their valence.

With positively charged sols, such as ferric oxide, it is the negative ion of the added electrolyte which is responsible for flocculation. Otherwise their behaviour is the same.

The Electrical Double Layer.—It must be kept in mind in connection with arguments of the foregoing type that sols are not merely charged particles suspended in a liquid, but that the particles are actually surrounded by two layers of opposite sign electrically, the entire particle thus being electrically neutral. Of these layers, the inner is to be regarded as firmly attached to the particle by adsorptive forces, whereas the outer layer is held in a loose way by the electrostatic forces resulting from the presence of the inner charged layer.

There are also cases in which the electrical double layer is to be regarded as at least partially made up of material from the particle itself, rather than of an adsorbed layer in the usual sense of the word. A striking example of this type is the silver bromide sol. If silver nitrate and potassium bromide are brought together in stoichiometric proportions a precipitate of silver bromide is formed which is not colloidal in nature. If, however, silver nitrate is present in excess, a silver bromide sol is obtained which is positively charged. On the other hand, if potassium bromide is present in excess, a negatively charged silver bromide sol is obtained. Now we can represent a crystal of silver bromide as shown in Fig. 48 (*a*). The atoms, or rather ions, on the surface are unsaturated in the sense that they could accommodate further silver bromide and allow the crystal to grow. If we added further silver bromide we would really be adding silver and bromide ions, and these would attach themselves to the lattice in appropriate positions. Suppose, however, that there is present in the solution not silver bromide but potassium bromide, i.e., potassium and bromide ions. The bromide ions can obviously add on to the lattice. There are, however, no silver ions to add on with them, so that only one layer of bromide ions can add on and the crystal will become negatively charged. Positive potassium ions will then be attracted by electrostatic forces, and an electrical double layer will be formed consisting of bromide ions which are definitely a part of the crystal lattice and an outer, loosely attached, layer of potassium ions. This is shown in Fig. 48 (*b*). Such a system really corresponds to that represented diagrammatically in Fig. 48 (*c*), i.e., to a negatively charged silver bromide sol. On the other hand, if silver nitrate is in excess, the silver ions will add on to the lattice, giving rise to a positive inner layer, with an outer layer composed of nitrate ions. Hence we shall have a positively charged silver bromide sol. Of course, if desired, this attachment of silver and bromide ions to the crystal may be

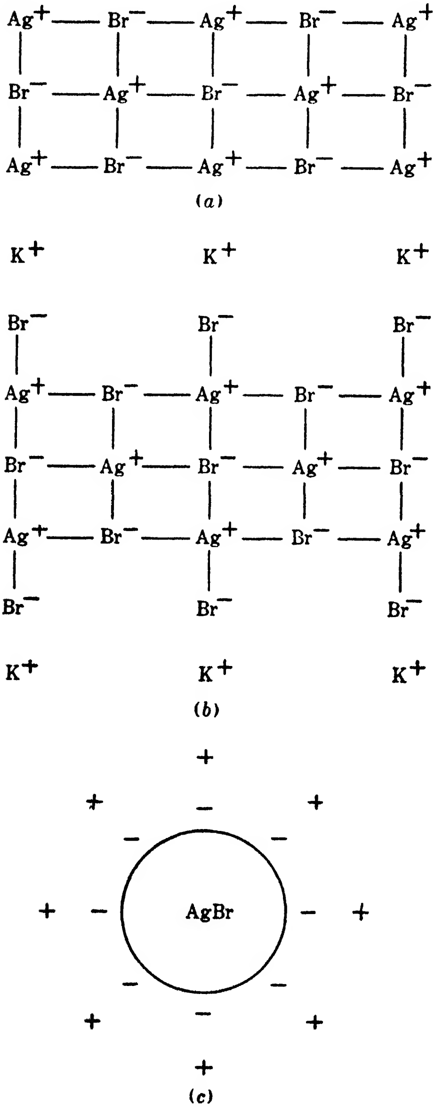

Fig. 48.

called selective adsorption, since chemical forces, forces in crystal lattices, and adsorptive forces are all essentially the same.

LYOPHILIC SOLS

Lyophilic sols are much more complex, and our knowledge of them is much less satisfactory than our knowledge of lyophobic sols. Lyophilic sols are almost always organic substances, and often occur in nature in the form of body fluids, etc. Many of them are formed spontaneously by merely bringing the disperse phase into contact with water or some other dispersion medium. Examples of this type are gelatin, albumin, and agar. They thus resemble true solutions to a greater extent than do lyophobic sols. This resemblance extends to many other properties and has its origin in the fact that the particles in a lyophilic sol are, in general, much smaller than those of lyophobic sols. The physical properties of lyophilic sols differ from those of the dispersion medium to a much greater extent than do those of lyophobic sols. This is particularly true of the viscosity.

The Viscosity of Lyophilic Sols and their Stability.—On the assumption that a sol consists of spheres of the disperse phase suspended in the dispersion medium, Einstein derived the equation

$$\eta = \eta_0(1 + 2.5\phi),$$

where η is the viscosity of the sol, η_0 the viscosity of the pure dispersion medium, and ϕ is the total volume of the disperse phase per unit volume of the sol. This equation has been found to hold well for lyophobic sols. In the case of lyophilic sols, however, there are very large discrepancies. Thus for an agar sol having a concentration of 0.3 per cent, assuming a density of 1 for the particles, we have

$$\eta_{sol} = \eta_{water}(1 + 2.5 \times 0.3 \times 0.01) = 1.007\eta_{water},$$

i.e., only very slightly greater than the viscosity of water. Actually the sol is found to have a viscosity 2.4 times that of water. It now appears certain that the cause of the discrepancy is that the agar particles absorb water, and their volume is consequently very much greater than the volume of the particles themselves. In the above example, if we equate the observed and calculated viscosities we can solve for ϕ, and hence determine the amount of water taken up by the particles. From this it appears that the volume of the particles must be about 200 times the volume of the agar itself, so that the sol particles are very highly hydrated.

If electrolytes are added to a lyophilic sol, it is found that the viscosity decreases greatly, the extent of the decrease being strongly dependent on the valence of the ion of sign opposite to that of the charge on the particles. The effect is thus strikingly similar to the coagulation of a lyophobic sol by the addition of electrolytes. The explanation is that since the particles are charged they repel one another; this is equivalent to an increase in their effective volume, and hence the viscosity of the sol is dependent on the charge on the particles. The viscosity of a lyophilic sol is thus a very useful property since it can give information concerning the electrical condition of the particles of the sol. This information can, in many cases, be confirmed by cataphoresis measurements.

In the case of lyophobic sols, flocculation occurs immediately if the charge on the particles is removed. With lyophilic sols, however, no flocculation occurs on removing the charge. Since the main difference between the two kinds of sols is the strong hydration of the lyophilic type, it is evident that the cause of the difference in behaviour is to be sought here. Apparently the water envelope surrounding the lyophilic particles prevents their coming into sufficiently intimate contact for the occurrence of coagulation. It may therefore be concluded that a lyophilic sol is stabilized by two distinct factors, its charge and its hydration.

In order to flocculate a lyophilic sol it is necessary to remove both the causes of its stability. Thus suppose that to an agar sol there is added a small quantity of an electrolyte such as aluminium chloride. This will result in the removal of its charge and the lowering of its viscosity. There is left, however, a sol which is perfectly stable, its coagulation being prevented by its hydration. Suppose that alcohol or acetone is now added to the sol. These substances are dehydrating agents, they cause the removal of the hydration of the particles, and since the charge is already gone the sol will flocculate immediately.

Since all that is necessary for the flocculation of a lyophilic sol is the removal of the two stability factors, it is possible to accomplish the same thing by reversing the sequence of the above operations. If alcohol is added to the sol first, the hydration of the particles is removed. Since the particles are still charged, no flocculation occurs. The viscosity, however, falls greatly and the sol changes in appearance and becomes a typical lyophobic (i.e., unhydrated) sol. If an electrolyte is now added the sol will flocculate immediately. The whole process has been summed up in a diagram of the type shown in Fig. 49 by Kruyt, who has been largely responsible for the explanation of the phenomenon.

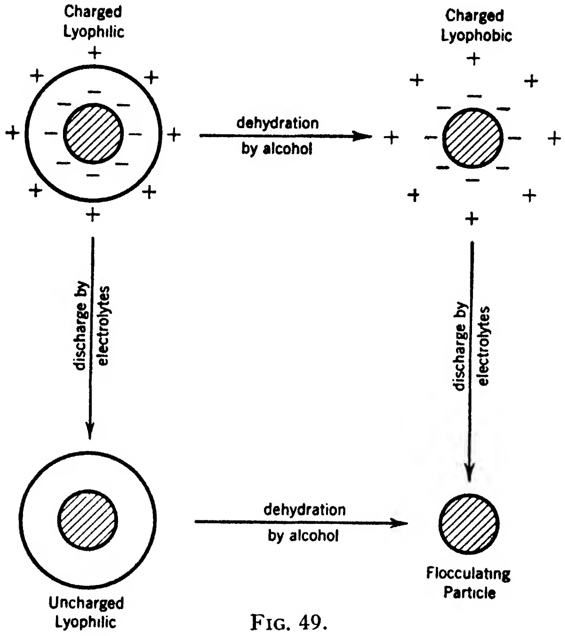

Fig. 49.

Salting Out.—As we have seen, traces of electrolytes merely remove the charge on lyophilic particles without causing the flocculation of the sol. If, however, very large quantities of electrolytes are added (i.e., sufficient to produce concentrations of several molar), it is found that flocculation can be brought about. This phenomenon is known as *salting out.* It is found that the relative efficiencies of different electrolytes are the same for all sols, and are dependent on both the anion and the cation, and independent of the sign of the charge on the particles. It is thus possible to arrange the ions in a series which shows their relative efficiency in salting out. This series, known as the *lyotropic series*, is

Decreasing Efficiency
→

Cations....... Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}
Anions........ $SO_4^{=}$, Cl^{-}, Br^{-}, NO_3^{-}, I^{-}, CNS^{-}

The lyotropic series is also met with in other phenomena. It is really merely the order of the ions in terms of the extent of their hydration. Hence in the case of salting out the electrolytes are merely acting as dehydrating agents at high concentrations as well as acting as discharging agents at low concentrations.

Protective Action.—If small amounts of a lyophilic sol are added to a lyophobic sol, the lyophobic sol will, in general, be protected against coagulation by electrolytes, that is, it will require much larger quantities of electrolyte than usual to cause coagulation. The effect appears to be due to a mere coating over of the large lyophobic particles by the smaller lyophilic particles. The resultant particle is thus really lyophilic in nature as far as its surface is concerned, and is therefore insensitive to electrolytes. This protective action of lyophilic sols is very important from a practical point of view.

It is usual to define the protective ability of a lyophilic sol in terms of its *gold number*. This is defined as the number of milligrams of protective colloid (disperse phase only) which when contained in 10 c.c. of a standard gold sol containing 1 per cent of sodium chloride will just prevent the sol from coagulating to an arbitrarily defined extent in 3 minutes. This protective action is sometimes surprisingly high, very small amounts of, say, gelatin having an enormous effect. The gold numbers of some typical lyophilic sols are:

Sol	Gold Number
gelatin	0.005–0.01
haemoglobin	0.03 –0.07
albumin	0.1 –0.2
dextrin	6–20
colloidal silica	infinite

GELS

If a few grams of gelatin are dissolved in 100 c.c. of water at, say, 40° C., and the gelatin sol thus produced is cooled to 20° C., the whole mass will set to form a solid gel, or jelly. In this process there is no separation into two or more phases: the whole mass, disperse phase and dispersion medium, sets together, and the resulting gel shows no visible heterogeneity.

In some cases the process of gelatinization can be made to occur not by cooling a sol, but by adding electrolytes to it. This effect is dependent on the valence of the ion of opposite sign to that of the sol, and the process thus appears to be analogous to flocculation. Gelatinization therefore appears to be merely the flocculation of very strongly hydrated particles in such a way that the network of flocculi occludes so much water that the whole system possesses more or less pronounced rigidity.

There are two distinct types of gel, elastic or swelling gels, and non-elastic or non-swelling gels. Thus when a gelatin gel is placed in water it imbibes more water and increases in volume, or swells. There is no limit to this process, the gel merely continuing to imbibe water till it becomes a sol. The process is reversible, and a swollen gel placed in a desiccator will lose water and shrink. On the other hand, a silicic acid gel will, over a certain range, take up or give up water without an appreciable change in volume.

QUESTIONS AND PROBLEMS

1. At 9.84 cm. pressure, 0.0274 gram of argon is adsorbed by 1 gram of charcoal; 0.0836 gram is adsorbed at 75.8 cm. pressure. Calculate α and n in the Freundlich adsorption equation. From these values find the amount adsorbed at 50 cm. pressure. *Ans.* $\alpha = 0.007856$
$n = 1.832$
$a = 0.0666$ gram.

2. Define the term *adsorption*.

3. Discuss the effect of temperature and pressure on the adsorption of gases by solids.

4. State the Freundlich adsorption equation, and discuss its use.

5. Discuss Langmuir's theory of adsorption.

6. Discuss adsorption at the solid-liquid interface.

7. Describe methods of distinguishing between colloids and solutions.

8. Define sol, gel, disperse phase, and dispersion medium.
9. State all possible types of dispersion, giving examples.
10. Describe the preparation of lyophobic sols.
11. Discuss the Brownian movement.
12. Discuss the relationship between the charge and the stability of lyophobic sols.
13. Define and discuss the "flocculation value."
14. Discuss the effect of valence on the flocculation value of ions.
15. Discuss the electrical double layer at solid-solution interfaces.
16. Discuss the viscosity of lyophilic sols.
17. Discuss the factors responsible for the stability of lyophilic sols.
18. Define and discuss "salting-out."
19. Write a brief account of the properties of gels.

CHAPTER XII

THE THEORY OF SOLUTIONS

In Chapter X various types of solution have been discussed from the point of view of their classification, mode of formation, and general properties. No attempt has been made, however, to formulate an hypothesis to explain the structure of solutions and the cause of their formation. Before the consideration of the cause of formation of solutions, and the extent to which substances are soluble in one another, we will discuss the properties of the solution once it is formed, irrespective of whether it is saturated or unsaturated.

In order to fix our ideas, we will consider throughout one definite solution, viz.: sugar dissolved in water. This particular example is chosen, first because solutions of solids in liquids are the most common and the most striking, and secondly because solutions of sugar in water have played an important part in the historical development of the theory of solutions.

The Diffusion of the Solute.—Suppose that a solution of sugar in water is brought into contact with a quantity of pure water. The solute will diffuse, and will spread itself throughout the system until its concentration is identical at all places. This diffusion will occur even against the action of gravity. The diffusion of the solute in a solution is thus similar to the diffusion of a gas. A gas will diffuse until it completely fills the containing vessel. In the same way the solute tends to spread itself throughout space. In the case of sugar, it cannot evaporate, and consequently the surface of the liquid phase prevents the solute from spreading further and thus behaves like the wall of a containing vessel.

It should be emphasized that the concentration of the solution may be varied continuously, by the addition of water, within wide limits. There is consequently no question of the existence of stoichiometric proportions between the solute and the solvent.

In the case of gases, the process of diffusion was explained by the assumption that gases are composed of small moving particles called molecules. These particles are in rapid motion and tend, in consequence, to spread themselves throughout the whole system bounded by the walls of the container. It is natural to attempt to explain the diffusion of the solute throughout the solvent in the same way. It is assumed that in the solution the dissolved substance consists of very small particles (which may or may not be molecules). These particles are in motion, and hence they tend to spread equally throughout the whole system bounded by the surface of the liquid phase.

In the case of gases, the hits recorded by the moving molecules on the walls of the container result in the development of a pressure. If the particles of the solute are in motion, they should register a pressure on a manometer in the same way. There is no sugar in the vapour phase above the liquid; the sugar particles must therefore be reflected from the surface of the liquid phase, just as gas molecules are reflected from the walls of the containing vessel. We cannot, therefore, measure the pressure due to the moving particles by means of a manometer, because as soon as we introduce the manometer we form a new liquid surface, and the particles are reflected from this surface and never reach the manometer.

In the case of a gas the moving molecules exert a pressure on the walls of the container. The gas tends to spread throughout space and is prevented from doing so by the walls of the container. In order to prevent this spreading, the material of which the container is made must have tensile strength to withstand the pressure due to the gas molecules. If the solute particles tend to spread, and are stopped by the surface of the liquid, then the liquid must possess tensile strength in order to withstand the pressure of the moving solute particles. Evidence of such a tensile strength has been mentioned previously, when discussing the liquid state.

The Pressure Due to the Dissolved Substance.*—One way of measuring the pressure due to the moving particles of the solute would be to overcome the tensile strength of the liquid in some way, and thus enable the particles to register their pressure on a manometer through the intermediary of the surface of the liquid phase. The liquid would then tend to expand and, if the expansion was prevented by the application of an external pressure, then the pressure due to the solute particles would be equal to the external pressure applied. The pressure due to the motion of the solute particles would thus be indirectly measured.

Suppose that we use an apparatus similar to that represented in Fig. 50. A tube filled with the solvent is dipped into the centre of a drop of the solution. The moving particles of the solute will tend to register their pressure on the end of the tube filled with solvent. Since there is no surface between the solution and the solvent, the tensile strength of the liquid will not prevent the registering of this pressure. The pressure, however, is immediately released by the diffusion of solute particles from the solution to the solvent. Such an apparatus is therefore useless, since it is like attempting to measure the pressure of a gas by introducing into it a tube leading to an unlimited evacuated space.

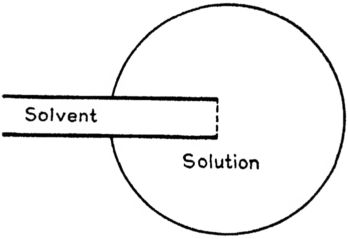

FIG. 50.

If it were possible to obtain a semi-permeable membrane, which was permeable to the molecules of the solvent but not to the particles of the solute, and if this were put across the end of the tube containing the solvent, the use of the apparatus illustrated above would now be feasible. An example of such a membrane would be a kind of sieve, which would permit the passage of the solvent molecules but not that of the larger particles of some solute.

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* The explanation of the pressure due to the dissolved substance which is given here is the classical one, and the one which is the most readily followed. There are those who prefer to attribute the phenomenon of osmotic pressure to the properties of the solvent, and to make use of the experimentally determined values without looking too closely into the mechanism of the phenomenon.

Semi-Permeable Membranes.—In practice it is not found to be possible to obtain a satisfactory semi-permeable membrane of the sieve type. We have seen previously that palladium acts as a semi-permeable membrane, which permits the passage of hydrogen but not that of other gases. This is due to the fact that hydrogen alone is soluble in palladium. By analogy it would therefore seem to be possible to make a semi-permeable membrane out of some substance which will dissolve water but not sugar. Such a membrane has been accidentally discovered.

If a 2.5 per cent solution of copper acetate is brought into contact with a solution of potassium ferrocyanide of similar strength, a precipitate of copper ferrocyanide is produced in the form of a gelatinous skin. This skin, or membrane, is readily permeable to water but is impermeable to a large number of dissolved substances, among which is sugar. The membrane formed in this way, however, has very little mechanical strength, cannot withstand high pressures, and is easily ruptured. A much more satisfactory membrane can be made by putting one of the reagents into a porous porcelain pot, and allowing the other reagent to diffuse in from outside. In this way the membrane is formed in the capillaries in the interior of the pot. As a result, the membrane in each capillary has a very small cross-section and will withstand a comparatively high pressure, in some cases 150 atmospheres.

The Measurement of the Osmotic Pressure.—The manner in which a semi-permeable membrane can be used to detect the existence of a pressure due to the particles of the solute can be illustrated by the apparatus shown in Fig. 51. The solution is completely enclosed in the vessel *A*, the sides and bottom of which are made of non-permeable glazed porcelain. A porous plate, *B*, containing a copper ferrocyanide membrane is cemented to one side of the top of the vessel. At the other side there is a piston, *C*, which at the start of the experiment registers no pressure, i.e., merely rests on the surface of the solution. The dissolved particles are confined by the boundary of the liquid phase, which transmits no pressure to the walls or piston on account of the tensile strength of the liquid. The whole apparatus is now immersed in an outer vessel, *D*, which is filled with water until the plate *B* is completely covered. Since water can pass through the membrane, the tensile strength of the liquid no longer comes into play and the solution will tend to expand. A pressure will therefore be registered on the walls of the container which is equal to the pressure caused by the change in momentum of the solute particles as they are reflected from the liquid surface. It is therefore necessary to apply an equal and opposite pressure to the piston to prevent it moving outwards.

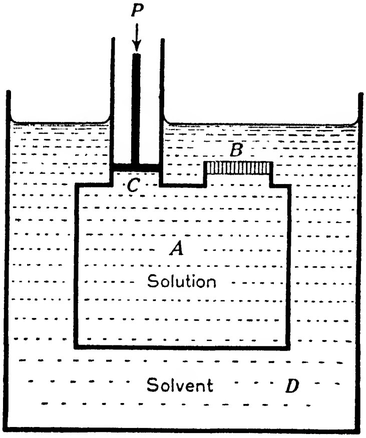

FIG. 51.

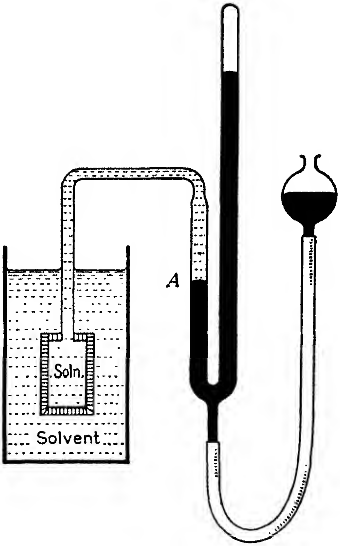

FIG. 52.

The pressure predicted above is actually found in practice. Thus a normal sugar solution is found to exert a pressure of 24.0 atmospheres at 20° C.

The type of apparatus generally employed in practice differs somewhat from that discussed above, and is represented in Fig. 52. The general principle of the apparatus is the same as that shown in Fig. 51, but the piston is replaced by a mercury manometer. The level of the solution is maintained at a fixed point, *A*, by raising or lowering the mercury in the manometer.

The term osmotic pressure is used to denote the pressure exerted by the particles of the solute, when the tensile strength of the liquid has been overcome by some method of compensation. The apparatus described above is therefore called an osmotic cell; and, for any solution, the pressure measured by means of an osmotic cell is called the osmotic pressure of the solution. It should be emphasized that there is nothing mysterious about the nature of osmotic pressure, and that it can be definitely predicted from the phenomenon of spontaneous diffusion in solution.

The next consideration is the magnitude of the osmotic pressure, and its relation to the variable factors which are met with in solutions. If the osmotic pressure is due to the movement of the particles of the solute, then we can regard these as analogous to the molecules of a gas, the confines of the solution corresponding to the containing vessel of the gas. By the application of Newton's laws of motion to the moving particles of solute, we can obtain relationships similar to those obtained with gases. We can therefore derive theoretical expressions, similar to the gas laws, giving the relation between the osmotic pressure and the temperature and concentration of the solution. We will now examine the experimental results, and compare them with the predictions of the theory.

The Variation of the Osmotic Pressure with Concentration.—In the case of a gas, the pressure exerted on the walls of the container depends on the kinetic energy of the moving molecules and on the number present. For a given number of molecules, therefore, the pressure will depend on the volume of the system. The osmotic pressure-volume relationships could theoretically be investigated by compressing the solute by means of a semipermeable piston. This is difficult experimentally, however, so that, instead, a series of solutions are made up with different concentrations of solute, and the osmotic pressure of each is measured.

It is found experimentally that

$$P = K_1C,$$

where P is the osmotic pressure in atmospheres, C the concentration in gram molecules per litre, and K_1 is a constant.

The concentration of a solution which contains a definite weight of solute is inversely proportional to its volume, i.e.,

$$C = K_2/V.$$

Hence, substituting for C in the above expression,

$$P = \frac{K_1K_2}{V} = \frac{K}{V},$$

or

$$PV = K.$$

Hence Boyle's law holds for the dissolved substance, just as it does for gases. An example of its applicability is given in the table below.

Cane Sugar Solution at 20° C.

Concentration, Gram Mols. per Litre	Osmotic Pressure, Atmospheres	
	Observed	Calculated from $PV = K$
0.05	1.25	1.21
0.10	2.24	2.40
0.20	4.80	4.85
0.30	7.23	7.22
0.50	12.08	12.07
0.80	19.07	19.14
0.90	21.80	21.74
1.00	24.34	24.34

The Variation of the Osmotic Pressure with Temperature.—With gases at higher temperatures, the molecules move faster, they strike the manometer harder, and therefore register a higher pressure. Hence the pressure increases as the temperature is raised. This behaviour is expressed by Charles' law:

$$P = P_o(1 + \alpha t),$$

where α is a constant equal to 1/273, and t is the temperature in °C. If we use absolute temperatures this expression becomes

$$P = KT.$$

In the case of osmotic pressures, it is found experimentally that Charles' law holds for the dissolved substance. Not only is this true, but the constants in the above equations have identically the same values with solutions as with gases. The following table gives some typical results obtained with a solution of cane sugar in water.

Temperature, °C.	Osmotic Pressure, Atmospheres	
	Observed	Calculated
6.8	0.664	0.665
13.7	0.691	0.681
14.2	0.671	0.682
15.5	0.684	0.686
22.0	0.721	0.701
32.0	0.716	0.725
36.0	0.746	0.735

The agreement between the experimental and calculated values, though by no means perfect, is within the experimental error. Unfortunately a membrane cannot be prepared which can be used over a wide range of temperature.

The Size of the Dissolved Particles.—Since the same empirical laws hold for substances in solution as for gases, and the constants have the same values, the analogy between the two seems to be complete, and the assumption that the dissolved substance consists of small discrete moving particles is justified. The dissolved substance therefore behaves like a gas in every way.

We may combine the equations for the variation of osmotic pressure with volume, and with temperature, as in the case of a gas. We then have

$$PV = RT,$$

where P is the osmotic pressure in atmospheres, V is the volume of the solution in litres which contains one gram molecule, T is the absolute temperature, and R is a constant equal to 0.082 litre-atmosphere.

If we introduce Avogadro's hypothesis into the above equation we have, as with gases,

$$PV = \frac{w}{M}RT,$$

where w is the weight of the dissolved substance, in grams, contained in the volume V, and M is the "molecular weight of the particle," i.e., the weight of the particle referred to the oxygen atom as 16.

The following values have been obtained experimentally with a typical sugar solution:

Volume of solution = 1 litre
Mass of sugar = 342 grams
Temperature = 273° Absolute
Osmotic pressure = 22.4 atmospheres

Hence we have

$$22.4 \times 1 = \frac{342 \times 0.082 \times 273}{M}.$$

Whence $M = 342$.

The Molecular Weight of the Solute Particles.—The definition of the molecular weight of a substance has been given in a previous chapter. According to this definition, the "molecular weight" of the dissolved substance will be the weight of a single particle compared with the weight of an oxygen atom as 16. These particles of the solute have freedom of translational and rotational movement, and all the atoms constituting such a particle keep their relative positions unaltered during any displacement of the particle. There is therefore nothing new in the idea of the molecular weight of the solute particles, or in regarding the solute particle as a molecule.

It is of interest to consider the relationship of such molecules of solute to the constitution of the substance in the solid state. In the case of sugar, volatilization is impossible on account of decomposition, and the nature of the sugar molecule in the gaseous state cannot be determined. By combustion, the analysis of solid sugar corresponds to the stoichiometric proportions given by the empirical formula $C_{12}H_{22}O_{11}$. This number of atoms, therefore, or some integral multiple of them, must always be connected together in order that the resultant substance shall have the properties of sugar. In the solid state this integral multiple will be so large that it includes the whole crystal. In solution, as we have seen above, the molecular weight of the solute particle is 342, corresponding to $C_{12}H_{22}O_{11}$. It may therefore be inferred that, if vaporized, the sugar molecule might possibly have this composition. Hence molecular weight determinations of *solute particles* are sometimes referred to as the determinations of the molecular weight of the *substance*, with the inference that it has the same complexity in solution as in the gaseous state. In a case like that of sugar, where the "molecular weight" determined in solution corresponds to the simplest possible empirical formula, there is perhaps some justification for such an inference. It must be remembered, however, that such a molecular weight does not correspond to that of the solid substance, any more than the molecular weight of a gas corresponds to that of a solid.

In the case of sugar, the chemical reactions which it undergoes have enabled the organic chemist to assign a structural formula to it. This formula for the sugar "molecule" is really a short-hand representation of its chemical behaviour only, since such a molecule cannot exist in the solid state. It has real physical significance only when the sugar is in solution, since in that case its size corresponds to that of a particle of solute. The identity of size between structural formula and solute particle is by no means the general rule, and the attempt to find the size of the structural formula from molecular weight determinations in solution has often led to erroneous results. As an example we may consider the case of ethyl alcohol. Its molecular weight determined in benzene solution corresponds to a particle containing many times the number of atoms in the structural formula. In addition to this, the size of the solute particle, as will be seen later, varies with the concentration of the solution.

Molecular weight determinations in solution can therefore only be looked upon as giving some confirmatory evidence for the structural formula as determined by chemical means. At times, of course, such confirmatory evidence may be of considerable value.

The Mechanism of the Semi-Permeable Membrane.—The manner in which the semi-permeable membrane acts is not a matter of very great importance. The osmotic pressure is a property of the dissolved substance, and the value obtained by measurement is independent of the mechanism of the membrane, so long as it behaves efficiently in permitting the passage of the solvent molecules and preventing the passage of those of the solute. That the osmotic pressure is independent of the membrane is shown by the fact that other membranes give the same values for a sugar solution as that described above. Some examples of such membranes are gelatin tannate, Prussian blue, and various animal membranes.

It is nevertheless of some interest to discover the mechanism by which the semi-permeable membrane functions. The gelatinous copper ferrocyanide membrane contains a large amount of water, which is apparently in solution. Sugar, on the other hand, is quite insoluble in copper ferrocyanide. This is analogous to the action of palladium which dissolves hydrogen, but not other gases, and will therefore permit the diffusion of hydrogen through it, but not that of other gases. As previously seen, hydrogen will diffuse through palladium from one vessel to another until its partial pressure, or concentration, is the same in each. In a sugar solution the concentration of water molecules must be less than their concentration in pure water. The copper ferrocyanide membrane, therefore, presumably functions by solution in the same way as a palladium membrane. It has also been suggested that the membrane might function like a sieve, and permit the passage of small solvent molecules, but not that of comparatively large molecules such as sugar. There is, however, little evidence to support such an hypothesis.

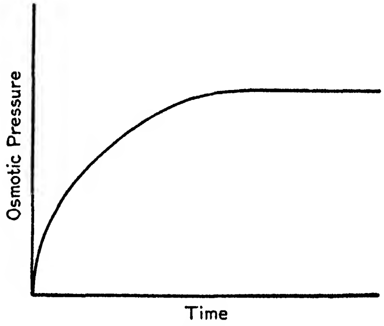

Fig. 53.

The Time Required to Reach Osmotic Pressure Equilibrium.—If a vessel containing a gas is connected to a similar evacuated vessel, by means of a capillary tube of moderate size, pressure equilibrium will be reached in a few seconds or tenths of a second. With a sugar solution, owing to the great resistance to flow introduced by the membrane, it takes much longer for the attainment of pressure equilibrium. There is, however, no fundamental difference between the two processes. A typical osmotic pressure-time curve is shown in Fig. 53.

With some solutions, other than sugar, a curve of an entirely different type is obtained when the osmotic pressure is plotted against time. Thus if we have a tenth normal solution of propyl alcohol in water, the calculated osmotic pressure will be 2.24 atmospheres at N.T.P. Actually, however, we obtain a curve similar to that represented in Fig. 54, the osmotic pressure increasing to a maximum, and then falling off without ever reaching the calculated value. This is found to be due to the fact that propyl alcohol slowly leaks through the membrane. Eventually, therefore, the concentration of propyl alcohol becomes the same on both sides of the membrane, and no osmotic pressure is registered.

In the case of a large number of solutions, it has been impossible to find a suitable semi-permeable membrane. It has been found to be possible, however, to make use of indirect methods of measurement, from the results of which the osmotic pressures can be calculated. Such methods give results which are in perfect agreement with direct osmotic pressure measurements, in the case of substances like sugar. It is therefore justifiable to use them to calculate the osmotic pressures of solutions for which a suitable semi-permeable membrane cannot be found. In the following pages such indirect methods of determining the osmotic pressures of solutions will be discussed.

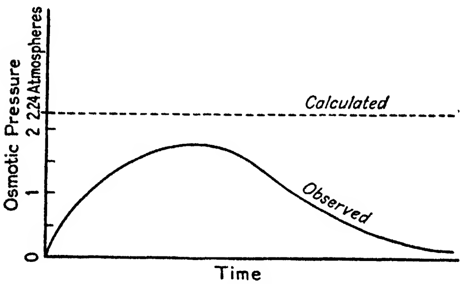

FIG. 54.

The Vapour Pressure of Solutions.—Consider a pure liquid in equilibrium with its own vapour. The faster-moving molecules of the liquid are continually escaping and entering the vapour; molecules from the vapour are also continually returning and entering the liquid. At equilibrium, the number of molecules leaving is equal to the number returning, and there is a constant pressure in the vapour phase which is the vapour pressure of the liquid.

If we now add a non-volatile solute to the liquid, there will be fewer molecules of solvent per unit volume than before.*

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* This is not strictly true in all cases. Sometimes the volume of the solution is less than that of the pure solvent. In such cases, however, strong attractive forces

There will thus be fewer molecules per unit volume which possess the energy necessary to enable them to escape from the liquid. Fewer molecules, therefore, will leave the liquid and enter the vapour in unit time. In consequence there will be more molecules leaving the vapour than are entering it. The number of molecules in the vapour will therefore decrease, and the vapour pressure will fall until equilibrium is again established. The vapour pressure of the solution is thus lower than the vapour pressure of the pure solvent. This is true in all cases.

Since the magnitude of the vapour pressure lowering depends upon the concentration of the solution, upon which the magnitude of the osmotic pressure also depends, it is natural to suppose that there will be some connection between the osmotic pressure and the lowering of the vapour pressure. If this is so, it will be possible to calculate the osmotic pressure from the vapour pressure, in the case of those solutions whose osmotic pressures cannot be directly measured.

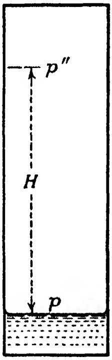

FIG. 55.

The Relation between the Osmotic Pressure and the Lowering of the Vapour Pressure.—It will first be necessary to discuss the variation of the pressure of a vapour with the height above a liquid surface. Consider a confined space which contains a liquid and its vapour, all air being absent (Fig. 55). Let the vapour pressure at the surface of the liquid be p, and the pressure of the vapour at a height H above the surface be p''. Then p must be greater than p'' by the hydrostatic pressure due to the weight of the column of vapour of height H. Hence

$p - p''$ = the weight of the vapour in a column of unit cross-section and height H,

or

$$p - p'' = dH,$$

where d is the density of the vapour, and p and p'' are expressed

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between the molecules of solute and solvent come into play. In consequence, the solvent molecules need more energy to enable them to escape, and again the vapour pressure is less than that of the pure solvent.

in grams per square centimetre. Or, expressing pressures in atmospheres,

$$76 \times 13.59(p - p'') = dH,$$

$$p - p'' = \frac{dH}{1033}.$$

Suppose that we now introduce into the above system an osmotic cell which contains a solution. Owing to the osmotic pressure, water will enter the cell until the solution has risen to such a height that the osmotic pressure is equal to the hydrostatic pressure exerted by the column of liquid, which thus serves as its own manometer. (See Fig. 56.) When this rise has taken place, the two pressures balance one another, and the system is in equilibrium. At equilibrium, let the vapour pressure of the solution at the top of the column be p', the vapour pressure at the surface of the solvent be p, and the pressure of the vapour at a height H above the solvent be p''.

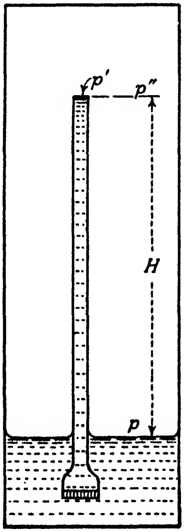

FIG. 56.

Then p' must be equal to p'', for, if not, suppose that p' is less than p''. In this case molecules of vapour will condense out on the surface of the solution. The solution will thereby be diluted, its osmotic pressure will decrease, and solvent will leave the cell through the semipermeable membrane. At the the same time, since molecules of vapour have condensed out on the surface of the solution, the space above the solvent will no longer be saturated with vapour, and the solvent will therefore evaporate. There will therefore be a continuous cyclic motion of solvent molecules, which evaporate from the surface of the solvent, condense out on the solution, leave the osmotic cell, and again evaporate, etc. This would result in a mass motion of matter which would continue indefinitely. Such ordered directional movement of molecules, as opposed to the ordinary chaotic movement which exists in a gas, could be used to obtain energy, for example by placing a small turbine in the vapour. The flow of vapour would drive such a machine, and energy would be obtained which could be used external to the system.

This is impossible as shown in Chapter VIII, and hence p' cannot be less than p''. Similarly it may be shown that p' cannot be greater than p'', and hence p' must equal p''. If p' is equal to p'', then there will be no tendency for such ordered movement of molecules to occur, and the system will be in equilibrium. When such equilibrium is reached, let P be the osmotic pressure of the solution. Then we have

P = weight of a column of solution of unit cross-section and height H,

$= SH$, where S is the density of the solution and P is expressed in grams per cm.^{2},

$= \frac{SH}{1033}$, where P is expressed in atmospheres.

But

$$H = \frac{1033(p - p'')}{d},$$

$$= \frac{1033(p - p')}{d}.$$

Therefore

$$P = \frac{S \cdot 1033 \cdot (p - p')}{d \cdot 1033},$$

$$= \frac{(p - p')S}{d}.$$

and

$$d = \frac{pM'}{1000\,RT},$$

where M' is the molecular weight of the solvent.

Therefore we have:

$$P = \frac{(p - p')S \cdot 1000\,RT}{pM'},$$

or

$$P = \frac{1000\,RST}{M'} \cdot \frac{p - p'}{p}.$$

Hence, if we know the difference between the vapour pressure of the solvent and that of the solution we can calculate the osmotic pressure of the solution.

The above expression is an approximation, and will hold for dilute solutions only. The approximate nature of the expression is due to the fact that we have assumed *d*, the density of the vapour, to be constant. Actually, *d* varies with height, and for more concentrated solutions it is necessary to use a more accurate expression, which takes this variation into account.

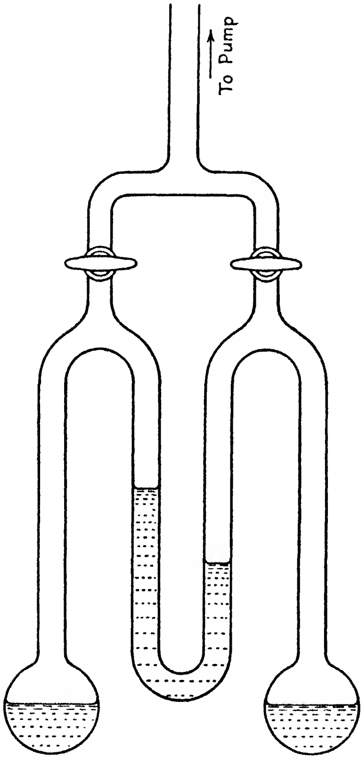

Fig. 57.

The Experimental Measurement of the Lowering of the Vapour Pressure.—The type of apparatus employed is illustrated in Fig. 57. The pure solvent is used as the manometer liquid. The apparatus is thoroughly evacuated, and is then filled with solution and solvent as indicated, and immersed in a constant temperature bath. The difference in the height of the liquid in the two arms of the manometer gives the difference between the vapour pressure ot the solvent and that of the solution.

The great disadvantage of the method is the very small difference in vapour pressure which must be measured. Thus suppose that water is the solvent, and that the solution is fifth normal. Let the density of the solution be 1.0 and the temperature be 20° C. The osmotic pressure of such a solution will be 4.80 atmospheres. The vapour pressure lowering of such a solution is, however, extremely small as is shown by the following calculation.

The vapour pressure of water at 20° C. is 17.5 mm. = 0.023 atmosphere.

Hence we have

$$4.80 = \frac{1000 \times 0.082 \times 1.0 \times 293}{18} \times \frac{p - p'}{0.023},$$

whence

$$
\begin{aligned}
p - p' &= 0.0000828 \text{ atmosphere,} \\
&= 0.0000828 \times 760, \\
&= 0.0630 \text{ mm. of mercury,} \\
&= 0.0630 \times 13.59, \\
&= 0.86 \text{ mm. of solvent.}
\end{aligned}
$$

It follows that the method can be employed only at temperatures where the vapour pressure is high, and for concentrated solutions.

Small differences in temperature can be measured more conveniently and accurately than small differences in pressure. Two other indirect methods of determining osmotic pressures have therefore been developed, which depend on the difference in vapour pressure between the solvent and the solution, but which involve the measurement of temperature rather than pressure. These methods, which involve the determination of the boiling and freezing points of solutions, are described below.

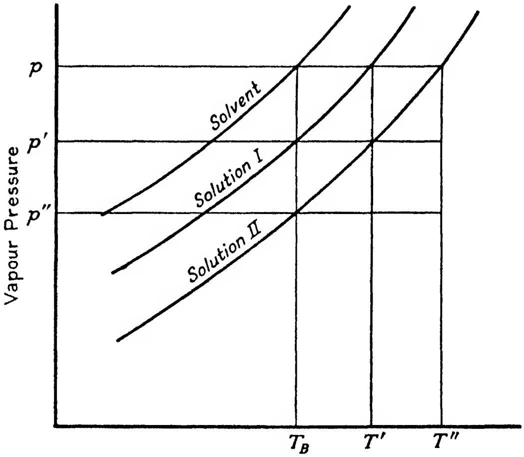

Fig. 58.

The Rise in the Boiling Point of Solutions.—Since the vapour pressure of a solution is always less than the vapour pressure of the pure solvent, and since the boiling point is merely the temperature at which the vapour pressure is equal to one atmosphere, it follows that the boiling point of a solution will always be higher than that of the pure solvent. If we plot the vapour pressures of the solvent, and of two solutions of different concentration, against the temperature, a regular series of curves is obtained as shown in Fig. 58, T_B representing the boiling point of the solvent, and T' and T'' those of the solutions.

Since these constitute a regular family of "parallel" curves, it may be said that the lowering of the vapour pressure is approximately proportional to the rise in the boiling point of a solution. Hence we have

$$\frac{p - p'}{T' - T_B} = \frac{p - p''}{T'' - T_B},$$

or, if Δt represents the rise in the boiling point of the solution as compared with the pure solvent,

$$\frac{p - p'}{\Delta t'} = \frac{p - p''}{\Delta t''}.$$

Or, in other words,

$$p - p' = K\Delta t'.$$

But

$$P = \frac{1000RST}{M'} \cdot \frac{p - p'}{p}.$$

Whence, since $p = 1$ atmosphere at the boiling point,

$$P = \frac{K\Delta t' \cdot 1000RST_B}{M'},$$

where T_B is the boiling point of the solvent.

For a given solvent R, T_B, and M' are constant, hence

$$P = K_1\Delta t' \cdot 1000S,$$

where K_1 is a new constant which includes K, R, T_B, and M'.

Since the density of a dilute solution differs only slightly from that of the solvent, the density of the solution in the above equation is approximately equal to that of the solvent, and hence is constant for a given solvent. The osmotic pressure is therefore proportional to the rise in the boiling point, and the proportionality factor is independent of the solute, i.e.,

$$P = K_2\Delta t',$$

where K_2 depends on the solvent only. The constant K_2 can be evaluated experimentally by means of a measurement carried out with a sugar solution, for which the osmotic pressure has been determined directly. It is also possible to calculate it from the known properties of the solvent, and such calculations give a result which is in agreement with the experimentally determined value.

The Experimental Measurement of the Rise in the Boiling Point of Solutions.—The boiling point of a liquid is usually measured by putting the thermometer in the vapour, and not in the liquid, as there is then the possibility of superheating. This method cannot be employed when measuring the boiling point of a solution. The vapour coming from the solution, and condensing out on the thermometer, is that of the pure solvent. The temperature at which it condenses is that at which the condensing liquid and the vapour are in equilibrium, i.e., the boiling point of the solvent. Hence, in order to measure the boiling point of a solution, we must immerse the thermometer in the solution. On this account it is necessary to take great precautions in order to prevent the superheating of the liquid. This is best done by using an electrical heating element which is immersed in the liquid (*A*, Fig. 59). In addition, some small pieces of platinum should be immersed in the liquid to provide a large number of points on which bubbles can form. A thermometer, *B*, which is graduated in hundredths, and which may be read to thousandths, of a degree, is placed in the tube containing the liquid and the heating element. This tube is surrounded by a jacket, in which some of the pure solvent is boiled. The solution is thereby kept near its boiling point, and only a small amount of heat need be supplied by the heating element in order to boil the solution. In consequence the element need not be at a temperature much higher than the boiling point of the solution, and the possibility of superheating is reduced to a minimum. Both inner and outer vessels are provided with reflux condensers to prevent the escape of vapour.

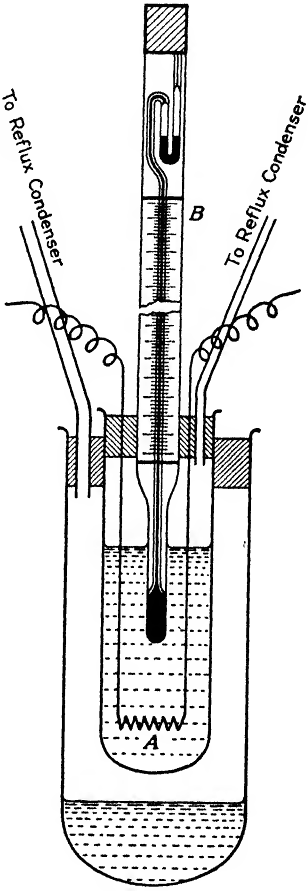

FIG. 59.

In carrying out an experiment, the boiling point of the pure solvent is first determined. A weighed quantity of the solute is then added, and the boiling point of the solute is determined. The above is an outline of the principles involved in the boiling point method. Modifications have been devised which give more accurate results.

The Lowering of the Freezing Point of Solutions.—Consider a pure liquid which is in equilibrium with its own solid at the freezing point. As we have already seen, solid molecules will be entering the liquid at a constant rate, while liquid molecules will also be entering the solid state. At equilibrium, the number of molecules leaving the solid will be equal to the number returning, and there will thus be a constant amount of solid present.

Suppose that a quantity of a solute is now added to the system. If the added substance is soluble in the solid and in the liquid to the same extent, both will be equally diluted by its addition. The number of molecules leaving the solid in unit time, and the number returning to it, will therefore both be decreased to the same extent, and the equilibrium will consequently be unaltered. The solution will therefore have the same freezing point as the pure solvent.

If the added substance is more soluble in the solid than in the liquid, however, the solid will be diluted to a greater extent than will the liquid. The number of molecules leaving the solid in unit time will therefore be cut down to a greater extent than the number entering the solid from the liquid. All the liquid will therefore disappear, and in order to again have liquid present it will be necessary to raise the temperature. In other words, the freezing point of the solution will be higher than that of the pure solvent.

If, on the other hand, the added substance is more soluble in the liquid than it is in the solid, the reverse will be true, and the freezing point of the solution will be lowered. In the case of aqueous solutions, the dissolved substance is usually insoluble in the solid, i.e., in ice. In consequence, the freezing point of aqueous solutions is lowered by the presence of the dissolved substance, and the solid separating out is generally the pure solid solvent. Only such cases will be considered in the following discussion.

If we plot the vapour pressure curves for the pure solvent, and for two solutions of different concentrations, we obtain the diagram shown in Fig. 60. As in the case of the curves shown in Fig. 58, these are practically "parallel." It has already been pointed out that the vapour pressure of a pure liquid is the same as the vapour pressure of the solid at the freezing point, since there can be equilibrium only when such equality of vapour pressure exists. Consequently the vapour pressure curve of the liquid solvent, *AB*, meets the vapour pressure curve of the solid, *BC*, at the freezing point of the pure solvent, T_F.

Since the vapour pressure of a solution is always less than the vapour pressure of the solvent, the vapour pressure curve of a solution will cut the vapour pressure curve of the solid at a lower temperature, T' or T''. At such a temperature the vapour pressure of the solution must be the same as that of the pure solid solvent. Hence this temperature must represent the freezing point of the solution.

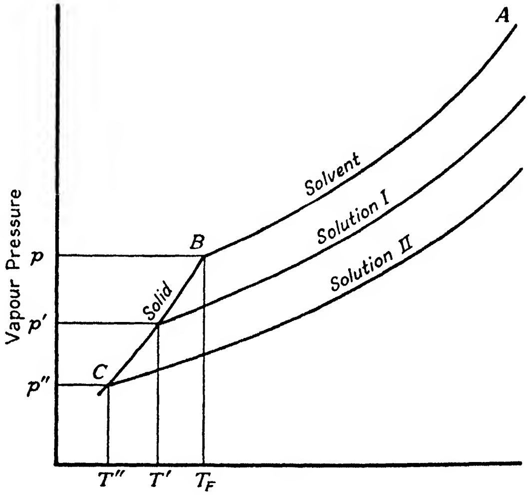

FIG. 60.

As in the case of the boiling point rise, the lowering of the freezing point, $(T_F - T')$ or $(T_F - T'')$, is proportional to the amount of the dissolved substance. It is also proportional to the lowering of the vapour pressure, since the curves form a regular family. We therefore have

$$\frac{p - p'}{T_F - T'} = \frac{p - p''}{T_F - T''},$$

or, if Δt is the lowering of the freezing point,

$$\frac{p - p'}{\Delta t'} = \frac{p - p''}{\Delta t''}.$$

Therefore

$$p - p' = K\Delta t'.$$

But, as before,

$$P = \frac{1000RST}{M'} \cdot \frac{p - p'}{p}.$$

Hence

$$P = \frac{1000RST_F}{M'} \cdot \frac{K\Delta t'}{p}.$$

For a given solvent R, T_F, M', and p are constants, and S is practically constant as before.

Therefore we have

$$P = K_1\Delta t',$$

where K_1 is a constant which depends on the solvent only, and can be calculated, or evaluated experimentally, for any solvent.

The Experimental Measurement of the Lowering of the Freezing Point.—Since it is necessary to measure very small changes in temperature, a thermometer must be used which can be read to 0.001° C. It is impossible to make such a thermometer of convenient dimensions, with a range of more than five or six degrees. It would therefore be necessary to have a very large number of different thermometers, in order to cover the range of one or two hundred degrees required for the measurements of boiling and freezing points in various solvents. In order to avoid this, Beckmann devised a thermometer with a range of five or six degrees, which is provided with a mercury reservoir, by means of which mercury may be removed from, or added to, the thermometer, which therefore can be employed for any desired temperature range. In order to use this thermometer in the determination of the lowering of the freezing point, it is first set so that the freezing point of the pure solvent is somewhere near the top of the scale. The freezing points of the solvent and the solution are then determined, and the difference between the two readings gives the lowering of the freezing point.

The apparatus ordinarily employed is represented in Fig. 61. It consists of a test-tube which is filled with the solution or solvent whose freezing point is to be determined. This tube is provided with a cork, through which pass the Beckmann thermometer and a small glass stirrer. This apparatus is fitted into another test-tube, so as to be surrounded by an air jacket. The outer tube is immersed in a jar, which contains a freezing mixture at a temperature several degrees lower than the freezing point to be measured.

In determining the freezing point of a substance the possibility of supercooling must not be overlooked. If a solid is heated to its melting point, fusion commences immediately, and the solid cannot be superheated, i.e., heated above its true melting point. On the other hand, if a liquid is fairly pure and free from dust, it is possible to cool it several degrees below its true freezing point, and to keep it at such a temperature for a long time without the formation of any of the solid phase. If we then lower the temperature still more, or introduce a small crystal of the solid, freezing will suddenly commence. As soon as freezing starts, the heat liberated (the latent heat of fusion) will cause the temperature of the liquid to rise until the true freezing point is reached. The temperature will then remain constant at the freezing point until all the liquid has disappeared, and will then fall steadily as the solid cools. Thus if we plot the temperature against time for a cooling substance we obtain a curve such as that given in Fig. 62.

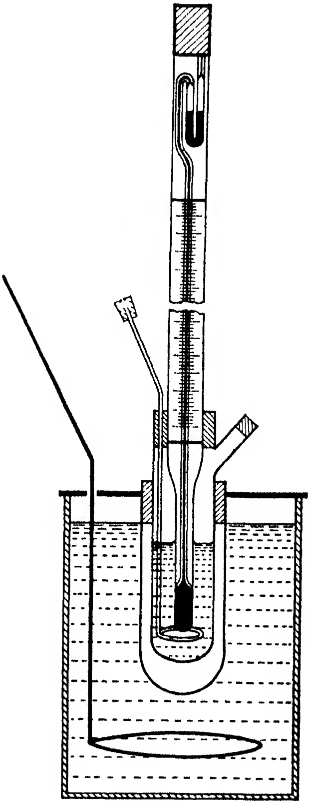
Fig. 61.

To determine the freezing point lowering due to a dissolved substance the following procedure is adopted. A weighed quantity of the solvent is first placed in the test-tube, and the outer bath is brought to a temperature a few degrees below the freezing point of the substance. If the solvent is water, an ice-salt mixture is used and the bath is maintained at about −5° C. The solvent is kept stirred, and the temperature, as indicated by the Beckmann thermometer, falls steadily, passing the true freezing point on account of supercooling. The temperature rises quickly as freezing starts, and then remains constant at the true freezing point of the solvent.

A weighed quantity of the solute is then introduced, dissolved by stirring, and the same procedure is again followed. The temperature at first falls below the true freezing point owing to supercooling, and then rises to the freezing point as solidification commences. As the solid freezing out is the pure solid solvent, the solution becomes more and more concentrated as freezing progresses. As a result the freezing point falls steadily. The true freezing point of the original solution is taken as the highest temperature reached after the supercooling. The difference between the two freezing points, thus determined, gives the lowering of the freezing point due to the presence of the dissolved substance.

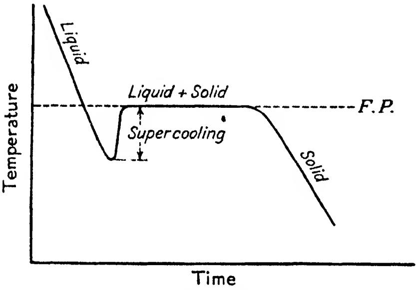

Fig. 62.

The Relation between the Molecular Weight of the Dissolved Substance and the Rise in the Boiling Point and Lowering of the Freezing Point.—It has been shown above that the osmotic pressure is connected with the molecular weight of the solute particles by the relationship

$$P = \frac{wRT}{MV}.$$

In many cases the molecular weight of the dissolved substance is of more interest than its osmotic pressure, and hence it is convenient to substitute this relationship for the osmotic pressure in the boiling and freezing point equations.

Thus, for the rise in the boiling point we have the equation

$$P = K_1 \Delta t,$$

where P is the osmotic pressure, Δt is the rise in the boiling point and K_1 is a constant which depends on the solvent only. Substituting for P, this becomes

$$M = \frac{wRT_B}{K_1\ V\Delta t},$$

or

$$M = \frac{wK_2}{V\Delta t},$$

where V is the volume of the solution, and K_2 is a constant for any particular solvent which includes K_1, R, and T_B. In dilute solutions, V, the volume of the solution, is approximately equal to the volume of the pure solvent, which in turn is approximately proportional to W, the weight of the pure solvent. Hence we have

$$M = \frac{Kw}{W\Delta t},$$

where w is the weight of solute dissolved in W grams of solvent, and K is constant for any particular solvent.

Here again, K can be evaluated experimentally by using a sugar solution whose osmotic pressure, and hence molecular weight, can be determined directly and compared with the observed rise in the boiling point. In the case of water the value of K is found to be 520.

A similar relationship holds between the molecular weight of the solute and the lowering of the freezing point. The value of the constant K is different, however, and in the case of water is 1860.

The following example will illustrate the application of the above equation.

Suppose that we have a solution of one gram of ethyl alcohol in 100 grams of water, and that the freezing point of the solution is 0.399° C. lower than that of pure water. Then the equation

$$M = \frac{Kw}{W\Delta t}$$

becomes

$$M = \frac{1860 \times 1}{100 \times 0.399},$$

$$= 46.4.$$

Isotonic Solutions.—The foregoing hypothesis of the nature of osmotic pressure and allied phenomena was developed by van't Hoff. Long before the development of this hypothesis, however, osmotic phenomena had been noticed, and regularities had been observed in connection with the lowering of the freezing point. For example, it was recognized that all molal solutions had their freezing points lowered to the same extent, viz.: 1.86° C., and this regularity was known as Raoult's law. In its more general form, this law stated that solutions of the same molal concentration had the same freezing point lowering (in the same solvent). In the light of van't Hoff's hypothesis, the reason for this is obvious, since all such solutions have the same osmotic pressure. Such solutions, i.e., those which have the same osmotic pressure, no matter what the solute may be, are called *isotonic* solutions.

The phenomenon of diffusion through a semi-permeable membrane was first noticed by botanists, in particular by de Vries and Pfeffer. Thus it was observed that certain vegetable membranes and animal bladders, when filled with a solution and placed in pure water, would swell owing to the diffusion of water into the solution. It was also observed that no such swelling occurred when a bladder filled with a solution was immersed in another solution of the same molal concentration. This phenomenon was called osmosis, and the absence of swelling of a bladder was used as a test for isotonic solutions. Such phenomena are, of course, readily understood in the light of the above hypothesis.

Aberrations from the Laws of Ideal Solutions.—So far nothing has been said concerning the exactness with which the various relationships dealing with osmotic pressure hold. In connection with the gas laws, it was shown that discrepancies occurred under certain conditions. In a similar way aberrations from the osmotic laws take place.

For example, in the case of gases, if we know the pressure-volume-temperature relationships, the molecular weight can be calculated from the equation

$$PV = \frac{w}{M}RT.$$

At high pressures gases deviate from the ideal gas law, and hence if the molecular weight is calculated from observations at different pressures we obtain a curve such as that previously given in Fig. 15.

The same type of aberration occurs if the molecular weight of a dissolved substance is calculated from observations of the rise in the boiling point, or lowering of the freezing point, carried out with solutions of different concentrations. Thus with a solution of naphthalene in benzene the following results are obtained.

Concentration of Solution (Gram Molecules per Litre)	Calculated Molecular Weight
0.0692	128.5
0.1384	128.9
0.2076	129.3
0.2768	129.7

The results given in the above table are plotted in Fig. 63. It will be seen that the value for the molecular weight of naphthalene is 128, when the curve is extrapolated to zero concentration. This agrees, within the experimental error, with the value obtained for naphthalene in the gaseous state by extrapolation to zero pressure. Hence it may be said that the relationships derived above hold, within the experimental error, for very dilute solutions, i.e., when the results are extrapolated to zero osmotic pressure. A solution which is so dilute that the osmotic laws hold with perfect accuracy is called an "ideal solution."

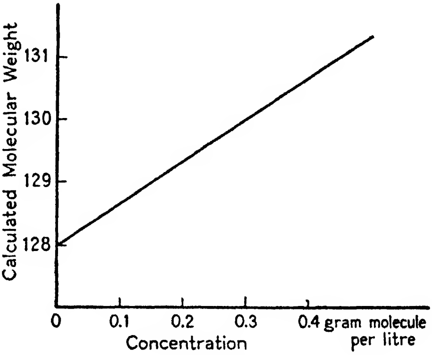

FIG. 63.

The aberration from the laws of ideal solutions at any specified concentration depends upon the intrinsic properties of the solute and solvent. Some solutions show only very slight aberrations even at high concentrations, just as gases such as helium obey the ideal gas law up to fairly high pressures. In solutions, the aberrations which occur are due principally to attractive forces between molecules. Such aberrations are complicated, and difficult to treat theoretically, since we are dealing with two different species of molecule.

Association and Dissociation.—In determining the molecular weight of a substance, a solvent should be chosen which is as similar to the solute as possible. Thus, when the molecular weight of alcohol dissolved in water is determined by the lowering of the freezing point, there is only a very small increase in the apparent molecular weight with increasing concentration. A curve is obtained for the results which is very similar to that given for naphthalene in Fig. 63. If a solution of alcohol in benzene is used, however, there is a very large variation of the apparent molecular weight with increasing concentration, as shown below.

Alcohol in Benzene

Theoretical Mol. Wt. = 46

Concentration (Gram Molecules per Litre)	Calculated Molecular Weight	Association
0.100	50	1.09
0.250	62	1.35
0.500	82	1.78
1.000	115	2.50
2.000	162	3.52
3.000	198	4.30

The abnormally high molecular weights obtained in such a case may be attributed to association. This is analogous to the similar assumption made in connection with the molecular weights of certain gases, such as sulphur vapour. For a given weight of substance in solution, the freezing point lowering, or boiling point elevation, depends upon the number of dissolved particles. The smaller the size of each particle, the larger will be the number of particles. In consequence, the aggregation of molecules to form larger particles will lead to a high value for the molecular weight calculated from the freezing point lowering. The last column in the above table gives the association at various concentrations, i.e., the number of single molecules which are aggregated to give the larger particle. It will be seen that this association factor, as given above, is not an integral number. This merely means that complexes are present which contain various numbers of molecules, and the average number of single molecules in an aggregate is that given in the table.

There are a large number of substances which behave in a similar manner, and in all cases the observed results can be reasonably explained by the assumption of association.

In the case of acids, bases, and salts, the molecular weight calculated from the rise in boiling point or lowering of the freezing point, instead of being too high, is too low, and decreases still further as the solution is diluted. This is similar to the behaviour of ammonium chloride in the gaseous state. It would therefore be expected that this behaviour could be interpreted by the assumption of dissociation. Some examples of molecular weights of this type are given below.

Substance	Theoretical Molecular Weight	Molecular Weight Calculated from Freezing Point Lowering of Very Dilute Solutions
$NaCl$	58.5	29.2
$NaOH$	40.0	20.0
H_2SO_4	98.0	32.6

Some of the most important conceptions regarding chemical reactions and the electrical properties of matter have been based on observations of the type given in the above table. These conceptions will be discussed in Chapter XVI, and the further discussion of dissociation in solution will therefore be deferred.

Volatile Solutes.—When alcohol is dissolved in water, the vapour above the solution is found to contain an appreciable amount of alcohol, even if the solution is very dilute. All the deductions which have been made previously regarding the vapour pressures of solutions will still be valid, provided that we consider, not the total pressure in the vapour phase, but merely the partial pressure of water vapour. The total pressure of vapour above the solution, i.e., water plus alcohol, will not necessarily be lower than the vapour pressure of the pure solvent, and may in fact be considerably greater than this in certain cases. As a result the methods previously described for the measurement of the lowering of the vapour pressure and the rise of the boiling point can no longer be used. The freezing point method is therefore the most suitable for the determination of the molecular weights of volatile solutes.

It should be again emphasized that the terms solute and solvent are used merely for convenience, and that there is no fundamental difference between the two. In a solution each constituent is to be regarded as dissolved in the other. Consequently, while alcohol lowers the partial vapour pressure of water, the water will also lower the partial vapour pressure of the alcohol. The total vapour pressure above the solution will therefore depend upon the relative proportions of the two substances in the solution. If, therefore, two substances were brought together in equimolecular proportions, and if they formed an ideal solution, the partial vapour pressure of each would be half the vapour pressure when pure. The total vapour pressure would consequently be the average of those of the constituents. This is not true in the case of alcohol and water, since the strong attractive forces which come into play between the two types of molecule cause large aberrations from the laws of ideal solutions.

Solubility.—Up to this point we have been considering the behaviour of the dissolved substance in a solution. It is now necessary to discuss the mechanism of the process by which one substance dissolves in another to form a solution.

It has often been suggested that solubility depends upon the formation of a compound between the solute and the solvent. There are, however, grave objections to this viewpoint. In the first place, the basic criterion of the existence of a solution is the possibility of the continuous variation of the composition, which thus eliminates the possibility of the existence of stoichiometric proportions as would be expected in the case of compound formation. Again, diffusion phenomena, and direct and indirect osmotic pressure measurements, show that the solute is free to move about the solution in particles whose sizes often correspond to that of the molecule of the solute as it exists in the vapour state. This, however, does not conclusively prove the absence of compound formation. The solute molecules may unite with one or more solvent molecules, and this aggregate as a whole may constitute the unit particle. Even if this is so, however, these resultant aggregates will move about in the solution, and will constitute a real solution in the sense of the hypothesis of van't Hoff.

It is impossible to discuss here the methods which have been employed in an attempt to determine whether such "solvation" of solute molecules occurs. It has been concluded that in some cases there is solvation (or hydration in the case of aqueous solutions), but that in a large number of cases it does not occur. If solvation does occur, the osmotic pressure of a dilute solution is not affected to an appreciable extent, because the number of particles remains the same whether the solute molecule exists alone, or has one or more solvent molecules attached to it. In concentrated solutions, however, serious aberrations from the osmotic laws may occur due to solvation, since the withdrawal of solvent for purposes of solvation results in the further concentration of the solution.

The nature of a solution may therefore be regarded as fairly well established, and we are left only with the discussion of the phenomenon of solubility, i.e., the saturation concentration. The nature of the solute particles is understood, but it is still necessary to explain why the number of particles which can exist in stable equilibrium in a solvent should be subject to an upper limit.

Suppose that we consider the case of solid iodine in equilibrium with its own vapour. Owing to molecular attraction, the solid possesses a definite surface tension. There is thus a downward force on the molecules at or near the surface, which tends to prevent evaporation. Only those molecules which possess an unusually large amount of energy can overcome this downward force and escape into the vapour above. When equilibrium is established, the number of molecules returning from the vapour is equal to the number evaporating, and there will be a definite vapour pressure. This vapour pressure is directly dependent on the downward attractive force at the surface, and anything which will affect this force will affect the vapour pressure. If, for example, oxygen is added to the vapour phase, owing to the attraction of oxygen and iodine molecules for one another, the resultant downward force at the surface is decreased. More iodine molecules are thus enabled to escape into the vapour phase, and the vapour pressure of iodine is thus raised by the addition of oxygen.

Suppose that we now consider some solid sugar in an evacuated space. The downward attractive force at the surface of the solid is so large that no appreciable number of sugar molecules can escape from the solid and enter the vapour phase. It is thus impossible to detect the existence of any vapour pressure, although there are undoubtedly a few sugar molecules in the vapour state. If the attractive forces at the surface could be overcome in any way, sugar molecules would be enabled to escape in larger numbers. If, therefore, water is brought into contact with the sugar, the force at the surface will be greatly reduced in intensity on account of the mutual attraction between molecules of water and sugar. Sugar molecules will therefore be able to escape from the solid, and to move about freely in the liquid. Solution is thus completely analogous to evaporation.

Like evaporation, solution is a dynamic equilibrium. Thus sugar is continually leaving the solid and entering the solution; at the same time molecules from the solution are continually returning to the solid. In consequence, if sugar is brought into contact with water, the number of sugar molecules in the solution will continually increase until the number entering the solution in unit time is equal to the number leaving the solution. When this equality is reached we have a condition of equilibrium, the number of molecules of sugar in the solution is constant, and the concentration of sugar is called the saturation concentration. We can thus regard the tendency of the sugar molecules to enter the solution as a solution pressure, which is in every way analogous to vapour pressure.

The above hypothesis of the mechanism of solubility may appear at first sight to be purely *ad hoc.* There is, however, outside evidence in its favour. By means of what are called radioactive indicators, it has been possible to prove conclusively that solution is a dynamic equilibrium. Furthermore, evidence regarding the forces of molecular attraction, obtained from the investigation of other phenomena, often enables successful predictions to be made concerning the solubility of a substance in various solvents. These details cannot be further amplified here, and are given merely to indicate that there is further evidence to confirm the plausibility of the above hypothesis.

The Effect of Temperature on Solubility.—By analogy with vapour pressure it would be expected that the solution pressure, and hence the solubility, of a substance would increase as the temperature rises. This is found to be the case with most solutions. There are, however, several complicating factors. In the first place, some solvents consist of associated molecules. If the complexity of these changes with changing temperature, complications will obviously be introduced into the variation of the solubility with temperature. Again, if solvation of the solute occurs, an increase in temperature will decrease the extent of solvation, and this will tend to decrease the solubility. Furthermore, association of the solute may occur; such association decreases with increasing temperature, and again complicates the solubility relationships. As a result of these complications the solubility sometimes remains constant, or even decreases, as the temperature is raised.

We may therefore say that although the general relationship between solubility and temperature is that which would be predicted, there are so many possible complications that in many cases it is impossible to estimate the effect of temperature on the solubility of a substance.

QUESTIONS AND PROBLEMS

1. One gram of a substance is dissolved in water to form 100 c.c. of solution. The osmotic pressure of the solution is found to be 50 cm. of mercury at 20° C. Calculate the osmotic pressure when the solution is diluted to 240 c.c.
Ans. 20.8 cm.

2. Calculate the osmotic pressure of the solutions in question 1, when the temperature is 50° C., neglecting the change in the volume of the solution when the temperature changes. *Ans.* 55.1 and 22.9 cm.

3. Calculate the osmotic pressure at 27° C. of a 0.0666 M solution of a solute which is neither associated nor dissociated. *Ans.* 1.642 atm.

4. Calculate the osmotic pressure of a solution at 70° C., 100 c.c. of which contain 1 gram of cane sugar (molecular weight = 342) and 1 gram of glucose (molecular weight = 180). *Ans.* 2.39 atm.

5. Five grams of a substance are dissolved in water to form 1 litre of solution. The osmotic pressure is 80 cm. at 20° C. Find the molecular weight of the solute. *Ans.* 114.3.

6. Calculate the height to which a 1 per cent sugar solution will rise in an osmotic cell of the form shown in Fig. 52. Assume the density of the solution to be 1.0, and the temperature to be 27° C. Neglect the dilution of the solution by the water which enters the cell. *Ans.* 743.6 cm.

7. The vapour pressure of water at 25° C. is 23.763 mm. Calculate the partial pressure of water vapour in a closed system 10 metres above a water surface. *Ans.* 23.747 mm.

8. The osmotic pressure of an aqueous solution at 100° C. is 1.2 atmospheres. The density of the solution is 1.05. Calculate the vapour pressure of the solution at this temperature. *Ans.* 759.6 mm.

9. An aqueous solution contains 5 grams of solute per litre. The vapour pressure of water at 50° C. is 92.17 mm. The vapour pressure of the solution is 92.02 mm. The density of the solution is 1.01. Calculate the molecular weight of the solute. *Ans.* 55.0.

10. One gram of a substance is dissolved in 100 grams of water. The freezing point lowering of the solution is 0.430° C. Find the molecular weight of the dissolved substance. *Ans.* 43.25.

11. Calculate the rise in the boiling point of the solution referred to in question 10. *Ans.* 0.120° C.

12. Calculate the boiling point rise and freezing point lowering of a molar solution. *Ans.* 0.520° C., 1.860° C.

13. The freezing point lowering of a 1 per cent aqueous solution is 0.235° C. Find the concentration of a cane sugar solution which would be isotonic with this. Assume the densities of both solutions to be 1.0. *Ans.* 0.126 M.

14. The freezing point lowering of a solution which contains 1 gram of solute to 100 grams of water is 0.195° C. The freezing point lowering of a solution of the same substance which contains 3 grams of solute to 100 grams of water is 0.570° C. Find graphically the molecular weight of the dissolved substance at zero concentration. *Ans.* 94.1.

15. The lowering of the freezing point of an aqueous solution of a substance is 0.500° C. Calculate the freezing point lowering of a solution of the same substance in benzene, the concentration by weight being the same as that of the aqueous solution. The freezing point constant for benzene is 5120. *Ans.* 1.376° C.

16. Describe the method of measuring osmotic pressures.

17. Discuss the determination of the molecular weights of dissolved substances.

18. Discuss the mechanism of osmotic membranes. Show that the measured osmotic pressure is independent of the mechanism of the membrane.

19. Derive the relationship between the osmotic pressure and the lowering of the vapour pressure of a solution.

20. Describe the experimental measurement of the lowering of the vapour pressure of a solution.

21. Derive the relationship between the osmotic pressure and the rise in the boiling point of a solution.

22. Describe the experimental measurement of the boiling point rise of a solution.

23. Derive the relationship between the osmotic pressure and the lowering of the freezing point of a solution.

24. Describe the experimental measurement of the lowering of the freezing point of a solution.

25. Derive the relationship between the molecular weight of a dissolved substance and the rise in boiling point or lowering of the freezing point.

26. Discuss isotonic solutions.

27. What is an ideal solution? Discuss aberrations from the laws of ideal solutions.

28. Discuss association and dissociation of solutes.

29. Discuss the mechanism of solution, and the effect of temperature on solubility.

CHAPTER XIII

THE PHASE RULE

Introduction.—While equilibria in homogeneous systems can best be studied with the help of the mass law, equilibria in heterogeneous systems are generally examined with the help of the phase rule. The latter is a relationship which was first deduced by Willard Gibbs from thermodynamic principles, and thus should hold without exception as has been found to be the case.

By means of the phase rule heterogeneous systems may be classified and the necessary conditions for the stability of a heterogeneous system can be predicted with exactitude. With the simultaneous application of Le Châtelier's principle and the phase rule, it is possible to predict qualitatively from a diagram the influence of changing pressure, temperature, or concentration on the equilibrium in a heterogeneous system.

An example of a simple heterogeneous system, namely that of a pure liquid in equilibrium with its own vapour, may well be taken in order to lead up to the phase rule itself. In this system pressure and temperature are the factors which influence the stability of the system. If, of these two, the temperature remains constant, the pressure is automatically defined and remains unaltered as long as the two phases exist. An attempt to increase the pressure by reducing the volume of the system results in condensation of some of the vapour, the pressure remaining constant. Thus when the temperature of such a system has been arbitrarily fixed at a definite value the pressure cannot be altered, and hence only one factor governs the stability of the system. When the volume of such a system is reduced to a point where only the liquid phase is left, then beyond that a further reduction in volume can be brought about only by an increase in pressure, even though the temperature is maintained at a constant value. Hence, to define conditions under which the compressed liquid exists, it is necessary to state both temperature and pressure. Arbitrarily fixing one of them does not define the other. The above facts follow (as was shown elsewhere) from the molecular kinetic concept of the structure of liquids and gases. The phase rule enables one to predict that for equilibrium between a liquid and its vapour only one of the factors influencing the equilibrium can be arbitrarily fixed, whereas, when the liquid alone exists, two factors must be defined. This prediction is independent of any concept of the nature of structure of matter.

The phase rule is expressed symbolically as follows: $P + F = C + 2$, where P stands for the number of phases, C the number of components, and F the degrees of freedom of the system under examination. The number of phases is the number of homogeneous physically distinct and mechanically separable portions of matter that are in equilibrium. Thus when water is in equilibrium with its vapour, $P = 2$, i.e., the liquid and the vapour. If this system is cooled down to the temperature where ice forms, $P = 3$, i.e., solid, liquid, and vapour, or, symbolically, S, L, V. If a small amount of ether is added to a system consisting of liquid water and completely dissolves, $P = 1$. Then on the gradual addition of more ether a second layer forms, a solution of water in ether, and $P = 2$. If now succinic nitrile is added to the system in sufficient quantity a third liquid layer forms and $P = 3$. There can be any number of liquid phases in a system. Similarly, there can be any number of solid phases in a system, and in the case of certain elements and compounds there may be two solid phases in a system containing only one pure substance. Thus, for instance, solid monoclinic and rhombic sulphur are in equilibrium with one another in the absence of the vapour at 95°, and here $P = 2$. Since all gases are soluble in one another in all proportions, there can be only one gaseous phase in any system, but as the above illustrations show, there may be any number of liquid and solid phases present.

The Components of the System.—In the application of the phase rule it sometimes requires a little thought to estimate the number of components. The following definition is the best one to employ in this connection. As components in a system we choose the smallest number of independently variable constituents by means of which the composition of each phase participating in the equilibrium may be defined. This definition may be elucidated by means of a number of illustrations.

Before taking these up, however, it may be well to point out that a constituent is here represented by a chemical formula which is not meant to be indicative of molecular structure but of stoichiometric proportions of the elements. Suppose we consider the system ice, water, and its vapour when in equilibrium at its freezing point. The composition of the water vapour is given by the chemical formula H_2O which has the meaning, in so far as the definition of components is concerned, that for every gram of hydrogen there are eight grams of oxygen present in this phase. The other two phases have the same composition, and therefore can also be represented by the same chemical formula. In this system then, $C = 1$, and it is called a one-component system. In the liquid water it is believed that there are molecular species H_2O, $(H_2O)_2$, $(H_2O)_3$, which are in equilibrium with one another. The definition of components is not concerned with molecular complexity, but solely with the chemical formulae giving the composition of the liquid. Suppose one next considers the number of components in the system where sodium chloride is dissolved in water in contact with its vapour. The composition of the liquid phase can then be given by $X\ NaCl + Y\ H_2O$, where X and Y are variables and depend on the amount of sodium chloride which has been dissolved. The vapour phase can be expressed by the chemical formula H_2O; thus by means of two chemical formulae it is possible to give the composition of each of the phases in this system. It is true that the sodium chloride is dissociated into sodium and chlorine ions, but that does not alter the fact that for every 23 grams of sodium there are 35.5 grams of chlorine. That ratio is fixed by the formula NaCl and not altered whether the sodium chloride be dissociated or not. If to this solution of sodium chloride potassium bromide is added, the composition of the liquid phase can be expressed by $X\ NaCl + Y\ KBr + Z\ H_2O$. Irrespective of the fact that four different ions as well as water are present in the solution, the three chemical formulae suffice to give the composition of this phase as it can be determined by analysis, irrespective of what the molecular complexity might be. It is therefore a three-component system. When calcium carbonate is heated, it dissociates in part into CaO and CO_2, $CaCO_3 = CaO + CO_2$. There are three phases present in this system: two solids and one gas. According to the definition, as components we must choose the smallest number of chemical formulae by means of which the composition of each phase may be determined and, in this case two suffice. The composition of the carbonate is given by $CaO + CO_2$, the composition of the lime by CaO, the composition of the vapour by CO_2. Hence this is a two-component system.

Another illustration which may help to qualify the definition of components is that of solid ammonium chloride in equilibrium with its vapour at a high temperature, where

$$\overset{\text{solid}}{NH_4Cl} = \overset{\text{gas}}{NH_3 + HCl}.$$

Though the vapour is largely decomposed into ammonia and hydrogen chloride, it would be a mistake to represent the gaseous phase by $NH_3 + HCl$, two chemical formulae, because it can be represented by NH_4Cl, the same as the solid phase. Analysis of the vapour would show that for every 14 grams of nitrogen there are 4 grams of hydrogen and 35.5 grams of chlorine, just as in the solid phase. Hence this is a one-component system. Should, however, excess HCl or NH_3 be added to the system, the composition of the gaseous phase can no longer be represented by NH_4Cl, but must be represented by $x\ NH_3 + y\ HCl$. The solid phase can be represented by $1\ NH_3 + 1\ HCl$. Two chemical formulae therefore suffice to represent the phases in equilibrium in the system, which is therefore a two-component system.

It is important at this point to indicate certain cases where care must be taken in evaluating the number of components. For instance, when acetaldehyde is added to paraldehyde, a liquid is obtained which under certain conditions appears to act as a two-component system although the composition of a liquid can be represented by one chemical formula, namely C_2H_4O. The reason why this system appears to act as a two-component system is that the equilibrium between acetaldehyde and paraldehyde, 3 $C_2H_4O = (C_2H_4O)_3$, is not always rapidly established, and consequently the properties of the liquid will vary depending on the extent to which true equilibrium has been reached. The phase rule, based on thermodynamic principles, does not take into account any time factor, and is only applicable to systems which are in true equilibrium. Care must therefore be taken in the phase rule applications to ascertain that the true final equilibrium conditions have been reached.

The Degrees of Freedom of the System.—As degrees of freedom we choose the number of variable factors such as pressure, temperature, and concentration, which must be arbitrarily fixed in order that equilibrium may be perfectly defined. The meaning of this definition will be clarified when some systems are examined by means of the phase rule. Before going on to this, a few further points had best be taken up. As was mentioned before, in phase rule applications, use is made of the principle of LeChâtelier, namely, that when one of the factors governing equilibrium is changed, the equilibrium is altered in such a direction as to minimize the magnitude of the change. Thus an increase in pressure will bring a change in equilibrium which is accompanied by a reduction in volume. A rise in temperature will produce a change in such a direction that there will be an absorption of heat, thus those phases will be stable at high temperature which are formed with the absorption of heat. Therefore one can predict that a rise in temperature will change a liquid phase into the vapour phase. An increase in pressure will bring about a change from a phase having a large volume to a phase having a small volume. Thus an increase in pressure will change the gas phase into the liquid phase.

The One-Component System—Water.—The first system to be examined, keeping the above applications in mind, is the one-component system of water. Following a procedure which is most useful, a list is made of the phases in which the component can exist, and then all possible systems and their degrees of freedom are tabulated. In the case of water, there are only three phases possible: water vapour, liquid water, and solid water (ice),* which it is convenient to designate again by V, L, and S. Possible systems:

$$\begin{array}{ccc} P = 1 & P = 2 & P = 3 \\ \left.\begin{matrix} S \\ L \\ V \end{matrix}\right\} F = 2 & \left.\begin{matrix} SL \\ LV \\ SV \end{matrix}\right\} F = 1 & SLV\} F = 0 \end{array}$$

In the above compilation it is seen that there are three possible systems in which there is only one phase present, three in which there are two phases present, and one in which there are three phases present. Since in a one-component system the phase rule reduces to $P + F = 3$, the degrees of freedom are 2, 1, and 0 in these systems respectively. According to the definition of component, in a one-component system concentration does not enter, and pressure and temperature are the only factors governing the equilibrium. Two degrees of freedom mean therefore that both pressure and temperature have to be fixed in order that the equilibrium is defined. In graphic representation an area will represent a system having two degrees of freedom since the location of any point in the area requires a measurement both along the ordinate axis and along the abscissa axis in order to fix the point in the area. Where the system has two degrees of freedom it is known as a divariant system.

Where two phases are present it follows from the phase rule that there is only one degree of freedom. Such a system can therefore be represented graphically by means of a line, because if the abscissa is fixed the line determines the ordinate, and *vice versa*.

Where three phases are present it follows from the phase rule that there are 0 degree of freedom, and such a system is called an invariant system. It must be represented graphically by a point which admits of no variation of either ordinate or abscissa.

The three divariant systems will then be represented by areas, the three univariant systems by lines, and the non-variant systems by a point. It also follows that where any two lines representing the univariant systems meet, say SL and LV,

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* Water can exist in solid crystalline forms other than natural ice. These formations, which only occur under enormous pressures, will not be considered here.

since S, L, and V are all three represented it must be the invariant point, and through it also must pass the third line representing the univariant system SV. The above sounds rather abstract until the graphs are drawn representing all possible systems of water (see Fig. 64*). AB represents the vapour-pressure curve of liquid water, that is, where L and V are in equilibrium with one another. Suppose one takes a temperature T_1, the line AB fixes the pressure P_1 which is necessary for the equilibrium of the system; that is, it is possible to arbitrarily choose any temperature, but as long as the two phases L and V are present the pressure is defined by the choice of the temperature. If a higher temperature T_2 is chosen, a higher pressure, P_2 is defined by this choice of temperature. It is possible to choose the pressure instead of temperature. Suppose a pressure P_3 is chosen, then the system, if in equilibrium, must be at a temperature T_3, as given by the position of the line AB. To make this clearer, one can refer to Faraday's method of

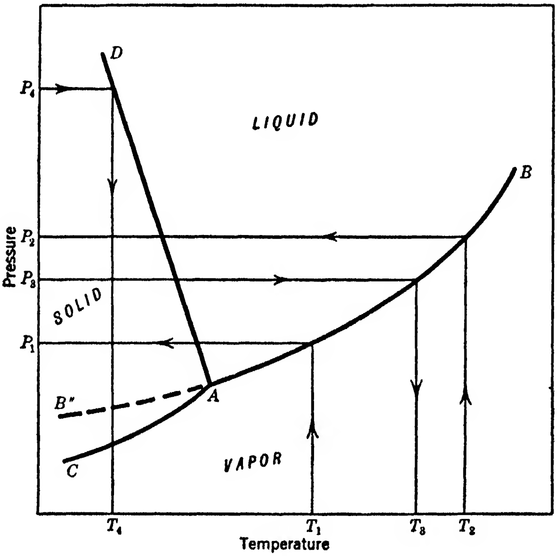

FIG. 64.

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* Temperatures are plotted as abscissae, and pressures as ordinates.

producing low temperatures by subjecting a liquid to a low pressure. If by means of a pumping system the pressure above the liquid is kept at a constant value, the temperature of a liquid remains constant at a value given by the position of the line *AB*, as indicated in Fig. 64.

The phase rule therefore predicts what has already been discussed: the nature of a vapour-pressure curve of a liquid. This requires that independent of the relative amounts of the two phases liquid and vapour, a liquid at a constant temperature has a constant vapour pressure, or a liquid-vapour system maintained at a constant pressure has a constant temperature. The phase rule predicts the existence of such a vapour-pressure curve, but it does not define its limits. We know from the molecular kinetic theory that, if a high enough temperature (the critical temperature) is reached, liquid and vapour become identical, and if a low enough temperature is reached, the liquid will freeze. However, it is possible to supercool a liquid below the freezing point; and, as there are then two phases present as before, it remains a univariant system, as represented by the dotted line *AB*—a continuation of the graph *BA*. For a supercooled liquid in contact with its vapour there is one degree of freedom, and, as before, when the temperature is arbitrarily fixed, the pressure is defined.

All that has been said in regard to the system liquid-vapour also follows in regard to the system solid-vapour, as represented by the curve *CA*. At any temperature arbitrarily chosen, the vapour pressure of ice, according to the phase rule, must have a definite value. Where the two curves representing the univariant systems *SV* and *LV* meet, (*A*, Fig. 64), since this point is on the curve where *S* and *V* are in equilibrium, and on the curve where *L* and *V* are in equilibrium, all three phases *S*, *L*, and *V* must be in equilibrium. Hence the meeting point of these two curves represents the invariant system *SLV*, that is, where solid, liquid, and vapour are in equilibrium. The meaning of invariant is that it is impossible to fix either temperature or pressure arbitrarily and have these three phases in equilibrium with one another. This point is called the melting or freezing point of the substance, and neither pressure nor temperature can alter the freezing point of a pure substance, that is, as long as it is a one-component system with its own vapour phase present.* That is why the constancy of the freezing point of a substance is a criterion of its purity. Through *A* must pass a line representing the univariant system solid-liquid, since at *A* solid and liquid are in equilibrium with one another. It is represented in Fig. 64 by the line *AD*.

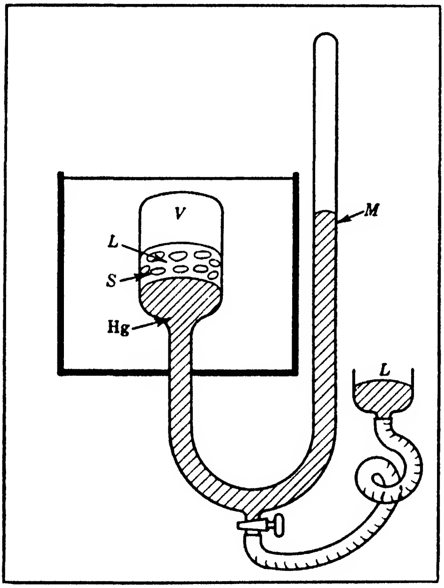

Fig. 65.

At this stage it may be of help in understanding the *SL* system to discuss the experimental method of determining the univariant system *SL*. As shown in Fig. 65, the system is enclosed by means of mercury in a little bulb surrounded by a thermostat whose temperature can be accurately regulated. The mercury is connected from the bottom of the bulb to an evacuated manometer *M*, and a leveling bulb *L* is attached as shown in the figure, so that the system can be subjected to any desired pressure. The pressure and temperature of the system are adjusted to begin with so that *L*, *S*, and *V* are in equilibrium with one another. This pressure and temperature cannot be altered without destroying one of the three phases present. If the temperature is lowered, the liquid freezes completely, and the pressure will then fall to some value given on curve *AC*, Fig. 64. If temperature is raised, the solid will melt, and the pressure rise to some point on the curve *AB*, corresponding to

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* It has become common practice to speak of 0° C. as the freezing point of water. This is due to the fact that in calibrating thermometers it is convenient to bring ice and water together in the presence of air at atmospheric pressure. Actually 0° C. is 0.0075° below the "triple point," where solid, liquid, and gaseous water are in equilibrium (in the absence of air) to give what is called, in phase-rule terminology, the invariant point.

this temperature. If, on the other hand, an attempt is made to increase the pressure, the vapour phase will disappear, after which, unless the temperature is lowered, the solid will disappear. To prevent the disappearance of the solid with increased pressure, the temperature has to be lowered, and the point thus obtained on the curve *AD*. For any increase in pressure above the vapour pressure at the invariant point *A*, the temperature has to be lowered to keep liquid and solid in equilibrium in contact with one another. With the disappearance of the vapour phase, the univariant system solid-liquid as given by the curve *AD* is obtained. For this system, if a temperature is arbitrarily chosen, the pressure is defined or in other words has to be brought to a definite value in order to keep an equilibrium between the solid and liquid. In practice, what is done is to increase the pressure, and maintain it at a given value, say P_4 (Fig. 64), then the temperature of the thermostat is adjusted to T_4 until the liquid does not freeze, and the solid does not melt. Owing to the difference in volume between liquid and solid this temperature can be readily determined because, when a change from one phase to the other is taking place, the level of the mercury in the manometer *M*, Fig. 65, keeps changing.

The system solid-liquid is known as a condensed system, a name given to any system in which the vapour phase is absent. Condensed systems differ markedly from systems in which the vapour phase is present inasmuch as a small change in temperature corresponds to an enormous change in pressure; thus, in the case of the one-component system water, an increase of one atmosphere means a lowering of temperature of only approximately 0.0075° C. The curve *AD* is actually much steeper than would be indicated on the diagram. For convenience condensed systems when depicted simultaneously with systems containing the vapour phase are drawn on an enormously greater pressure scale so that the direction of slope can be indicated.

The divariant systems representing a single phase are denoted by areas bounded by the univariant curves. Suppose one considers any point *E* on curve *AB* representing the univariant system *LV*, and that at T_1 the pressure is P_1. If an attempt is made to lower the pressure, the volume has to be increased, and the pressure remains constant as long as any trace of liquid remains, evaporation of the liquid supplying the vapour to bring about this increase in volume. When the last trace of liquid has disappeared, $F = 2$, and now an increase in volume will reduce the pressure. In other words, if desired, a point E' below the curve AB will be reached. The area below the curve AB represents the system V. In order to define the equilibrium of this system, both the pressure and the temperature have to be set. That is, arbitrarily fixing the temperature T_1, it is still possible arbitrarily to fix any pressure on the ordinate T_1E and have the system exist as a vapour phase. Similarly, starting again with point E, where liquid and vapour are in equilibrium, an attempt to increase the pressure will bring about a reduction in volume, the pressure remaining constant until the vapour has completely condensed, after which the pressure can be increased to any arbitrarily desired value E'', the liquid phase only being present. The area above the curve AB represents the divariant system—liquid.

It follows from the same line of reasoning that the area below the curve CA represents vapour and the area above, solid. The area representing the liquid phase and the area representing the solid phase are bounded by the univariant system liquid-solid, curve AD. If we take any point F on this curve it indicates that at a temperature T_4 liquid and solid are in equilibrium provided the system is subjected to the pressure P_4. An attempt to decrease the pressure, maintaining the temperature constant, will result in the disappearance of the phase having the larger volume,* namely, in the case of water, the ice; and thus it is possible at this temperature to have this system, the solid phase, in equilibrium at any desired pressure below F after the liquid has disappeared. In other words, the area below F represents the system—solid. Similarly, the area above the curve AD represents the system where only the liquid phase is present.

Stable and Unstable Phases.—There are a number of other considerations which may well be pointed out in connection with any one-component system. The univariant systems LV and

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* Le Châtelier's rule.

SV have been shown to meet in such a way that the supercooled liquid has a greater vapour pressure than the solid (Fig. 64, and Fig. 66 (*a*)). They might have met so that the reverse were the case (Fig. 66 (*b*)). The phase rule cannot be resorted to in order to decide which is the correct representation. As it is a matter which enters into almost every phase-rule diagram, it is worth discussing to some extent. Figure 66 (*a*) is the correct representation because it is an invariable rule that an unstable phase has a higher vapour pressure than a stable phase. Figure 66 (*b*) represents the reverse of this, and therefore is incorrect. The criterion of the relative stability of two phases is to bring them in contact with one another at a constant temperature, whereupon the unstable phase will change into the stable one. As has been discussed before, a supercooled liquid when brought into contact with its crystalline form immediately starts to freeze, and will solidify completely if a constant temperature is maintained. This also follows from phase-rule considerations. As long as liquid and vapour are in contact, there is one degree of freedom, and at a given temperature they can exist together even below the freezing point. The moment a crystal of the solid is added, three phases are present, and the system is invari-

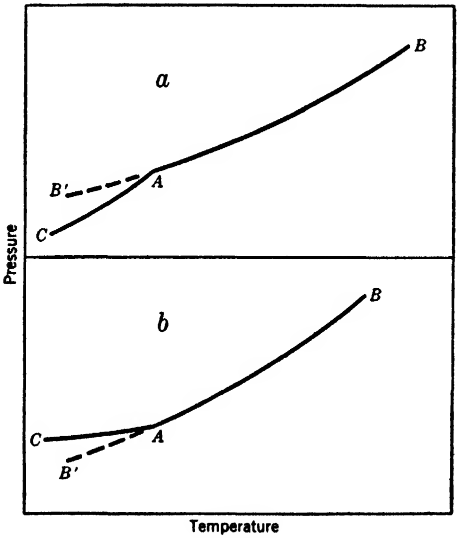

FIG. 66.

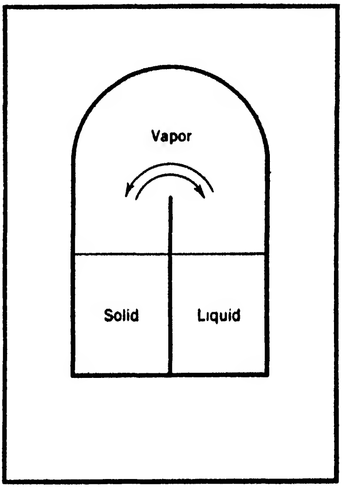

FIG. 67.

ant so that temperature and pressure will have to change to correspond to the invariant point or if the temperature is kept constant one of the phases (the unstable one) will have to disappear.

Going back to the question of the relative vapour pressures of the stable and unstable phases, one can imagine the supercooled liquid and the solid to be separated from actual contact except by means of the vapour as indicated in Fig. 67. If brought into contact, liquid will spontaneously change into solid; therefore the vapour pressure of the liquid must be greater than the vapour pressure of the solid in order to enable that change to take place spontaneously by the evaporation of the liquid and condensation of vapour on the solid. Otherwise it would be possible to devise a directional circulation of molecules which is contrary to the second law of thermodynamics. As shown in Fig. 64 and Fig. 66 (*a*), therefore, the curve AB must be placed relative to curve CA in such a way that BA produced to B' lies above CA. It is convenient to represent a univariant unstable system by means of dotted lines as has been done for $B'A$.

The Ice-Point.—It might seem that there is some discrepancy in connection with the invariant point. The melting point of ice and water, a fixed point in thermometry, is taken as 0° C. Thus ice and water, in the presence of air at atmospheric pressure, are in contact with their own vapour, whereas the freezing point as given in Fig. 64 is with liquid, solid, and vapour in contact at a much lower pressure. How is it that this supposedly invariant system can exist at more than one pressure? The answer is that in ordinary thermometry where ice and water are used, one is not dealing with a one-component system, as the water vapour is in contact with the air of the atmosphere. Therefore this gas phase cannot be represented by the chemical formula H_2O. Hence $P + F = 4$, and with three phases present $F = 1$. Consequently the pressure has to be arbitrarily fixed in order that the temperature is defined. The pressure which has been arbitrarily chosen for convenience is atmospheric pressure. Actually the true freezing point of water is approximately $+0.0075°$C., i.e., the freezing point when only water vapour is present and ice and liquid water are in equilibrium.

Other One-Component Systems.—Figure 68 represents the typical one-component system where the curves *B'AB*, *AC*, and *AD* represent respectively the univariant systems liquid-vapour, solid-vapour and solid-liquid. The solid liquid curve in Fig. 68 slopes in a different direction from that given in Fig. 64 for water. This is due to the fact that water is one of two known exceptions * to the general rule that the density of a pure liquid is less than that of the solid at its melting point. Change from solid to liquid is accompanied by an absorption of heat; hence rise in temperature must bring a change of phase from solid to liquid, as indicated by going from *a* to *b*. A rise in pressure must bring about a change of phase such that a smaller volume results. Hence, as indicated on going from *c* to *d*, a rise in pressure brings about a change from liquid to solid. The direction of the curve *AD* is governed by these two factors.

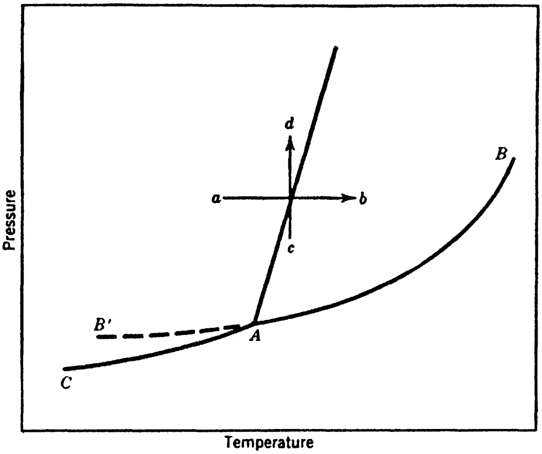

FIG. 68.

The Sulphur System.—The next system to be considered is one where more than one solid modification can exist, and the sulphur system is the classic illustration for this purpose. It will be used here to exemplify how a phase-rule diagram can be systematically built up on the basis of very little information.

Sulphur exists in two solid modifications, rhombic and monoclinic, which for convenience will be represented later on

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* Tin is the other exception.

by the letters *R* and *M*. The change from rhombic sulphur to monoclinic sulphur is accompanied by an absorption of heat, and by an increase in volume. The solid rhombic and monoclinic sulphurs are in equilibrium with one another, and with their vapour at 96° C., and this is known as the transition temperature. Rhombic sulphur has a melting point of 114° C. Monoclinic sulphur melts at 120° C. This information is sufficient to enable one to draw a phase-rule diagram indicating the relative positions and stability of all possible sulphur systems. These are first of all tabulated below together with their degrees of freedom.

$$\begin{array}{ccc} P = 1 & P = 2 & P = 3 \\ \left.\begin{array}{r} R \\ M \\ L \\ V \end{array}\right\} F = 2 & \left.\begin{array}{r} RV \\ MV \\ LV \\ RM \\ RL \\ ML \end{array}\right\} F = 1 & \left.\begin{array}{r} RMV \\ RLV \\ MLV \\ RML \end{array}\right\} F = 0 \end{array}$$

It is seen that the existence of two solid phases produces a considerable increase in the number of possible systems, there being four divariant, six univariant, and four invariant systems possible.* The phase rule predicts also that the four phases, rhombic, monoclinic, liquid, and vapour cannot exist together under any condition of temperature and pressure to form a stable system, as this would mean that $F = -1$, since $P + F = 3$.

In building up the phase-rule diagram, it is convenient to start with an invariant system; and *RMV*, which is the lowest temperature invariant system, can be considered first. Through the point representing it must pass the lines representing the three univariant systems *RV*, *MV*, and *RM*. The information that the change from rhombic to monoclinic is accompanied by an absorption of heat means that the monoclinic is stable at high temperatures, and the rhombic at low temperatures. Consequently, the *MV* and *RV* curves meet in the manner indicated in Fig. 69 (*a*), for, when produced, the metastable phases (dotted lines) have a higher vapour pressure than the stable

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* These will have to be represented by four areas, six curves, and four points in the phase-rule diagram.

phases. Thus above the transition temperature (96° C.), rhombic sulphur has a higher vapour pressure than monoclinic, and below the transition temperature the monoclinic has a higher vapour pressure than the rhombic. The relative positions of the *RV–MV* curves are thus definitely fixed. The third curve *RM* must pass through the point where *RV* and *MV* meet, and its direction of slope is given by the fact that the change from monoclinic to rhombic is accompanied by decrease in volume. The area above *MV* represents solid monoclinic sulphur, the area above *RV* solid rhombic sulphur, the area below both curves representing the vapour phase. Starting at some point *a* with monoclinic sulphur, an increase in pressure

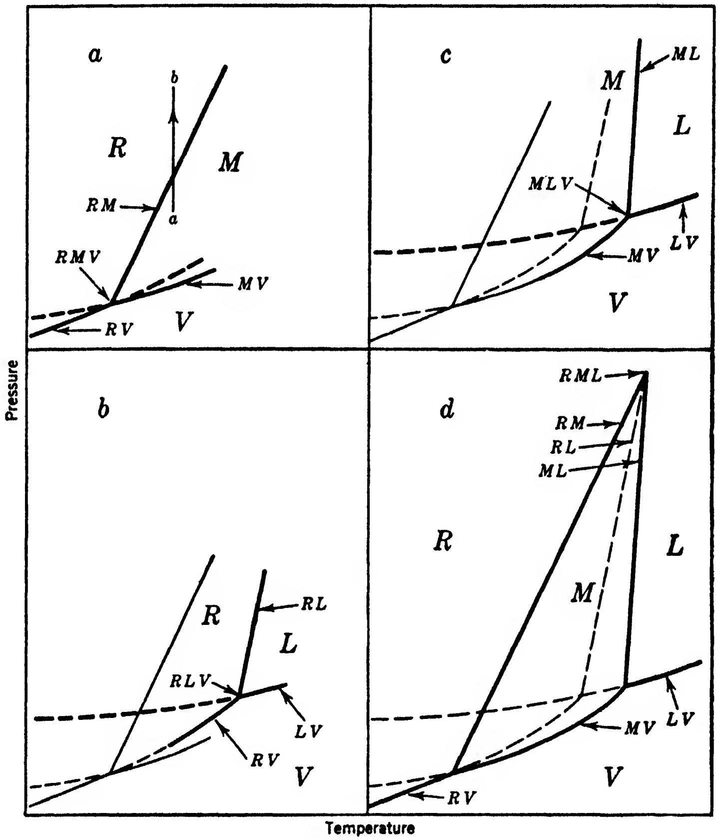

Fig. 69.

from *a* to *b* as indicated will bring about a change such that the phase having a smaller specific volume is formed.

In the absence of monoclinic sulphur, rhombic sulphur can be heated above the transition temperature until it melts at 114°. This gives the second invariant point *RLV* through which the three univariant systems *RV*, *LV*, and *RL* must pass. Of these the univariant system *RV* has already been established. The *LV* system must join with the *RV* system in such a way that the vapour pressure of the liquid is greater than that of the rhombic below its melting point. The *RL* system must slope to the right, as shown in Fig. 69 (*b*), as the change from liquid to solid is accompanied by a decrease in volume. In Fig. 69 (*b*) the heavy lines show how this univariant point must be placed relative to the systems first worked out, and already shown in Fig. 69 (*a*).

In Fig. 69 (*c*) the heavy lines show univariant systems passing through the third triple point *MLV*, the melting point of monoclinic sulphur, 120°. Two of these have been previously established, namely *LV* and *MV*, which must come together at the melting point of the monoclinic sulphur. There remains only the *ML* curve which must slope to the right, as shown in Fig. 69 (*c*).

The fourth invariant point (*RML*) is governed by the direction of the curves representing the univariant condensed systems. If two of these meet, say the *RM* and the *RL* curves, *R*, *M*, and *L* are in equilibrium, and therefore the curve representing the univariant system *ML* must also pass through this point. The complete phase-rule diagram is given in Fig. 69 (*d*).

The area below the curves *MV*, *RV*, and *LV* represents the divariant system vapour. The area above *LV* and to the right of *ML* represents the divariant system liquid. The area above *RV* and to the left of *RM* represents the divariant system solid *R* as the stable phase with the possibility of supercooled liquid and metastable solid *M* existing in this region, the liquid phase being the least stable of the phases, and, lastly, below the dotted lines in this area, vapour. Thus, if a crystal of monoclinic sulphur below 96° C. is brought into contact with the supercooled liquid, it will change into solid monoclinic and consequently, as indicated in the diagram, the vapour pressure of the liquid is higher than that of the monoclinic solid. If a crystal of rhombic sulphur is brought into contact with monoclinic sulphur in this region (i.e., below 96° C.), the monoclinic changes into the rhombic, and the vapour pressure of the former must be greater. The area enclosed by the curves RM, MV, and ML represents the divariant system M, as a stable phase. To the left of RL and above LV solid R can exist as a metastable phase.

The Phosphorus System.—When two solid modifications exist in a one-component system, then if the transition temperature lies above the melting point of the lower melting modification, the number of possible systems is greatly decreased since it is impossible to heat a solid above its melting point.

The phosphorus system is a good example of this. Phosphorus exists in two solid forms known as red and yellow phosphorus, the former having a melting point of 590° C., and the latter 44° C. The change from yellow phosphorus to red phosphorus is accompanied by an evolution of heat. The transition temperature cannot be determined as it lies above the melting point of either modification. Leaving this aside for the moment, the possible systems are tabulated below. For convenience the solid modifications yellow and red phosphorus are represented by Y and R and liquid and vapour phases by L and V.

$P = 1$	$P = 2$	$P = 3$
Y	YV	YRV
R	RV	YRL
L	LV	YLV
V	RL	RLV
	YL	
	RY	
$F = 2$	$F = 1$	$F = 0$

Of the above systems, starting with the invariant systems, the first two are impossible, since R and Y cannot exist in contact with one another. It follows also that the univariant system RY cannot exist. Starting with the invariant system YLV, the univariant systems YV, LV, and YL must have the relative positions indicated in Fig. 70 based on reasoning similar to what has been gone into before. Through the other invariant point RLV, one of the univariant systems LV has already been given. The line representing the RV univariant system must have a direction such that it lies everywhere below not only the LV system but also the YV system. The latter fact follows from the observation that the change from yellow to red phosphorus is accompanied by an evolution of heat. Red phosphorus is therefore the stable modification at low temperatures. Red phosphorus, therefore, cannot be changed directly into yellow phosphorus. The vapour pressure of the latter must always be greater than that of the former, it being always a metastable phase relative to the red modification.

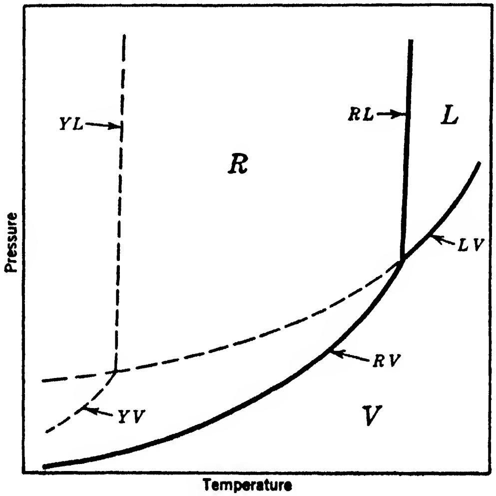

FIG. 70.

Two-Component Systems.—The above suffices to illustrate the phase-rule applications to one-component systems. In two-component systems, a new factor, namely that of concentration, enters into the establishment of equilibrium. It may be well to emphasize at the start that concentration is used in its true sense, namely to give the composition of any phase participating in the equilibrium whose composition can be varied continuously. For instance, in the case of a saturated solution in contact with its solid solute and its vapour, there are three phases and, since $P + F = 4$, $F = 1$. Consequently, if concentration is arbitrarily chosen to have a definite value, both the pressure and the temperature are defined. The concentration refers to the amount of solute dissolved in the liquid phase. Any amount of solid solute can be present without influencing the equilibrium.

With three variable factors influencing equilibrium, the question of graphic representation becomes much more complicated. Three axes at right angles, representing pressure, temperature, and concentration, would serve for this purpose. Then a point in space would represent an invariant system, a line in space a univariant system, and a surface in space a divariant system. Space models have been used, but to consider these is beyond the scope of an elementary textbook. Instead, only two variables will be represented at a time, as even with this method much interesting information can be obtained.

The simplest two-component system is one where the two components are soluble in one another in all proportions in the liquid state, but insoluble in the solid state, and where no compounds form between the two components. Representing the two components in the solid state by the letters A and B, and L and V representing the liquid and vapour phases respectively, one can tabulate the following possible systems:

$$\begin{array}{cccc} P = 1 & P = 2 & P = 3 & P = 4 \\ \left.\begin{array}{l} A \\ B \\ L \\ V \end{array}\right\} F = 3 & \left.\begin{array}{l} AB \\ AL \\ BL \\ AV \\ BV \\ LV \end{array}\right\} F = 2 & \left.\begin{array}{l} ABL \\ ABV \\ ALV \\ BLV \end{array}\right\} F = 1 & ABLV\} F = 0 \end{array}$$

The four one-phase systems and the two-phase systems AV and BV are part of the one-component systems of pure A and pure B. The divariant systems AL and BL are condensed systems, but very few such systems have been studied. L, it must be remembered, represents a solution, and the system AL, for instance, a saturated solution in which A is a solid phase, the vapour phase being absent. This means that there are two degrees of freedom, and the temperature alone will not define the concentration, the pressure having to be defined; in other words, the solubility depends on the pressure. Since solution is generally accompanied by a decrease in volume, an increase in pressure will increase the solubility. Thus the solubility of sodium chloride at 25° C. increases from 26.42 per cent by weight at atmospheric pressure to 27.01 per cent when subjected to a pressure of 1000 atmospheres. As is usual with condensed systems, a large change in pressure is accompanied by only a small change in concentration. The system *AB* is of no interest since it consists of two solids that are insoluble in one another. The only divariant system of general interest is that of *LV*, which will be considered later on.

Univariant systems *ABL* and *ABV* have not as yet been studied. The first is similar to the condensed systems *AL* and *BL*, except that three phases are present (two solid and one liquid); one of the variable factors arbitrarily fixed will govern its equilibrium. The system *ABV*, since the solids are not soluble in one another, simply involves the combined vapour pressure of the two solids when in contact with one another.

From all these possible systems then the only ones left for general discussion are listed below.

$P = 2$	$P = 3$	$P = 4$
$LV\}F = 2$	$\left.\begin{matrix}ALV\\BLV\end{matrix}\right\}F = 1$	$ABLV\}F = 0$

The univariant systems *ALV* and *BLV* are commonly called the freezing-point curves of the two-component system, and sometimes *BLV* is known as the solubility curve of *B* in *A* as the solvent. The graphic representation of these systems is best carried out by plotting the relationship between temperature and concentration. The pressures corresponding to these systems are generally of smaller interest. In Fig. 71 a typical freezing-point diagram is represented. Concentrations are plotted as abscissae in terms of molecular percentages of *A* and *B*. Thus the first point signifies pure *A*; a point one-fourth way along the bottom axis signifies 75 per cent *A*, 25 per cent *B*; a point one-half way along signifies 50 per cent *A*, 50 per cent *B*; and so on. Temperatures are plotted as ordinates.

The system *ALV* starts with the melting point T_A of pure *A*. There the liquid in contact with the solid and vapour has as yet none of *B* dissolved in it. As has been shown in a previous chapter, the addition of *B* lowers the freezing point of *A*, that is, a lower temperature is required for the equilibrium between solid *A* and the solution. A curve *ac* is therefore obtained which represents the system ALV. Similarly, starting with pure B, at its melting point, T_B, the curve *bd* is obtained representing the system BLV. These curves must eventually meet at some point *e*. At this point all four phases, A, B, L, and V, are in equilibrium with one another. It is an invariant point, and has been called the eutectic. The area above the curve *ae* and *eb* represents the divariant system LV. The area below these curves has no physical significance.

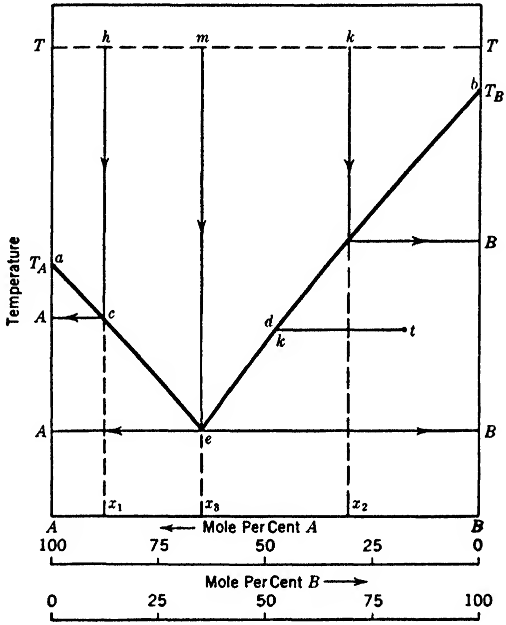

Fig. 71.

The meaning of the above statements will now be amplified. Suppose we start with the point *h*. This has the significance of a solution at a temperature T_1 and concentration x_1, in contact with its vapour. As concentration and temperature have been arbitrarily fixed, this solution will have a definite vapour pressure. Cooling this solution means following a curve parallel to the temperature axis, and, when this meets the univariant system represented by *ae*, solid A is formed. The system has now become univariant, and the temperature and pressure are defined. A further attempt at cooling by the abstraction of heat results in the formation of more solid A which can only occur by a decrease in concentration of A, the concentration falling along curve ce.

Similarly, starting with a solution at T_1 at a concentration x_2 (point k), on cooling, pure B precipitates out when point d on the univariant system BLV is reached. After this, with further cooling, the solution becomes less concentrated in B, i.e., more concentrated in A. If a solution is chosen having the concencentration x_3 (point m) corresponding to the concentration of the eutectic, then, on cooling down until the point E is reached, there are four phases present, A, B, L, and V. At this point $F = 0$, and therefore it is impossible to vary either pressure, temperature, or concentration and still have the four phases existing. It is possible to abstract heat from the system, resulting in the formation of solids. Both these solids A and B must form in exactly the same percentage as they exist in the solution. This invariant point has then all the appearance of the melting point of a pure substance, for, on cooling the solution having the eutectic concentration to where freezing starts, complete solidification takes place without a change in temperature. As this is what happens with a pure substance, the eutectic concentration was at one time looked on as being in the nature of a compound. But even before the phase-rule interpretation gave the correct explanation, it was recognized that this was not the case. In the first place the composition of the eutectic was never found to correspond to simple molecular proportions of A and B, and in the second place the examination of the solid showed that there were two solid phases present, the crystalline forms of pure A and pure B, although these sometimes were in the form of such minute crystals that microscopic examinations were necessary to distinguish the crystalline forms from one another.

The Experimental Determination of Freezing-Point Curves.—When the solution is transparent, the experimental determination of freezing-point curves can be carried out as follows. A solution is made up of known composition, placed in a test-tube in which a thermometer is centred, and equipped with a stirrer, very much like the apparatus previously described for the molecular-weight determination by the lowering of the freezing point, except that a long-range thermometer replaces the Beckmann. The test-tube is then cooled down until crystals form, whereupon the solution is allowed to warm up slowly with vigorous stirring, and the temperature observed at which the last crystals disappear.

Where the solution is not transparent, in the case, for instance, where *A* and *B* are metals, a different technique has to be resorted to. As this will also help to elucidate the meaning of the freezing-point diagram, it is worth describing. The two metals, *A* and *B*, in known amounts, are brought together in a crucible and heated until all solid has disappeared. The crucible is then placed in a closed vessel made of heat-insulating material and allowed to cool. The temperature change with time is noted by means of a thermocouple thermometer. The arrangement is such as to ensure that the system loses heat at a constant rate. In Fig. 72 are plotted the time-temperature observations in conjunction with the freezing-point diagram. Suppose the concentration and temperature of the liquid corresponds to point *a*. As cooling occurs, the temperature drops in a continuous manner as indicated by the curve *a′b′*. During this heat is being lost by conduction at a constant rate and the rate of cooling depends on the specific heat of the solution. At *b* solid *A* starts to form, and additional heat is required for

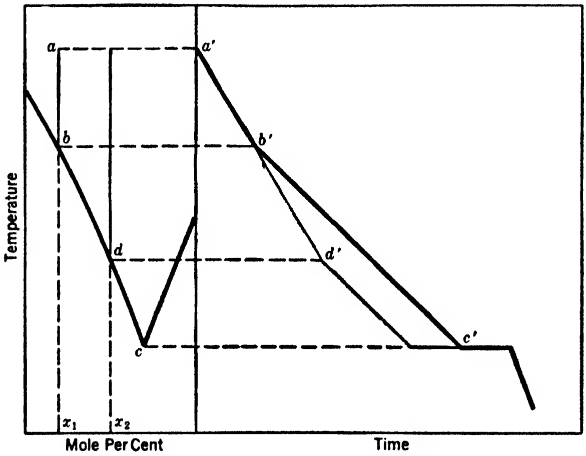

FIG. 72.

the latent heat of fusion. Consequently, cooling takes place more slowly and there is a break in the time-temperature curve in the direction $b'c'$. Where curves $b'c'$ and $a'b'$ intersect is the temperature at which the solid phase of a solution of concentration x_1 forms. In other words, it is the freezing point of that particular solution. With continued cooling, when point c is reached both A and B precipitate out. The temperature remains constant as indicated by the part $c'd'$ of the time curve. This then is the temperature of the eutectic, but from this observation alone its composition is not given. It is possible to determine the whole freezing-point curve in this way. Starting with a liquid having a different concentration, x_2, the curve $a'b'$ continues beyond b' to d', where a break occurs, thus giving the freezing point of a solution having this composition. By making up various solutions of A and B, choosing their compositions judiciously, the whole freezing-point curve can be established.

It was mentioned before that the area below the freezing-point curves has no physical significance. Suppose we consider a point t in Fig. 71 lying below the freezing-point curve be. Its meaning would be that there is a homogeneous phase whose composition at that temperature is given by point t. This, however, is impossible. True enough solid A and solid B can be brought together at the temperature indicated by point h and in the proportions corresponding to the concentration given by point h. Soon though, if a constant temperature is maintained, a liquid would form corresponding to a solution having the concentration given by point k, some of the solid B being left over. That is what is meant by saying that the area below the freezing-point curves has no physical significance. The area above has; it gives the composition and temperature of the system LV, that is, the system solution vapour.

Molecular Compounds.—Very often freezing-point curves have more than one invariant point. Thus in Fig. 73 (a), when B is added to A its freezing point is lowered, giving the system ALV. When A is added to B its freezing point is lowered, giving the system BLV. But before they meet at e, a break occurs in each giving two eutectics e_1 and e_2, with a rise in freezing point between them. Applying the phase rule, one can come to certain interesting conclusions. Both e_1 and e_2 are invariant points which in a two-component system means that there are four phases present. But four phases can exist only at one temperature, pressure and concentration. Therefore the same four phases cannot be present at e_1 and at e_2. Since above these freezing-point curves we have the phases L and V present, both L and V are present at the invariant points e_1 and e_2. Further, at e_1 the third phase is A, as the line ae represents the system ALV. Similarly, at e_2 there must be present the solid phase B. Since the curve e_1ce_2 is continuous, it must be the same solid phase which forms along this curve. Let us call this phase C.

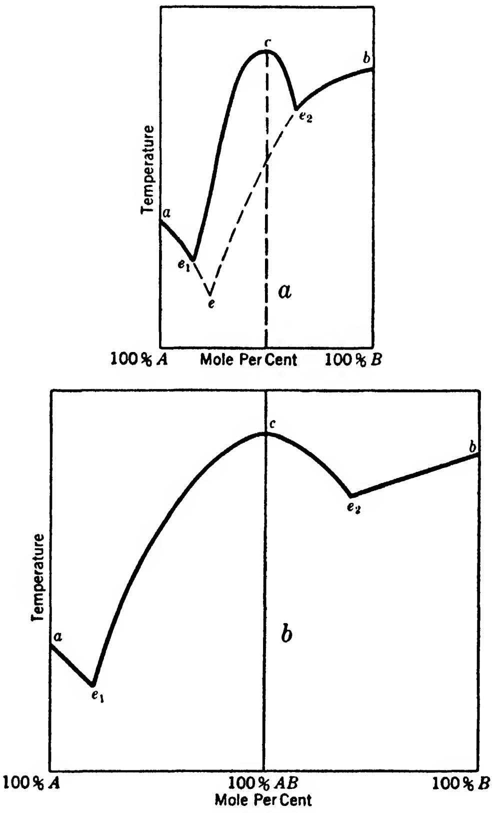

FIG. 73.

It has been established, therefore, that the four phases at e_1 are $ACLV$ and at e_2, $BCLV$. Only components A and B are present and C cannot be A or B alone, and yet must be a homogeneous phase. C must therefore be a crystalline form of a compound of A and B. Hence a curve of this type having two eutectics proves that a crystalline compound of A and B has been formed.

The composition of this compound can also be established from the freezing-point curve. It must correspond to the maximum temperature C of the curve between the eutectics e_1 and e_2. This is indicated in Fig. 73 (*b*). If, instead of considering the system AB, we consider two systems A and C and C and B, where C is a compound of A and B, then two freezing-point curves are obtained by starting, first, with a liquid having the composition of C and A, and, second, a liquid having a composition of C and B, since the addition of either A or B to C will lower its freezing point, as indicated in Fig. 73 (*b*). The highest temperature C, Fig. 73 (*a*), must correspond to the composition of the molecular compound. Going to the left, i.e., adding A, means a lowering of freezing point, or going to the right, i.e., adding B, brings about a lowering of the freezing point.

Hence freezing-point curves can serve a useful purpose as a means of determining whether molecular compounds are formed, and, if so, what their nature is when two components are brought together. It must be remembered that this is no proof of the extent to which this compound exists in the liquid state but goes to prove that it must be there to a greater or less extent, as on cooling down a solid is formed from the complexes existing in the liquid.

Solid Solutions.—There are systems of two components which give freezing-point curves radically different from any that have been discussed so far. In Fig. 74 (I) the freezing-point curve is shown to be continuous from the freezing point of pure A to that of pure B. An example of this is given by the system silver-gold, when A corresponds to silver and B to gold. This differs from the others in two ways. In the first place there is no eutectic, and in the second place the addition of B to A actually raises the freezing point of the solution. If the phase rule is correct, then the absence of the eutectic means that there is no invariant point ($F = 0$), and it follows that at no time can four phases exist together. As the freezing-point curve represents the equilibrium between three phases, gas, liquid, and solid, it follows that the solid phase must be the same from 100 per cent *A* to 100 per cent *B*, and therefore in the two-component system neither pure *A* nor pure *B* can separate out at any stage. The only explanation is that the solid separating out must be in the nature of a solid solution, *A* and *B* being soluble in one another in all proportions in the solid state, just as they are soluble in one another in all proportions in the liquid state.

Although it does not concern the application of the phase rule, an explanation of the rise in freezing point when component *B* is added to component *A* is of interest. As was discussed in a previous chapter, the freezing point of any system is the temperature at which the liquid is in equilibrium with the first trace of solid formed on cooling the liquid. There is a dynamic equilibrium between molecules in the liquid and molecules formed from the solid surface. Starting with one component *A*, the addition of a second component *B* will lower its freezing point provided pure crystals of *A* separate out. This is due to the fact that the "concentration" of potential *A* molecules in the solid is unaltered, whereas the "concentration" of the *A* molecules in the liquid has been decreased owing to the presence of *B* molecules. Thus the number of *A* molecules returning to the crystal in unit time is decreased while the number leaving the crystal has remained the same, and the latter will therefore disappear unless the temperature is lowered. If, however, the crystal formed contains potential *B* molecules dissolved in it the concentration of potential *A* molecules has also been lowered in the solid. Should the concentration change in the solid and be less than in the liquid, there would still be a lowering of the freezing point, but not nearly as much as calculated on the basis of Raoult's law. If the concentration of *B* molecules in the solid is greater than in the liquid, then there will actually be a rise in freezing point, as at the freezing point of pure *A* there would now be fewer potential *A* molecules leaving the solid to go into the liquid than *A* molecules in the liquid settling on the solid, and the liquid would disappear unless the temperature was raised. To sum up, when a solution of *B* in *A* is formed, and at the freezing point a solid solution obtained containing a lower concentration of A molecules than the solution, there is a lowering of the freezing point (though not as great as that given by Raoult's law); and, if the solid solution contains more B molecules than the liquid solution, there will be a rise in freezing point.

The dotted line shown in Fig. 74 (I) is known as the "melting-point" curve as compared to the undotted line, the "freezing-point" curve. Its significance is brought out by considering a solution having the composition given by point a. When this solution is cooled, solid forms at b and, since the freezing point T_f is higher than that of pure A, the solid solution must be richer in B than the liquid solution. The composition of the solid formed at the freezing point is given by a point c. Since continued abstraction of heat produces solid solutions richer in B than the liquid solutions, the composition of the liquid changes as shown until point d is reached, that of the

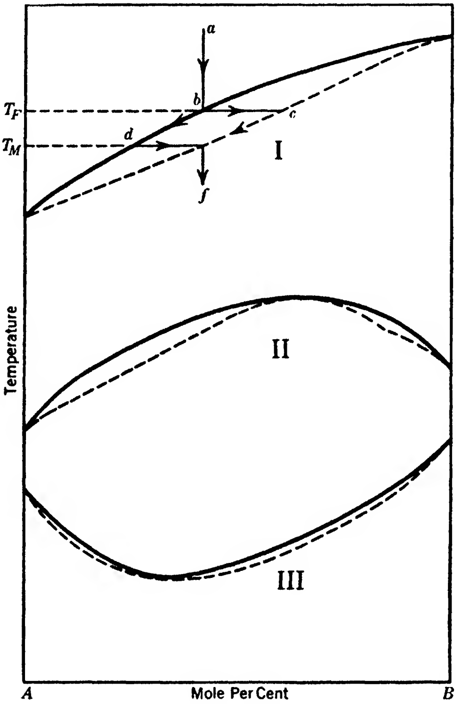

Fig. 74.

solid changing until point f is reached. At this point all the liquid has disappeared, a solid solution having been formed which perforce must have the same composition as the original liquid solution. If after cooling down the solid solution it is reheated, exactly the reverse will occur. The solid melts at T_M, the melting point. The melting-point curve, therefore, always lies below the freezing-point curve and gives the composition of the solid (point c for instance) corresponding to the freezing point (point b). The area above the freezing-point curve represents the system liquid-solution-vapour; the area below the melting-point curve represents the system solid-solution-vapour; the area enclosed by these curves has no physical significance, as any system made up to have a composition and temperature to correspond to a point in this area will separate into three phases, a liquid and a solid phase having concentrations given by points on the melting-point and freezing-point curves at that temperature, as well as the vapour phase.

When the addition of A to B as well as the addition of B to A cause a rise in temperature, the freezing-point curve passes through a maximum (Fig. 74 (II)). Conversely, when the addition of B to A causes a lowering of the freezing point as well as the addition of A to B, the freezing-point curve passes through a minimum (Fig. 74 (III)). In both cases, of course, solid solutions are formed miscible in all proportions; otherwise the curves would not be continuous. The melting-point curves are indicated by the dotted lines. The concentrations corresponding to a maximum or minimum composition of solid and liquid solutions are the same at the freezing points, and hence complete solidification takes place without change in temperature.

There are systems in which two solids are not soluble in one another in all proportions. As the solubility increases with rise in temperature, their mutual solubility curve may be represented as shown in Fig. 75. Suppose that B is added to A at temperature T_1; a solid solution of B in A is obtained. Then if, when the concentration represented by point a is reached, a saturated solution of B in A is formed, further addition will bring the formation of a second solid phase, namely a solution of A in B, represented in composition by point b. There are now three phases present, two solid phases and the vapour phase, so that the system is univariant. Further addition of *B* cannot change the concentrations of these phases but will change only their relative amounts, the one richer in *B* growing at the expense of the other phase. When the relative amounts of *A* and *B* brought together correspond to the composition given by *b*, the phase having a composition given by point *a* disappears and only one phase is left, the solution of *A* in *B*. The system is now divariant and further addition of *B* increases its concentration. At a higher temperature T_2, *B* is more soluble in *A*, and a point *d* is reached showing this higher concentration. As *A* will also be more soluble in *B* at this higher temperature, the point *e* giving the composition of the second solid phase will be richer in *A* than at the lower temperature. Curve *ad* represents the solubility of *B* in *A* and *eb* the solubility of *A* in *B*; these curves meeting at *c* in a continuous manner as *a d c e b* represent a univariant system. This is known as the mutual solubility curve of the two solids. Above this curve the area represents the univariant system solid-liquid-solution-vapour. The area below has no physical significance. Above T_3, the temperature corresponding to the maximum of the mutual solubility curve, the two solids are soluble in one another in all proportions.

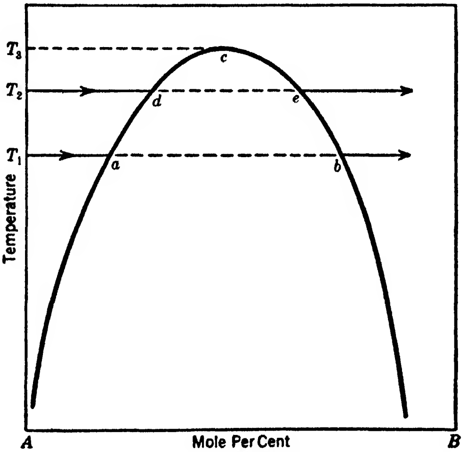

FIG. 75.

The freezing-point curves involving solid solutions considered so far are such that the melting-point curves at no point

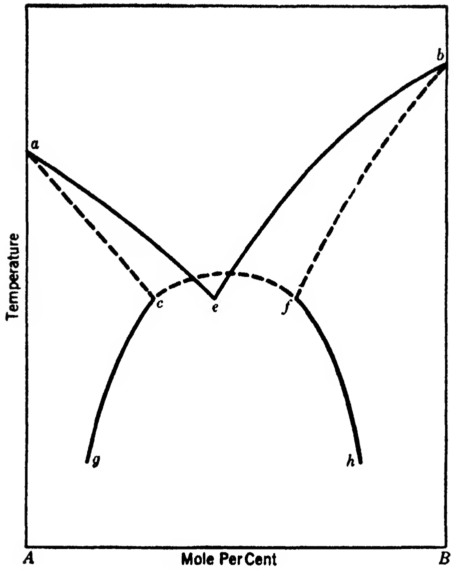
a
b
c
e
f
g
h
Temperature
A
Mole Per Cent
B

FIG. 76.

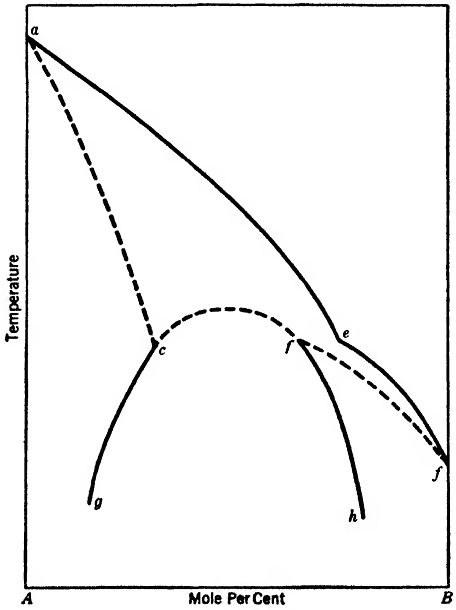
a
c
f
e
f
g
h
Temperature
A
Mole Per Cent
B

FIG. 77.

cross the mutual solubility curve of the solids. When this happens an invariant point is obtained, since at the mutual solubility curve two solid phases and the vapour phase are in equilibrium and on the melting-point curve a liquid phase as well as a solid and a vapour phase are in equilibrium. Two types of such a system are shown in Fig. 76 and Fig. 77. Where the melting-point curve *ac* cuts the mutual solubility curve *gc* a solid having the composition given by the other part of the mutual solubility curve *hf* at this temperature must be in equilibrium. Now the liquid solution, in equilibrium with the solid having a composition given by point *c*, must also be in equilibrium with a solid having a composition given by point *f*, since these two solids are in equilibrium with one another at this temperature. Hence the two freezing-point curves, one starting from pure *A* the other from pure *B*, must meet at the same point *e*. This is the invariant point and is equivalent to the eutectic mentioned before, two solid phases, a liquid phase, and the vapour phase being in equilibrium with one another.

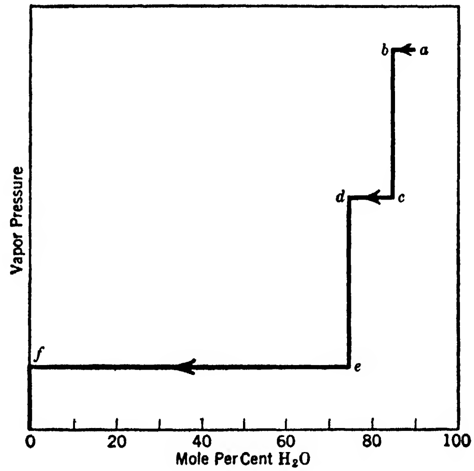

Fig. 78.

Hydrates.—Many substances form molecular compounds with water called hydrates. Thus copper nitrate forms three hydrates $Cu(NO_3)_2 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 2H_2O$. Starting with pure crystals of $Cu(NO_3)_2 \cdot 9H_2O$ (at a temperature below the melting point of this compound) it is found that it exhibits a constant vapour pressure if the temperature is kept constant, even when some water is removed (*ab*, Fig. 78). This is in conformity with the phase rule. The removal of water from the hydrate brings about the formation of a second solid phase, the lower hydrate according to

$$Cu(NO_3)_2 \cdot 9H_2O \rightarrow Cu(NO_3)_2 \cdot 6H_2O + 3H_2O.$$

There are thus three phases present, and if the temperature is

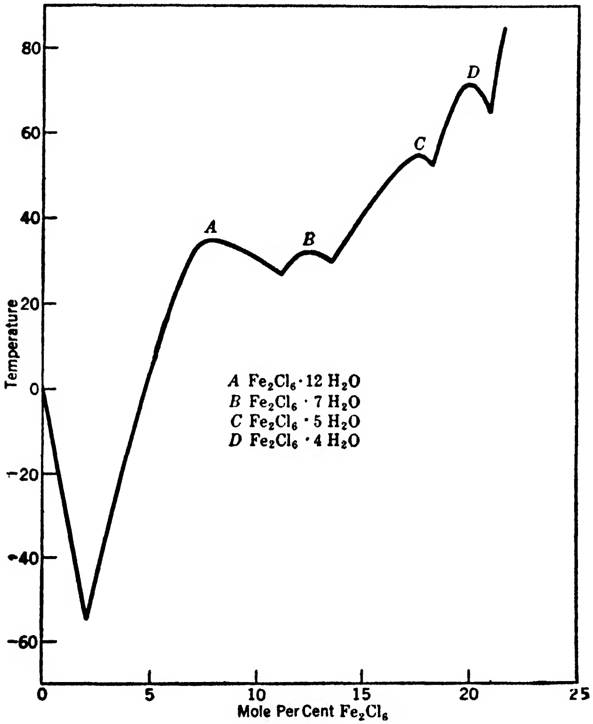

Fig. 79.

defined everything else is automatically determined, and thus the pressure remains constant until the removal of water vapour has used up all the $Cu(NO_3)_2 \cdot 9H_2O$ (point *b*). Then the pressure drops suddenly to a new value (point *c*, Fig. 78) but again remains constant with further removal of water vapour. Here again two solid phases are in equilibrium with the water vapour $Cu(NO_3)_2 \cdot 6H_2O \rightarrow Cu(NO_3)_23 \cdot H_2O + 3H_2O$. At point *d*, which corresponds to the composition of $Cu(NO_3)_23H_2O$, none of the higher hydrate is left, and the pressure falls to a new value given by point *e* and remains constant until all the water vapour has been removed, the three phases being represented by $Cu(NO_3)_2 \cdot 3H_2O \rightarrow Cu(NO_3)_2 + 3H_2O$. The presence of hydrates can thus be established by the removal of measured amounts of water vapour, the pressure remaining constant as long as two solid phases are present.

Another means of proving the existence of hydrates is by

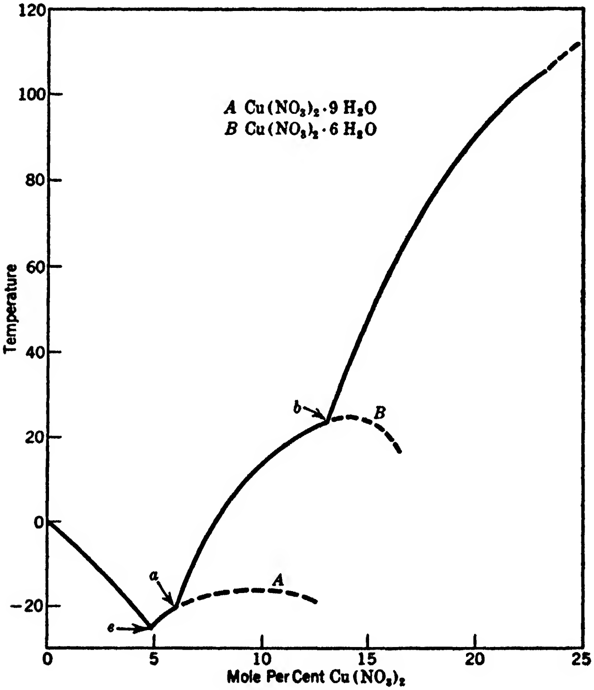

Fig. 80.

determining the freezing-point curves. A maximum between two eutectics proves the existence of a hydrate whose composition is given by that of the maximum. An example of this is shown in Fig. 79, which represents the system $Fe_2Cl_6 — H_2O$. At times, however, there are discontinuities in the freezing-point curves without a maximum occurring. This is illustrated by the system $Cu(NO_3)_2 — H_2O$ in Fig. 80. The reason for the absence of the maximum is as follows. As the first eutectic

$Cu(NO_3)_2 \cdot 9H_2O$ crystallizes out, but before the maximum as indicated by the dotted line is reached, a discontinuity, point *a*, is reached. A discontinuity means an invariant point and it is found that the second solid phase is $Cu(NO_3)_2 \cdot 6H_2O$. The question arises, why did the univariant system $Cu(NO_3)_2 \cdot 9H_2O$—solution—vapour not continue as expected? The answer is that in this particular system, at the temperature corresponding to point *b*, the vapour pressure of the hydrate $Cu(NO_3)_2 \cdot 6H_2O$ is the same as that of the solution and therefore also of the higher hydrate. The lower hydrate is thus in equilibrium with these two phases at that temperature and will therefore form. Similarly at point *b* the vapour pressure of $Cu(NO_3)_2 \cdot 3H_2O$ is the same as that of a solution having the composition and temperature corresponding to point *b*. In the absence of the crystalline lower hydrate it is possible to obtain freezing points given by the dotted curve. This, however, is a metastable system and, on the addition of a crystal of the lower hydrate, the higher hydrate disappears and the system reverts to a point on the undotted line.

QUESTIONS AND PROBLEMS

1. Discuss the purpose of the phase rule.

2. Define the terms *phases*, *components*, and *degrees of freedom* as used in the phase rule, and illustrate by means of examples.

3. Discuss methods of graphic representation used for one-component and for two-component systems.

4. What is meant by a condensed system? Describe an experimental method for measuring the relation between temperature and pressure in a one-component condensed system involving two phases.

5. Show why the vapour pressure of an unstable phase must be greater than that of a stable phase.

6. By means of Le Châtelier's principle show that the vapour pressure of a liquid must increase with rising temperature, starting with the facts that the change from liquid to gas is accompanied by an absorption of heat and that the specific volume of a vapour is greater than that of its liquid.

7. Discuss the melting point of ice and give reasons why ice melting under atmospheric pressure can be used as a fixed point in the thermometric scale.

8. Two condensed phases, *A* and *B* of a one-component system, are such that the change *A* to *B* is endothermic and accompanied by an increase in volume. Give a phase-rule diagram of all possible systems, including those in which the vapour phase participates, and give reasons for the direction and relative positions

of the curves representing the univariant systems. (A and B may be two solids or a liquid and a solid.)

9. A chemically pure substance exists in two solid modifications, A and B, having a transition temperature T_1; the change $A \rightarrow B$ is accompanied by an increase in volume and an evolution of heat. Discuss all possible systems and depict them graphically, working out in logical sequence the relative positions of the curves representing univariant systems when

$$\text{(i) } T_3 > T_2 > T_1,$$
$$\text{(ii) } T_1 > T_3 > T_2,$$

where T_2 and T_3 are the melting points of A and B respectively.

10. Discuss the systems of a two-component system of A and B where the solids are not soluble in one another in the solid state but where A and B are soluble in one another in all proportions in the liquid state, no molecular compound being formed between the two.

11. Discuss the freezing-point curves of the two-component system mentioned in question 10, and describe methods by means of which they can be determined experimentally.

12. Show why the presence of two eutectics shows the existence of molecular compound formation and why the maximum between such eutectics gives the composition and melting point of the compound.

13. Show how the solubility of two solids in one another will cause aberrations from Raoult's law and may even lead to a rise in freezing point.

14. Where two components are soluble in one another in all proportions in the solid state as well as the liquid states, depict the various possible freezing-point curves. Show clearly what is meant by the melting-point and the freezing-point curves in such systems.

15. Discuss what is meant by the mutual solubility curve of two solids.

16. Show how the mutual solubility curve of two components in the solid state may influence the freezing-point curve in a two-component system.

17. Discuss the vapour pressures of hydrates and indicate how the existence of hydrates may be proved by vapour-pressure measurements.

18. Indicate how the existence of hydrates may be determined from the freezing-point curves and explain why in some cases their presence is indicated by a discontinuity in the freezing-point curve without a maximum existing between two such discontinuities or between the eutectic and its nearest discontinuity.

19. Taking the various freezing-point curves shown in Chapter XIII, discuss the possibility and condition necessary for separating out one of the pure components by crystallization due to cooling.

CHAPTER XIV

CHEMICAL EQUILIBRIA

THE idea has long prevailed that the course of chemical reactions between substances is governed by some force, which for want of a better name has been termed chemical affinity. Until the middle of the nineteenth century this force, or affinity, was considered to be the only, or at least the all-important, factor in deciding whether or not a reaction will occur. An example of this viewpoint is found in the "affinity tables," in which the acids were arranged in a sequence such that any acid would drive the acids below it out of their salts. Thus sulphuric acid was supposed to be able to drive most of the other acids out of their salts, the implication being that the reaction would go to completion if a stoichiometric amount of sulphuric acid were present, thus

$$\mathrm{H_2SO_4} + 2\mathrm{Na}X \rightarrow \mathrm{Na_2SO_4} + 2\mathrm{H}X.$$

These ideas were shown to be untenable, when it was found that chemical reactions are reversible, and that the direction in which they proceed is governed, not only by the affinities of the substances concerned, but also by their relative quantities.

Cadmium sulphide, for instance, may be precipitated from a solution of cadmium chloride by the addition of hydrogen sulphide, thus

$$\mathrm{CdCl_2} + \mathrm{H_2S} \rightarrow \mathrm{CdS} + 2\mathrm{HCl}.$$

If the precipitate of cadmium sulphide is filtered off, however, and an excess of hydrochloric acid is added, the precipitate will again go into solution,

$$\mathrm{CdS} + 2\mathrm{HCl} \rightarrow \mathrm{H_2S} + \mathrm{CdCl_2}.$$

The complete reaction may therefore be written

$$\mathrm{CdCl_2} + \mathrm{H_2S} \rightleftarrows \mathrm{CdS} + 2\mathrm{HCl},.$$

the direction in which it proceeds being governed by the quantities of the various substances present.

That the reversibility of chemical reactions is not surprising may be shown by a mechanical analogy. This analogy is not in any way intended to represent the mechanism of chemical equilibrium, but merely to show that very often the direction in which a system changes is governed by two factors, one of which depends on what might be called the *intensity* of the forces coming into play, whereas the other depends on the size or *capacity* of the medium to which the forces are applied.

Consider, for example, the system shown in Fig. 81. A double cylinder is fitted with a double piston, one head of which has an area of 10 sq. cm. and the other 1 sq. cm. These are connected as shown to two closed volumes containing gas, the space between the two pistons being evacuated.

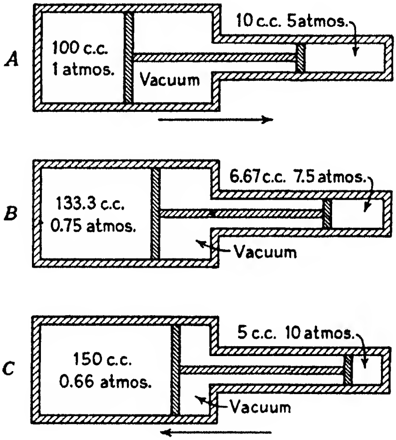

Fig. 81.

Suppose that the initial conditions are represented by the state *A*, the large volume being 100 c.c. and containing gas at one atmosphere pressure, while the smaller volume is 10 c.c. and is filled with gas at 5 atmospheres pressure. At first sight it might be expected that the piston would move from high pressure to low, i.e., from right to left in the diagram. The force on the piston tending to move it from left to right is given by the product of the pressure (i.e., force per unit area) and the area of the piston, viz., 1 × 10. The force tending to move the piston from right to left is similarly 5 × 1. The motion is therefore from left to right, i.e., from low pressure to high.

On the other hand if the piston is placed in the position indicated by *C* in the diagram, we have

$$\text{Force from left to right} = 0.66 \times 10 = 6.66.$$
$$\text{Force from right to left} = 10 \times 1 = 10.$$

The motion in this case is therefore from right to left.

In both the above cases, therefore, no equilibrium exists, the piston moving once against the high pressure and once with it. The governing factor is the total force on the piston, i.e., the product of the pressure and the area of the piston head. If the piston is started in either of the positions *A* or *C* and allowed to move freely it will finally come to rest in the position shown at *B*. Here we have

$$\text{Force from left to right} = 0.75 \times 10 = 7.5.$$
$$\text{Force from right to left} = 7.5 \times 1 = 7.5.$$

It should be specially emphasized that the attainment of equilibrium does not depend upon equality of pressure being reached, but on equality of the product (pressure) (piston area).

Chemical Equilibria.—In the previous section we have seen that some chemical reactions will proceed in either direction, depending upon the concentrations of the substances concerned. A mechanical analogy shows that a given system might behave in a similar way. If we therefore regard the two sides of a chemical equation as symbolizing two opposing reactions, we would expect that eventually equilibrium would be reached, no further change would take place, and the system would consist of a mixture of the various substances concerned having a definite constant composition.

It has been found that reactions between gases are the simplest and the easiest to investigate, and we will consider as a typical example the reaction

$$CO_2 + H_2 \rightleftarrows H_2O + CO.$$

It is found experimentally that when 1 gram molecule of carbon dioxide and 1 gram molecule of hydrogen are mixed at a temperature of 986° C., analysis shows that 0.44 gram molecule of hydrogen and of carbon dioxide are left, and 0.56 gram molecule of water and of carbon monoxide have been formed. That is, we have

	CO_2 +	H_2 →	CO +	H_2O
gram molecules	0.44	0.44	0.56	0.56

When this composition has been reached no further change will take place even over a long period of time.

If now 1 gram molecule of carbon monoxide and 1 of water vapour are mixed at the above temperature, they react to produce carbon dioxide and hydrogen. The reaction proceeds until the composition is identically the same as that found previously, i.e.,

$$\begin{array}{lcccc} & \mathrm{CO} + & \mathrm{H_2O} \rightarrow & \mathrm{CO_2} + & \mathrm{H_2} \\ \text{gram molecules} & 0.56 & 0.56 & 0.44 & 0.44 \end{array}$$

The reaction is therefore reversible, and it reaches a definite equilibrium which is exactly the same starting from either side.

The above behaviour has been found to be typical of all reversible reactions. An equilibrium is always reached which gives a definite composition of products and reactants. This equilibrium, at a constant temperature, depends solely on the molecular quantities of the substances present. The same behaviour is observed when the reaction takes place in solution as when it occurs in the gaseous state. Many reactions, which are normally regarded as going to completion, are in reality reversible, but the equilibrium position is so far to one side that it escapes notice. It seems certain that all reactions are really reversible, though in some cases the equilibrium is immeasurably far to one side. Thus, for example, the dissociation equilibria of some common gases at room temperature are given below:

Reaction	Percentage Dissociation at 25° C.
$O_2 = 2O$	2.6×10^{-39}
$H_2 = 2H$	2.0×10^{-34}
$N_2 = 2N$	1.9×10^{-58}
$Cl_2 = 2Cl$	2.3×10^{-17}
$Br_2 = 2Br$	4.0×10^{-13}
$I_2 = 2I$	1.4×10^{-9}

As an example of the effect of temperature on equilibria of this sort, data are given below for the reaction

$$2CO_2 = 2CO + O_2.$$

Temperature, ° K.	Equilibrium Constant, $K = \frac{P_{co}^2 \, P_{o_2}}{P_{co_2}^2}$, atm.
300	3.36×10^{-90}
600	7.40×10^{-41}
1000	4.00×10^{-21}
2000	1.87×10^{-6}
3000	0.112

The effect of a variation in the relative proportions of the reacting substances upon the position of the equilibrium was first thoroughly investigated by Guldberg and Waage. They found that for any reaction the product of the concentrations of the reacting substances, divided by the product of the concentrations of the substances formed, was constant at a constant temperature when equilibrium had been reached. Thus in the above example at equilibrium we have*

$$\frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.44)^2}{(0.56)^2} = 0.64.$$

If now 1 gram molecule of carbon dioxide is mixed with 4 gram molecules of hydrogen, 0.85 gram molecule of water and of carbon monoxide are formed, and 3.15 gram molecules of hydrogen and 0.15 gram molecule of carbon dioxide are left. We therefore have

$$\frac{(0.15)\ (3.15)}{(0.85)\ (0.85)} = 0.64,$$

the same value as before.

Again, if we mix 4 gram molecules of carbon dioxide, 3 of hydrogen, 2 of carbon monoxide, and 1 of water vapour, we have at equilibrium,

$[CO_2]$ = 2.73 gram molecules per litre
$[H_2]$ = 1.73 gram molecules per litre
$[CO]$ = 3.27 gram molecules per litre
$[H_2O]$ = 2.27 gram molecules per litre

and again

$$\frac{(2.73)\ (1.73)}{(3.27)\ (2.27)} = 0.64.$$

The above discovery of Guldberg and Waage is known as the law of mass action.

In a molecule the atoms are held together by what we may call chemical forces. It is not necessary for our purpose that their nature should be specified. The forces coming into play must be strong, however, since gases can often be heated to

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* Square brackets are used to denote the concentration in gram molecules per litre of the substance whose formula is enclosed between them.

very high temperatures before the impacts of the molecules become violent enough to cause the break-up of the molecules.

When two molecules react, as in the above example, new forces come into play at the moment of collision and these cause the formation of different molecules. The existence of such forces seems well established, and we will make use of their existence in discussing chemical reactions, without specifying their origin.

According to the experimental results of Guldberg and Waage, it is also necessary to take into account the number of available molecules of each substance concerned.

The Law of Mass Action.—Having discussed the experimental evidence for the existence of chemical equilibria, the next step is to attempt to formulate a mechanism, based on the atomic-molecular structure of matter, which will explain the observed facts.

The molecules of a gas, or mixture of gases, are widely separated from one another, and a chemical reaction can obviously take place only at the moment when molecules of the reactants collide. It is necessary therefore to consider what collisions will be effective in causing a reaction to occur, and what factors will govern this effectiveness.

On account of the very high speeds with which molecules move, the number of collisions per second in a gas under normal conditions is enormous. Calculation shows that if all collisions between molecules of the reactants were effective equilibrium should be reached practically instantaneously. As a matter of fact, considerable time is often required for the attainment of equilibrium, especially in the case of reactions between gases, or organic compounds in solution. Apparently then, not every collision between molecules of the reactants results in a reaction taking place. The molecules which do react must therefore be in an exceptional state of some kind.

Consider the diagram shown in Fig. 82 to illustrate the reaction between carbon dioxide and hydrogen. In order that carbon monoxide and water may be formed, the original molecules of carbon dioxide and hydrogen must be disrupted. In other words, the molecules shown in *A* must be distorted so that one oxygen atom is held to the remainder of the molecule less strongly than before, and the hydrogen atoms are also held together less strongly. At the moment of collision, therefore, conditions may be represented diagrammatically as in *B*. If reaction occurs, the oxygen atom will be united with the two hydrogens to give water, while the remainder of the carbon dioxide molecule has now assumed the configuration corresponding to carbon monoxide. This is illustrated by *C*.

It is fairly obvious that any vibration between the atoms of the reacting molecules will be of great assistance in furthering the disruption of the molecules, and hence will make them more reactive. The existence of such vibration has already been postulated in connection with the specific heats of gases. The kinetic energy of a molecule is a variable quantity, some of the molecules having much greater velocities than others. In the same way there will be a distribution of the vibrational energy of the molecules about a mean value. A very small fraction of the total number of molecules will possess an unusually high vibrational energy, which will be sufficient to enable a rearrangement of atoms to occur at the moment of collision. The tendency for the reaction to occur, and therefore the amount of the substances reacting in unit time, will consequently be proportional to the number of collisions between "activated" molecules, i.e., between molecules which have a high enough vibrational energy to react.

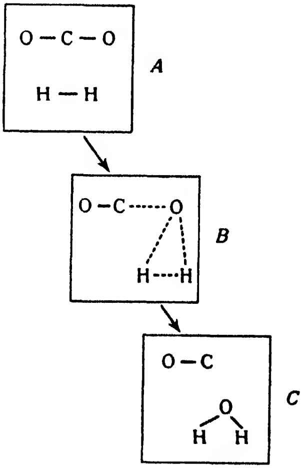


FIG. 82.

The total number of collisions in which a carbon dioxide molecule collides with a hydrogen molecule will be proportional to the number of each in unit volume. Let these numbers be n_1 and n_2, respectively. Then the total number of collisions between carbon dioxide and hydrogen molecules will be proportional to the product n_1n_2. The fraction of molecules of any kind which have a vibrational energy above a certain critical value is independent of the number of molecules. Let α and β represent the fraction of the carbon dioxide and hydrogen molecules which have this critical vibration, i.e., the fractions which are activated. The number of collisions in unit time between such activated molecules, and hence the number of molecules reacting in unit time, will therefore be proportional to

$$\alpha n_1 \cdot \beta n_2,$$

or

$$\alpha\beta n_1 n_2,$$

where α and β are constants at constant temperature. The amount of substance reacting in unit time, expressed in gram molecules, is called the velocity of the reaction. Hence we have

> Velocity of the reaction $CO_2 + H_2 \rightarrow CO + H_2O$ is proportional to $\alpha\beta n_1 n_2$.

But if we start with carbon monoxide and water vapour, the reverse reaction is possible. The same argument may therefore be applied to the reverse reaction, the velocity being proportional to the number of collisions between activated molecules of carbon monoxide and water.

Let γ and δ be the fractions of the molecules of carbon monoxide and water which are activated, and let n_3 and n_4 be the total number of molecules of each substance in unit volume. Then, as before,

> Velocity of the reaction $CO + H_2O \rightarrow CO_2 + H_2$ is proportional to $\gamma\delta n_3 n_4$.

There now remains the problem of the existence of an equilibrium in the above reaction. Suppose that n_1, n_2, n_3, and n_4 represent the number of molecules per unit volume of the various substances, as before, but that all four substances are present at once in the same container at constant temperature. α, β, γ, and δ are therefore constants. The velocities of the two opposing reactions at the start are given by

$$k_1 n_1 n_2,$$

and

$$k_2 n_3 n_4.$$

As the reactions proceed, n_1, n_2, n_3, and n_4 will vary. At any time, however, we may say that the velocities of the two opposing reactions are given by:

$$k_1 n_{CO_2} n_{H_2}$$

and

$$k_2 n_{CO} n_{H_2O},$$

where n_{CO_2}, n_{H_2}, etc., represent the numbers of the various kinds of molecule in unit volume, at the instant under consideration.

Suppose that

$$k_1 n_{CO_2} n_{H_2},$$

is greater than

$$k_2 n_{CO} n_{H_2O},$$

then n_{CO_2} and n_{H_2} will decrease as the reaction proceeds. This decrease, however, will cause an increase in n_{CO} and n_{H_2O}. As a result $k_2 n_{CO} n_{H_2O}$ will increase. Consequently the velocities of the two opposing reactions must eventually become equal, and an equilibrium is reached. At equilibrium we therefore have

$$k_1 n_{CO_2} n_{H_2} = k_2 n_{CO} n_{H_2O}$$

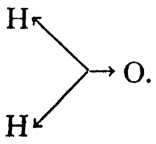
or

$$\frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}} = \frac{k_2}{k_1} = K.$$

It is obvious from the above derivation that k_1 and k_2 are dependent on α, β, γ, and δ. The magnitude of each of these is dependent upon the amount of vibrational energy required to cause the disruption of the molecule, which in turn is dependent upon the chemical forces holding the atoms together in their respective molecules. The ratio k_1/k_2, and therefore K, is dependent in consequence upon the relative magnitudes of the chemical forces involved, i.e., on the relative strengths of the forces

$$CO \longleftrightarrow O$$

and



The position of the equilibrium is therefore dependent upon which of these forces predominates.

In the above equilibrium relationship, the numbers of molecules per unit volume for each substance are involved. The number of molecules per unit volume is, of course, proportional to the number of gram molecules per unit volume, and therefore to the concentration. The equilibrium relationship may therefore be written

$$\frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = K.$$

This is the same as the experimentally found expression for the law of mass action.

In a later section further details will be given of the experimental methods employed, and of the manner in which the above equation may be used.

It is of interest in the derivation of any relationship to examine the various steps, in order to see if any assumptions have been made which are approximate or uncertain, or which will be true only under certain conditions. In the derivation of the law of mass action two postulates of this kind were made. These are: (1) that collisions between molecules depend solely upon chance, and are not influenced by concentration except in the way indicated by the kinetic theory; (2) that the chemical forces which come into play do so only at the moment of collision, and are not influenced by the concentration of the various substances.

With regard to the first of these assumptions, it is known that chemical forces have an appreciable effect at distances several times greater than the radius of a molecule. At high concentrations, therefore, these forces may influence the number of collisions, and molecules may collide which, in the absence of attractive forces, would have missed one another.

As far as the second assumption is concerned, it is certain that the forces which exist between the atoms of a molecule will be influenced by the presence of neighbouring molecules. Atoms are now known to be composed of electrically charged particles. The forces which hold the atoms together in a molecule are electrical in nature, and any electrical field due to an atom or molecule must have an effect on the stability of all the other molecules in the neighbourhood. The strength of the "chemical forces" which hold a molecule together will therefore be dependent upon the concentration of the substances present to some extent. Aberrations from the law of mass action would therefore be expected to occur at high concentrations. The law of mass action will apply rigorously only to ideal gases or solutions, or to real substances at very low concentrations.

In most cases the aberrations from the law of mass action are but slight. In certain cases, however, where the forces of attraction are very pronounced, as in electrolytic dissociation, very serious discrepancies occur.

The derivation of the law of mass action given above is based upon the kinetic theory; it is also possible to derive it from energy considerations. In such a derivation it is customary to use a quantity called the "activity" in place of the concentration. Under these circumstances the mass law becomes of universal validity, but the activities of the substances concerned must now be determined from experimental observations on the particular system involved.

The Experimental Application of the Law of Mass Action.—The great difficulty in the experimental verification of the law of mass action is the determination of the concentrations of the various substances at equilibrium, without disturbing the equilibrium in any way during the process of analysis. This is quite simple when the equilibrium is the result of two opposing reactions which take place very slowly compared with the time required for analysis. Reactions between organic compounds are often of this type, for example, the reaction between ethyl acetate and water:

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH.$$

In such a case the ingredients are mixed to form a homogeneous solution. After a short time a sample is withdrawn and analyzed. This procedure is repeated from time to time, until no further change occurs over a considerable period. The concentrations which exist at this equilibrium state are determined, and from them the mass law constant, or equilibrium constant, K, is calculated. By starting with various initial concentrations, we will obtain different concentrations at equilibrium. We can, however, test the law of mass action by calculating the mass law constants for each set of conditions and comparing their values.

Suppose that *a* gram molecules of acetic acid and *b* gram molecules of ethyl alcohol are mixed, and that at equilibrium *x* gram molecules of water and of ethyl acetate have been formed. Then if *v* is the volume of the solution, we have

$$\frac{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)} = K,$$

or

$$\frac{(a-x)\,(b-x)}{x^2} = K.$$

In order to solve this equation and obtain the value of *K*, the equilibrium constant, it is necessary to know only the original concentrations of ethyl alcohol and acetic acid, *a* and *b*, and the equilibrium concentration of one of the four substances concerned. In the following table are given various values of *a* and *b*, the experimentally determined amount of ethyl acetate, and the amount calculated from the law of mass action.

Gram Molecules of Acetic Acid, *a*	Gram Molecules of Alcohol, *b*	Gram Molecules of Ethyl Acetate, *x*	
		Observed	Calculated
1.00	0.05	0.050	0.049
1.00	0.18	0.171	0.171
1.00	0.50	0.414	0.423
1.00	1.00	0.667	0.667
1.00	2.00	0.858	0.845
1.00	8.00	0.966	0.945

In the above table it is seen that there is good agreement between the observed and calculated values of the concentration of ethyl acetate in the equilibrium mixture. The experiments thus constitute a verification of the law of mass action.

We will now describe the various experimental methods which may be used in investigating chemical equilibria. It is often impossible to use direct analysis as a method of determining the equilibrium concentrations, because the velocities of the reactions involved may be so high that a shift in the equilibrium will occur during the process of analysis.

It is a well-known fact that the velocity of a chemical reaction decreases as the temperature is lowered. This suggests a method of investigating equilibria at temperatures where the velocities of the opposing reactions are high. Thus consider the equilibrium:

$$H_2 + I_2 \rightleftarrows 2HI.$$

The velocities of the opposing reactions are very high at 300° C. At room temperature both these reactions occur only very slowly. It is thus possible to determine the amounts of hydrogen, iodine, and hydriodic acid in a mixture at room temperature by direct analysis. To investigate the equilibrium at 300° C., measured amounts of hydrogen and iodine are sealed up in a glass bulb. This is then kept in a thermostat at 300° C. until equilibrium is reached. If the bulb were cooled slowly to room temperature the equilibrium would shift, since the mass law constant, i.e., the equilibrium, varies with the temperature. If, however, the bulb is cooled more rapidly than the time required for an appreciable change in the concentrations of the various substances, the mixture will reach room temperature with its original composition unaltered. The bulb is therefore cooled suddenly by plunging it into a refrigerant. In order to prove that no shift in the equilibrium has occurred, several experiments must be carried out with various rates of cooling. If concordant results are obtained, then it may be assumed that the cooling is sufficiently fast.

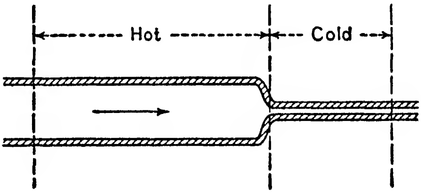


FIG. 83.

Another experimental method which is based on the same principles is known as the dynamic method. The apparatus employed is illustrated in Fig. 83. A gas mixture of known composition is passed slowly through a wide tube, which is maintained at the desired temperature. For example, nitrogen and oxygen may be passed through a platinum tube at 1500° C. This wide tube ends suddenly in a tube of capillary dimensions, which is immersed in liquid air. The gas mixture passes slowly through the wide tube and reaches equilibrium:

$$N_2 + O_2 \rightleftarrows 2NO.$$

This slow flow is changed into a rapid movement in the capillary tube, and as a result the gas is cooled suddenly to a low temperature. It may then be analyzed at room temperature, where the velocity of the reaction is immeasurably slow. The concentrations found at room temperature will be the same as those which existed in the equilibrium mixture at 1500° C., provided that the quenching was sufficiently fast. This is tested, as in the previous method, by altering the rate of the gas flow.

In both the above equilibria, the right-hand side of the equation represents a reaction in which two molecules of the same kind participate. It follows that the equilibrium constant will be given by

$$\frac{[H_2]\,[I_2]}{[HI]\,[HI]} = K_1,$$

or

$$\frac{[H_2]\,[I_2]}{[HI]^2} = K_1,$$

and

$$\frac{[N_2]\,[O_2]}{[NO]\,[NO]} = K_2,$$

or

$$\frac{[N_2]\,[O_2]}{[NO]^2} = K_2.$$

In other words, if more than one molecule of the same kind participates in a reaction, the concentration of the substance appears in the mass law equation raised to a power which is equal to the number of molecules concerned. Thus for example in the reaction

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

we have

$$\frac{[H_2]\,[H_2]\,[H_2]\,[N_2]}{[NH_3]\,[NH_3]} = K$$

or

$$\frac{[H_2]^3\,[N_2]}{[NH_3]^2} = K.$$

It should be noticed that when a reaction occurs which involves no change in the number of molecules in the system, the equilibrium constant is a pure number and it is immaterial what units are used to express the concentrations. Thus suppose that we have the reaction

$$\mathrm{A} + \mathrm{B} = \mathrm{C} + \mathrm{D}.$$

Then suppose that

$$\frac{[\mathrm{A}]\,[\mathrm{B}]}{[\mathrm{C}]\,[\mathrm{D}]} = K,$$

when the concentrations are expressed in moles per litre. Suppose that we now transform to moles per cubic centimetres. Then we have

$$\frac{\dfrac{[\mathrm{A}]}{1000}\cdot\dfrac{[\mathrm{B}]}{1000}}{\dfrac{[\mathrm{C}]}{1000}\cdot\dfrac{[\mathrm{D}]}{1000}} = K_1,$$

and obviously all the 1000's cancel and $K = K_1$, i.e., the value of the mass law constant is not changed by changing the units in which the concentrations are expressed. On the other hand, when the number of molecules changes during the reaction it is essential that the units of K be stated. Thus consider the reaction

$$\mathrm{A} + \mathrm{B} = \mathrm{AB}.$$

Again suppose that

$$\frac{[\mathrm{A}]\,[\mathrm{B}]}{[\mathrm{AB}]} = K,$$

when the concentrations are expressed in moles per litre. Transforming to moles per cubic centimetre, as before, we have

$$\frac{\dfrac{[\mathrm{A}]}{1000}\cdot\dfrac{[\mathrm{B}]}{1000}}{\dfrac{[\mathrm{AB}]}{1000}} = K_1,$$

i.e.,

$$K_1 = 1000K,$$

and the value of the constant depends on the units used to express the concentrations.

When dealing with gases, it is convenient to use a different method of representing concentrations. If c is the concentration of a substance, and n the number of gram molecules present in a volume v, we have

$$c = \frac{n}{v}.$$

From the ideal gas law

$$PV = nRT,$$

or

$$c = \frac{n}{v} = \frac{P}{RT}.$$

Hence at constant temperature

$$c = KP.$$

The concentrations can therefore be represented by the partial pressures of the gases which participate in the equilibrium. This also follows directly from the derivation of the law of mass action, since we had for the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O,$$

$$\frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}} = K.$$

According to Avogadro's hypothesis, the number of molecules present is proportional to the pressure at constant temperature. Hence we have

$$\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = K,$$

where P_{CO_2}, P_{H_2}, etc., represent the partial pressures of the various gases concerned. Similarly for the ammonia reaction we have

$$\frac{P^3_{H_2} P_{N_2}}{P^2_{NH_3}} = K.$$

If we know the amount of ammonia which was originally put into the reaction vessel, it is possible to calculate the partial pressures of the various substances at equilibrium from the total pressure. This method may therefore be used to calculate the equilibrium concentrations. This is true only in the case of a gas reaction in which a pressure change accompanies the reaction, i.e., when the total number of molecules present is altered as the reaction proceeds. In the hydrogen iodide and nitric oxide reactions this is not so, and hence the equilibrium cannot be investigated in this way.

Information regarding the effect of the *total* pressure upon the position of equilibrium can be obtained by the application of the principle of Le Châtelier. According to this principle, an increase in pressure will shift an equilibrium in such a way that a diminution in volume occurs. In the ammonia reaction, an increase in the pressure will therefore shift the equilibrium in the direction of the formation of ammonia. In the hydrogen iodide reaction, however, no change in volume accompanies the reaction, and the pressure is without influence upon the equilibrium.

A very convenient method of investigating the equilibrium concentrations is possible when a semi-permeable membrane is available, which will permit the passage of one of the reacting molecular species to the exclusion of the others. We have already seen that a palladium membrane will serve this purpose with hydrogen. This method has been used extensively to investigate a number of commercially important reactions which involve hydrogen. The experimental arrangement is similar to that previously illustrated in Fig. 41. The space between the manometer and the membrane is, however, made extremely small compared with the volume of the reaction vessel, so that the equilibrium is not appreciably altered by the loss of the hydrogen which diffuses into the space above the manometer. From the total pressure, and the partial pressure of the hydrogen at equilibrium, the mass law constant can be calculated.

A semi-permeable membrane could obviously be employed in the same way with reactions which occur in solution. The lack of suitable membranes for the majority of substances, however, makes this method of little practical value. If, however, the total number of molecules changes during the course of the reaction, the total osmotic pressure will change as the reaction proceeds. The equilibrium may then be investigated by indirect osmotic-pressure methods, such as the lowering of the freezing point of the solution. Many examples of such a method will be discussed in the next chapter, in connection with the dissociation of electrolytes.

Apart from the above methods of measuring equilibrium concentrations, it is also possible to determine them indirectly by means of the measurement of any physical property which varies with the concentration of one of the participants in the reaction. Such methods are of special importance in investigating equilibria between inorganic salts in solution, on account of the very high velocity of such reactions.

Heterogeneous Equilibria.—In the case of equilibria which involve more than one phase, some uncertainty arises as to the concentration which is to be assigned to a pure solid or liquid. It is impossible to vary appreciably the concentration (i.e., the number of gram molecules per litre) of a solid or liquid. It is true that a high pressure will alter the volume of a solid or liquid, but the compressibility is so small that the volume change is inappreciable under ordinary conditions. The concentration of a solid or liquid is therefore constant at constant temperature. If we have a gas in contact with a solid, for example, only the surface atoms of the solid can participate in any reaction. Since the surface of the solid exposed to the gas must be the same as the surface of the gas exposed to the solid, the effective concentration of the solid will be constant.

In the case of the dissociation of calcium carbonate, for example, we have

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

The law of mass action gives

$$\frac{[CaCO_3]}{[CaO]\,[CO_2]} = K_1.$$

Since $[CaCO_3]$ and $[CaO]$ are constants, we have

$$[CO_2] = K_2,$$

and hence

$$P_{CO_2} = K_3.$$

We can therefore deduce the fact that the pressure of the carbon dioxide in equilibrium with calcium carbonate, i.e., the dissociation pressure of the calcium carbonate, will be constant at a given temperature, and independent of the relative amounts of calcium carbonate and calcium oxide present. This has been confirmed experimentally.

Physical Equilibria.—The basic ideas involved in the law of mass action can also be applied to so-called physical equilibria, such as the evaporation or freezing of a liquid.

At a given temperature, the vapour pressure of a liquid is the pressure at which the number of molecules leaving the liquid is equal to the number returning from the vapour. The equilibrium will therefore be governed by the relative velocities of the two processes. Thus we have

$$\textsc{Liquid} \rightleftarrows \textsc{Vapour}.$$

Applying the law of mass action,

$$\frac{[\textsc{Liquid}]}{[\textsc{Vapour}]} = K_1.$$

But

$$[\textsc{Liquid}] = K_2.$$

Hence

$$[\textsc{Vapour}] = K_3,$$

or

$$P_{\text{VAPOUR}} = K_4.$$

We thus have a constant vapour pressure at a given temperature, which is independent of the relative amounts of liquid and vapour present.

By the addition of a solute $[\textsc{Liquid}]$ is reduced (i.e., the liquid is diluted by the dissolved substance). Hence since

$$\frac{[\textsc{Liquid}]]}{[\textsc{Vapour}]} = K_1,$$

$[\textsc{Vapour}]$ must also be reduced, that is, the vapour pressure of the solution is less than that of the pure solvent.

The same type of argument can also be used in the case of the freezing of a liquid. Here we have

$$\textsc{Liquid} \rightleftarrows \textsc{Solid}.$$

From the law of mass action therefore

$$\frac{[\textsc{Liquid}]}{[\textsc{Solid}]} = K.$$

Both [Liquid] and [Solid] are invariable, and hence the melting point is constant and independent of the relative amounts of solid and liquid.

In every dynamic equilibrium involving molecules we must be dealing with opposing processes whose velocities are equal. The mass law relationship may therefore be applied to all such cases.

The discussion of the influence of temperature on chemical equilibria will be given in the chapter on thermochemistry.

QUESTIONS AND PROBLEMS

1. One mole of ethyl alcohol is mixed with 1 mole of acetic acid. At equilibrium it is found that 0.667 mole of ethyl acetate has been formed. Calculate the mass law constant for the reaction. *Ans.* 0.25.

2. Using the value of K found in question 1, find the amount of ethyl acetate formed when 10 grams of ethyl alcohol and 15 grams of acetic acid are mixed. *Ans.* 13.6 grams.

3. One mole of acetic acid, 1 mole of water, 1 mole of ethyl acetate, and 1 mole of ethyl alcohol are mixed. Calculate the amounts of each at equilibrium.
Ans. 0.66 mole alcohol, 0.66 mole acetic acid,
1.34 moles water, 1.34 moles ethyl acetate.

4. Two grams of hydriodic acid are heated to 327° C. in a bulb having a volume of 100 c.c. Calculate the volume percentages of hydrogen, iodine, and hydrogen iodide at equilibrium. The value of the mass law constant for the reaction $2HI \rightleftarrows H_2 + I_2$ is 17.9 at 327° C., when the concentrations are expressed in moles per litre.
Ans. $HI = 67.90$ per cent, $H_2 = 16.05$ per cent, $I_2 = 16.05$ per cent.

5. Calculate the partial pressures of the reactants in question 4.
Ans. $HI = 5.22$ atm., $H_2 = I_2 = 1.235$ atm.

6. Two grams of hydriodic acid are heated to 527° C. in a bulb having a volume of 100 c.c. The bulb is then quenched in liquid nitrogen to a temperature of $-193°$ C. At this temperature the hydriodic acid and iodine have no appreciable vapour pressure. The equilibrium constant for the reaction at 527° C. is 9.1. Calculate the pressure in the bulb at $-193°$ C. *Ans.* 0.204 atm.

7. Two grams of hydrogen bromide are heated to 1200° C. in a 100-c.c. bulb. The equilibrium constant for the reaction $H_2 + Br_2 \rightleftarrows 2HBr$ is 9800 at 1200° C. Calculate the total pressure in the bulb when equilibrium is reached, and the volume percentages of the substances.
Ans. Total pressure = 29.9 atm., $HBr = 0.502$ per cent,
$H_2 = Br_2 = 49.749$ per cent.

8. How much HBr would have to be placed in the bulb mentioned in question 7 in order that the partial pressure of hydrogen would be 1 atmosphere at 1200° C.? *Ans.* 0.135 gram.

9. What is meant by chemical equilibrium? Illustrate by examples.

10. Derive the law of mass action.

11. Describe experimental methods of determining the concentrations of the substances involved in the hydrogen-nitrogen-ammonia equilibrium.

12. Show how the law of mass action may be tested experimentally.

13. Discuss the application of the law of mass action to heterogeneous and physical equilibria.

CHAPTER XV

THE RATE OF CHEMICAL REACTIONS

THE rate at which chemical equilibrium is attained and the factors which influence this rate are of considerable interest. The rate of a chemical reaction has already been defined as the rate of change of the concentration of the reactants. This rate of change is usually expressed in terms of the number of gram molecules reacting per second.

In many chemical reactions the position of equilibrium is so far to one side that only the products of the reaction can be detected analytically when equilibrium has been attained. Such reactions are usually called "irreversible." These reactions are very convenient for rate measurements, since the reverse reaction would otherwise introduce complications into both the experimental measurements and their theoretical interpretation. Reversible reactions can best be treated in the early stages of the reaction before the products have had time to accumulate.

One of the main reasons for the interest which is taken in the rate of a chemical reaction is that such measurements throw a great deal of light upon the mechanism of the process. A chemical equation represents the initial reactants and the final products of a reaction. The reaction, however, may really occur in several consecutive stages which are not indicated by the ordinary stoichiometric equation. The presence of such a series of stages may often be discovered by reaction-rate measurements.

We have already seen that the rate of a reaction such as

$$\mathrm{A} + \mathrm{B} + \mathrm{C} + \cdots \rightarrow \text{(Products)}$$

is given in its initial stage by

$$\text{Rate} = kC_AC_BC_C \cdots,$$

i.e., the rate is proportional to the product of the concentrations of the reacting substances at the time considered. The constant k is known as the rate constant of the reaction. Reactions are usually classified as follows:

Unimolecular Reactions are those in which only one molecule participates, for example,

$$\mathrm{A} \rightarrow \text{(Products)}.$$

Bimolecular Reactions involve two molecules, i.e.,

$$2\mathrm{A} \rightarrow \text{(Products)},$$

or

$$\mathrm{A} + \mathrm{B} \rightarrow \text{(Products)}.$$

Similarly *Termolecular* and *Quadrimolecular* reactions refer to

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \text{(Products)}.$$

and

$$\mathrm{A} + \mathrm{B} + \mathrm{C} + \mathrm{D} \rightarrow \text{(Products)}.$$

The rates of the various types of reaction are consequently given by the following expressions:

Unimolecular $\quad \text{Rate} = k_1\, C_A$

Bimolecular $\quad \text{Rate} = k_2\, C_A C_B,$

or $\quad = k_3\, C_A^2,$

if two molecules of the same kind are involved.

Termolecular $\quad \text{Rate} = k_4\, C_A C_B C_C,$

etc.

Order and Mechanism.—Consider the reaction

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \text{(Products)}.$$

This might occur directly, as indicated by the equation. In this case the expression for the rate would be

$$\text{Rate} = k\, C_A C_B C_C,$$

i.e., the reaction is termolecular. The reaction, however, might really occur in stages, such as

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D}$$

$$\mathrm{D} + \mathrm{C} \rightarrow \text{(Products)},$$

and thus involve a pair of successive bimolecular reactions. The chemical equation, therefore, does not necessarily represent the true course of the reaction. If the reaction occurs in stages, the rate of the whole process will depend on the relative rates of the two stages. If, for example, the first step is slow compared with the second, the reaction rate will be controlled by the rate of the first stage, and we will have

$$\text{Rate} = k\, C_A C_B.$$

As a result the whole process will appear to be a bimolecular reaction in spite of the fact that three molecules are really involved.

The majority of reactions which are represented by an equation involving more than two molecules has been found to be really of the above type, and to involve a series of bimolecular stages. This is not surprising, since a reaction of a higher order than the second would involve the simultaneous collision of three or more molecules and would therefore be a very rare event.

In order to avoid ambiguity it is customary to designate the number of molecules participating in any reaction, or stage of a reaction, as the *mechanism* of the reaction, and to classify the mechanisms as unimolecular, bimolecular, termolecular, etc. On the other hand, the *order* of a reaction is defined as the number of concentration terms involved in the rate expression. Thus, if the rate of a reaction is given by

$$\text{Rate} = k\, C_1 C_2,$$

it is a second-order reaction, irrespective of what the real mechanism may be. It follows that the order of a reaction is an experimentally determined quantity, whereas a knowledge of the mechanism involves the disentangling of the processes involved.

As an example of the above distinction, let us consider the case where one of the reactants involved is present in large excess. Thus in the inversion of a dilute solution of cane sugar, we have

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6,$$

and the water is present in very large amount compared with the sugar. The rate of the reaction should be given by

$$\text{Rate} = k\,[C_{12}H_{22}O_{11}]\,[H_2O].$$

For every molecule of sugar one molecule of water is involved in the reaction. In dilute solution, therefore, the percentage change in the concentration of water as the reaction proceeds is very small. In other words, the concentration of water remains practically constant whereas that of sugar varies from its initial value to zero. Hence the rate of the reaction, as experimentally determined, is proportional to the concentration of the sugar alone, i.e.,

$$\text{Rate} = k\,[C_{12}H_{22}O_{11}].$$

In consequence, although the reaction has a *bimolecular mechanism*, it is *first order.*

The Determination of the Order of a Reaction.—In the above discussion we have referred to the rate of reaction as a function of the concentrations of the reactants. In any actual reaction, however, the concentrations of the reactants continually change as the reaction progresses, and the rate at any moment is proportional not to the initial concentrations of the reactants, but to the concentrations at the moment considered. The important thing, therefore, is to determine the rate of the reaction as a function of the time. For example, consider a first-order reaction. If a is the initial concentration of the reactant, and if x is the amount which has reacted after the lapse of t seconds, we have

$$\begin{aligned}\text{Rate at time } t &= k\,[\text{A}],\\ &= k(a - x).\end{aligned}$$

It can be shown that this leads to the expression*

$$\log \frac{a}{a - x} = kt.$$

It follows that if we plot $\log a/(a - x)$ against the time, a straight line will be obtained, as shown by Fig. 84.

---

* It is impossible to discuss rates mathematically without the use of elementary calculus. For the sake of those who have some slight knowledge of calculus, this expression and the following one are derived in Appendix II.

For a second-order reaction of the type

$$2A \rightarrow \text{(Products)},$$

we get similarly

$$\frac{x}{a(a - x)} = kt.$$

It follows, therefore, that the order of a reaction can be found by determining which type of equation fits the experimental results.

In practice it is usually more convenient to determine the order of a reaction in a somewhat different way. Let us define the *time to half-value*, $t_{1/2}$, as the time at which one-half of the initial amount of reactant has disappeared by reaction. Then when $t = t_{1/2}$, $x = a/2$. Hence for a first-order reaction we have

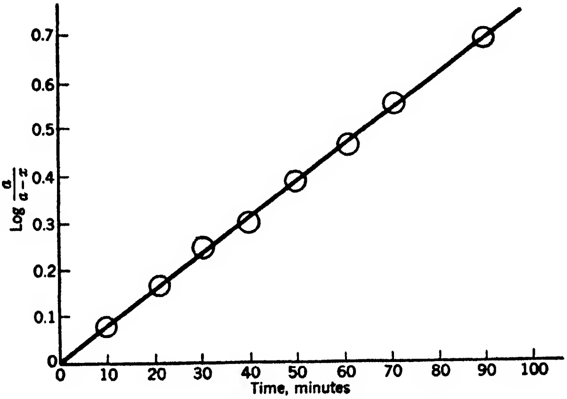


FIG. 84.—The Decomposition of Chloropicrin at 145° C.

$$\log \frac{a}{a - a/2} = kt_{1/2}.$$

Whence

$$t_{1/2} = \frac{\log 2}{k} = \text{Constant}.$$

Hence the time to half-value for a first-order reaction is independent of the initial concentration of the reactant.

For a second-order reaction we have similarly

$$\frac{a/2}{a(a - a/2)} = kt_{1/2},$$

whence

$$t_{1/2} = \frac{1}{ka}.$$

Hence in this case the time to half-value is inversely proportional to the initial concentration of the reactant. In general, for a reaction of the *n*th order,

$$t_{1/2} \propto \frac{1}{a^{n-1}}.$$

To determine the order of a reaction, therefore, all that is necessary is to determine the time to half-value corresponding to several different initial concentrations of the reactants.

We will now proceed to a discussion of reactions of various orders. This discussion will be almost entirely confined to reactions in gases, since these are the simplest and much more is known about them than about other reactions.

Bimolecular Reactions.—The classical example of a bimolecular reaction is the decomposition of gaseous hydrogen iodide. This was found by Bodenstein to proceed by the mechanism

$$2HI \rightarrow H_2 + I_2.$$

The reaction is definitely second order. The rate constants at various temperatures are given in the following table.

THE DECOMPOSITION OF HYDROGEN IODIDE

Temperature, ° C.	Rate Constant, *k*, Calculated with Time in Seconds, and Concentration in Moles per Litre
508	0.0395
443	0.00250
427	0.00116
410	0.000512
393	0.000220
374	0.0000859
356	0.0000302
302	0.00000122
283	0.000000352

The Effect of Temperature. Activation.—It has been found that reaction rates in general increase very rapidly with increasing temperature. The temperature coefficients of almost all reactions can be accurately represented by means of an equation originally proposed by Arrhenius. According to the *Arrhenius equation*,

$$k = Ae^{-E/RT},$$

where k is the reaction rate constant, A is a constant, e is the base of natural logarithms, and E is a constant called the activation energy. Taking logarithms of both sides, we may write the equation

$$\log_e k = \log_e A - \frac{E}{RT},$$

or

$$\log_{10} k = \log_{10} A - \frac{E}{2.3RT}.$$

If the gas constant, R, is expressed in calories per mole, the units of E are also calories per mole.

It was mentioned in the discussion of the law of mass action that, if every collision between the reactant molecules were effective in causing reaction, all reactions in gases would proceed practically instantaneously. Actually, however, as illustrated by the example of the hydrogen iodide decomposition, many gas reactions proceed at a slow and easily measurable rate. It is apparent, therefore, that the reacting molecule is in a condition different from that of the average molecule of the reactant. It is now known that this difference lies merely in the energy content of the molecule, molecules with high vibrational energies being those which react.

It can be shown that in a gas at a temperature T the fraction of the molecules with energy greater than some arbitrarily chosen amount E is given approximately by [fraction of the molecules with energy greater than E] $= e^{-E/RT}$. If, then, we assume that a molecule cannot react unless its energy content is greater than E, we have

$$\text{Rate} = k = \text{Constant} \cdot e^{-E/RT},$$

which is the Arrhenius equation. The constant E in the Arrhenius equation is therefore known as the activation energy, and it may be defined as the minimum amount of energy which must be acquired by N molecules of the reactant in order that they may react.

In a bimolecular reaction the activation energy may be considered to be the total energy of the pair of colliding molecules. In the case of the hydrogen iodide decomposition it is found from the temperature coefficient of the reaction that the activation energy is 44,000 calories per mole. In other words, if a pair of hydrogen iodide molecules collide and their combined energy is greater than $44{,}000/N$ calories, reaction will occur; otherwise they will be unable to react. Hence we may write for the rate of the reaction

$$
\begin{aligned}
k &= (\text{number of collisions per second between reactant molecules}) \times \\
&\quad (\text{fraction of collisions in which the combined energy of the two colliding} \\
&\qquad \text{molecules is greater than } E) \\
&= Ae^{-E/RT},
\end{aligned}
$$

and in this case the constant A in the Arrhenius equation is merely the number of collisions per second between molecules of the reactant.

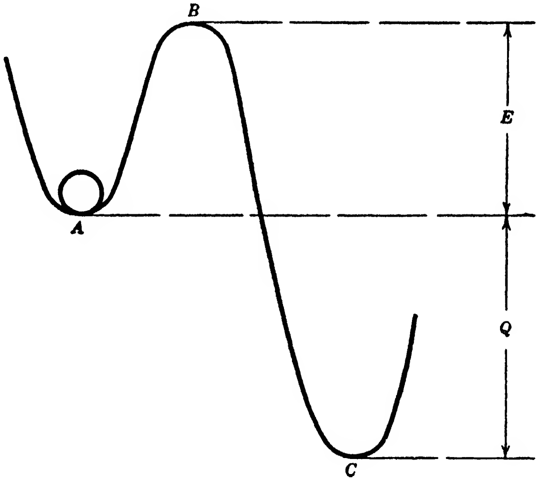


FIG. 85.

The activation energy should be clearly differentiated from the heat of the reaction. If a molecule undergoes reaction to form some other substance or substances, a certain amount of heat is in general absorbed from the surroundings or given out. This energy, the heat of the reaction, is obtained external to the system. The activation energy, however, has nothing to do with the final overall energy state of the system. It is merely a transitory localization of energy in certain molecules which react, and later give their excess energy back to the system whence it came.

As an analogy consider the diagram given in Fig. 85. Suppose that we have a ball in a valley at *A*. If this can fall to the lower valley *C*, the potential energy lost will be obtained external to the system in the form of heat or work. We may denote this amount by *Q*. However, in order that the ball may fall to *C*, it must first rise over the hump *B*. To get it over the hump we must supply energy to increase its potential energy by the amount *E*. When it falls from *B* to *C*, however, we will get back energy equal to *E* plus *Q*, and hence the net energy gain when the ball passes from *A* to *C* over the hump is still *Q*. In the case of a reaction, *Q* is analogous to the heat of the reaction and *E* to the activation energy.

Termolecular Reactions.—Very few third-order reactions are known. Of these the reaction

$$2NO + Cl_2 = 2NOCl$$

is the most thoroughly investigated. It obeys a third-order equation, i.e.,

$$\text{Rate} = k\,[NO]^2\,[Cl_2].$$

Although there is some difference of opinion on the subject, it appears probable that the reaction really proceeds by a pair of bimolecular steps:

$$2NO \rightleftarrows N_2O_2 \tag{1}$$

$$N_2O_2 + Cl_2 \rightarrow 2NOCl. \tag{2}$$

The first of these is rapid and involves the unknown compound N_2O_2. This, if formed, would be very unstable and would largely dissociate, so that the first step is reversible. Since this reaction is assumed to be very fast, we may consider that the equilibrium between NO and N_2O_2 is always established and write for the equilibrium constant of reaction (1)

$$\frac{[N_2O_2]}{[NO]^2} = K. \tag{3}$$

If the second step is the slow one, then it governs the rate of the entire process, and we have

$$\text{Rate} = k_2\,[N_2O_2]\,[Cl_2]. \tag{4}$$

But from (3), we have

$$[N_2O_2] = K[NO]^2.$$

Substituting this in (4), we obtain

$$\text{Rate} = k_3 [NO]^2 [Cl_2],$$

i.e., the expression for a third-order reaction. It may therefore be concluded that most third-order reactions are not of the true termolecular type, but involve a pair of bimolecular steps.

Unimolecular Reactions.—A large number of unimolecular reactions are known. An example is the decomposition of gaseous chloropicrin,

$$CCl_3NO_2 = COCl_2 + NOCl.$$

In general, the decomposition of almost every organic compound is a first-order reaction, and the whole question of the stability of organic compounds is merely a question of the rates of unimolecular decomposition reactions.

As we have seen, bimolecular reactions can be interpreted as occurring whenever in a collision the reactant molecules have energy equal to or greater than the activation energy. Unimolecular reactions also occur at measurable rates in certain temperature ranges, and they have high temperature coefficients which are adequately expressed by the Arrhenius equation. It may therefore be concluded that activation is necessary in unimolecular reactions also.

The process by which the activation energy is acquired in a unimolecular reaction presented considerable difficulty in the early days of the development of reaction-rate theory. Since the reaction is unimolecular, only one molecule is involved in the reaction process. Hence, it was argued, the reaction process occurs with isolated molecules. If this is the case, it is difficult to see how an isolated molecule can acquire the necessary activation energy. We cannot assume simply that this is acquired by collision, since a collision involves two molecules, and the number of collisions in a gas is therefore proportional to the square of the concentration. Hence if the rate were proportional to the number of collisions the reaction would be second order.

These difficulties were solved by the following suggestion of Lindemann. Suppose that we assume that activation is by collision, but that there is a time lag between activation and reaction, and that most activated molecules lose their energy by suffering another collision before they have had a chance to react. That is, we have

$$\text{Normal molecules} \rightleftarrows \text{Activated molecules} \tag{1}$$

$$\text{Activated molecules} \rightarrow \text{Products.} \tag{2}$$

If we assume that the activation and deactivation processes are fast, then the rate of (2) will be the controlling factor in the rate of the reaction. Now provided that comparatively few of the activated molecules react to form products, the occurrence of (1) will not be appreciably affected by the presence of (2), and we may assume that the ordinary equilibrium number of high-energy molecules will exist in the gas. Hence, applying the mass law, we have

$$\frac{[\text{Activated molecules}]}{[\text{Normal molecules}]} = K = e^{-E/RT}.$$

Now the activated molecules are few in number, and hence almost all the molecules are normal ones. We may therefore substitute [Reactant] for [Normal molecules]. Hence we have

$$[\text{Activated molecules}] = [\text{Reactant}]\, e^{-E/RT}. \tag{3}$$

Now the rate of reaction is the rate of (2), i.e.,

$$\text{Rate} = k_2\, [\text{Activated molecules}]. \tag{4}$$

Hence, substituting (3) in (4), we have

$$\text{Rate} = k_2\, [\text{Reactant}]\, e^{-E/RT},$$

$$= \text{Constant } [\text{Reactant}].$$

Hence we can account for a first-order rate in spite of the fact that activation occurs by collision.

This explanation accounts satisfactorily for the first-order rate at ordinary pressures. However, if the pressure is very low, the time between collisions becomes large, and most activated molecules react rather than are deactivated. As a result the fraction of molecules activated begins to fall below the equilibrium value, and the rate diminishes. This "falling-off" in rate at low pressures has been confirmed experimentally, and is strong confirmation for the Lindemann hypothesis.

Complex Reactions.—A considerable number of reactions are known in which the order is not integral. Thus for a reaction of the type

$$X + Y \rightarrow (\text{Products}),$$

it is sometimes found that the rate is given by an expression such as

$$\text{Rate} = kC_x^a C_y^b,$$

where a and b are not integers. In all such cases the overall reaction is the summation of a series of steps, and no one of the steps is sufficiently slow for its rate to control the rate of the overall process.

Reactions in Solution.—In general, the same principles govern reactions in solution as do those in the gaseous state. The temperature coefficients of reactions in solution are well expressed by the Arrhenius equation, and activation appears to be a necessary preliminary to reaction. The theory of such reactions, however, is in a much less advanced state, since comparatively little is known about the kinetic theory of the liquid state.

Catalysis.—Substances are known which influence the rate of certain chemical reactions without altering, or participating in, the final equilibrium which is reached. This phenomenon is known as catalysis, and a substance which causes catalysis is called a catalyst. Since a catalyst does not affect the position of equilibrium in a reaction, it follows that it must influence the rates of the two opposing reactions to the same extent. A catalyst has no stoichiometric relationship to the amounts of the reacting substances, its sole effect being to increase the reaction rate. The effect of a catalyst can therefore best be measured by determining the rate constant of the reaction in the presence of varying amounts of the catalyst. The extent to which the reaction rate increases is found to be, in general, dependent on the amount of catalyst present. It is obvious that a catalyst may play a very important rôle from a practical point of view, since by means of catalysts substances can sometimes be brought into equilibrium in a few minutes which would otherwise require years to reach equilibrium.

Catalytic reactions may be classified under two main divisions, homogeneous and heterogeneous catalysis, depending upon whether the catalyst plus reaction mixture forms a homogeneous or a heterogeneous system.

Homogeneous Catalysis.—A good example of homogeneous catalysis is furnished by the inversion of cane sugar:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6,$$

which is catalysed by the addition of acids. (The actual catalyst is hydrogen ions derived from the acid.) In dilute solution it is found that the rate of the reaction is approximately proportional to the amount of acid added.

Another example of homogeneous catalysis is the action of sodium hydroxide on the decomposition of hydrogen peroxide solutions:

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2.$$

Pure hydrogen peroxide solutions decompose only exceedingly slowly. The addition of a trace of sodium hydroxide makes an enormous difference in the rate of the decomposition.

In both the above examples the catalyst is found to be present in unchanged amount at all stages of the reaction. It is therefore obvious that a small amount of catalyst can be effective in the transformation of a large amount of material.

In certain catalytic reactions the catalyst is one of the products of the reaction. The amount of catalyst in the system therefore increases as the reaction proceeds, and this results in a continual acceleration of the reaction. This phenomenon is known as *autocatalysis*. For example, the hydrolysis of ethyl acetate,

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH,$$

is catalysed by acetic acid, which is one of the products of the reaction.

A very large number of cases of homogeneous catalysis are known. In the majority of these the catalyst is either an acid or a base. These reactions are of diverse kinds, and the mechanisms by which the catalysts function are often complex. In some cases the reactions undoubtedly proceed through the alternate formation and decomposition of an unstable intermediate compound formed between the catalyst and one of the reactants.

Heterogeneous Catalysis.—Heterogeneous catalysis is of very frequent occurrence. In this phenomenon, as the name implies, the catalyst constitutes a phase which is not that which contains the reactant or reactants. Thus, for example, in the reaction

$$KClO_3 \rightarrow KCl + 1\tfrac{1}{2}O_2,$$

the rate at which oxygen is evolved is greatly increased by the addition of manganese dioxide to the potassium chlorate.

The most interesting cases of heterogeneous catalysis are those in which a solid catalyses a reaction between gases or substances in solution. A well-known example of this type, which is of great commercial importance, is the contact process for the manufacture of sulphuric acid, i.e., the oxidation of sulphur dioxide to sulphur trioxide in the presence of finely divided platinum, viz.,

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3.$$

The equilibrium in this reaction is on the sulphur trioxide side at low temperatures, and on the sulphur dioxide side at high temperatures. To obtain reasonable yields of sulphur trioxide a low temperature is therefore necessary. The reaction, however, is immeasurably slow at such temperatures. In the presence of a catalyst the reaction may be made to proceed at reasonable speeds at temperatures where the equilibrium is sufficiently on the sulphur trioxide side for practical purposes. The feasibility of the process is therefore entirely dependent on the presence of a suitable catalyst.

Heterogeneous catalysis is of particular importance in gas reactions, many of which take place entirely at the walls of the containing vessel, rather than in the gas phase. For example, the oxidation of carbon monoxide to carbon dioxide is completely catalytic under ordinary conditions, and occurs entirely at the wall of the container.

In heterogeneous catalysis it should be remembered that the reaction is taking place at the surface of the catalyst, and hence the extent of the surface of the catalyst is of great importance, rather than its mass. For this reason catalysts are usually employed in the form of fine powders which have a very large surface.

The Specificity of Catalysts.—The great specificity in the action of catalysts is noteworthy. As an example we may consider the decomposition of gaseous formic acid. At ordinary temperatures equilibrium calculations show that formic acid is quite unstable and tends to decompose according to one of the two alternative mechanisms:

$$HCOOH \rightarrow H_2O + CO \qquad (1)$$

$$HCOOH \rightarrow H_2 + CO_2. \qquad (2)$$

Actually, however, in the absence of a catalyst such decomposition occurs immeasurably slowly, and hence formic acid is "stable." It is found that copper and other metals catalyse reaction (2) but have little effect on (1), whereas alumina and other oxides catalyse reaction (1) without having much effect on (2). Hence by a suitable choice of a catalyst either set of products may be obtained at will.

Adsorption and Catalysis.—It now appears certain that the mechanism of catalysis in systems such as the above involves adsorption of the reactants on the surface of the catalyst. The reaction then occurs in the adsorbed layer. The forces which exist between the catalyst and the adsorbed gas may be regarded as straining the adsorbed molecules and thus allowing reactions to occur which would ordinarily not take place. Adsorption may therefore be regarded as a necessary preliminary to catalysis. However, the mere fact that a solid will adsorb certain gases is no indication that it will be an efficient catalyst for reactions between them. It may, however, be predicted that in general the most efficient catalysts will be those which are in such a physical state that large adsorption of the reactants is favoured.

Since reactions on a catalytic surface are really occurring in an adsorbed layer, it is obvious that applications of the law of mass action, etc., should really be made only to the adsorbed gas, and not to the gas in the gas phase, since the gas phase is merely acting as a reservoir to keep up the supply of adsorbed gas on the surface. Actually, however, the progress of the reaction is usually followed by analysing the gas in the gas phase. Thus, suppose that we have a gas reaction

$$\mathrm{A} \rightarrow \text{(Products)}$$

proceeding on the surface of a catalyst. Then we should have

$$\text{Rate} = k\,[\mathrm{A}]_{\text{in adsorbed layer}}.$$

Now according to the Freundlich adsorption equation,

$$[\mathrm{A}]_{\text{in adsorbed layer}} = k_1 P_A^n.$$

Hence

$$\text{Rate} = k_2 P_A^n,$$

and the reaction is apparently of the *n*th order. Now *n* is usually not an integer; hence in catalytic reactions the order is often fractional, and is frequently difficult to interpret.

Catalytic Poisons, Etc.—The word "poison" has been applied to substances which destroy the activity of heterogeneous catalysts. Their action is undoubtedly due to their being themselves strongly adsorbed by the catalyst. As a result the free surface available for the adsorption of the reactants is diminished, and the efficiency of the catalyst is thus decreased. An example of such poisoning is found in connection with the sulphur dioxide-oxygen reaction on the surface of platinum. A trace of arsenic will render the platinum catalytically inert.

In all the examples of heterogeneous catalysis given above the catalyst is found to be chemically unchanged at all stages of the reaction. It is found, however, that in some cases physical changes occur in the catalyst. Thus if crystalline manganese dioxide is used to catalyse the decomposition of potassium chlorate, it is found after the reaction to have changed into a fine powder. A physical change of this kind means a change in the extent and nature of the surface of the catalyst, and this change sometimes results in the catalyst losing its activity. In this connection, a particular type of poisoning may be mentioned. The coagulation of colloidal particles is, as we have seen, often caused by the addition of certain substances. Hence the catalysing power of a colloidal catalyst may be destroyed by the addition of a substance which causes the coagulation of the colloid.

Another type of loss of catalytic power occurs when a product is formed in the reaction which itself partially poisons the catalyst. Thus in the decomposition of nitrous oxide on the surface of platinum,

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2,$$

the oxygen formed in the reaction is very strongly adsorbed, and thus cuts down the activity of the catalyst.

The Effect of Temperature on Catalytic Reactions.—The effect of temperature on the rates of catalytic reactions is similar to that with homogeneous reactions. The Arrhenius equation fits the results, and it appears that activation is a necessary preliminary to reaction. In general, the activation energies of catalytic reactions are found to be lower than those of the corresponding uncatalysed reactions, and it appears that the main function of the catalyst is to lower the activation energy of the reaction.

Some catalysts, however, are physically altered by a rise in temperature, and hence their catalytic power may be decreased. A rise in temperature has two opposing effects in such a case, and hence there may be a temperature at which the reaction rate is a maximum, the velocity decreasing at higher temperatures owing to the partial destruction of the catalyst. This is particularly true with colloidal catalysts, since a rise in temperature may cause their coagulation. Thus a platinum sol has an optimum temperature at which its efficiency in catalysing the decomposition of hydrogen peroxide is a maximum.

Negative Catalysis.—The velocity of a homogeneous reaction is sometimes *decreased* by the addition of a small amount of some substance. Such a substance is called a *negative catalyst.* In most cases such substances act by merely destroying some catalyst which is present. An example of this action is furnished by the addition of certain acids to hydrogen peroxide solutions. The presence of the acid prevents the decomposition of the peroxide being catalysed by traces of alkali which are dissolved from the glass container.

Negative catalysis also frequently occurs in oxidation reactions, in which the overall reaction is the summation of a complex series of steps involving the transitory participation of unstable substances. In these cases the catalyst acts by changing the course of some of the reaction steps, destroying the unstable substances, and thus preventing their further participation in the reaction.

Enzyme Reactions.—A special class of heterogeneous catalysts, which are of great importance in biochemistry, are known as enzymes. An enzyme is a complicated organic compound of colloidal dimensions which is produced in life processes. The catalytic action of enzymes is in every way similar to that of ordinary heterogeneous catalysts. The activity of enzymes is particularly striking because of their highly specific nature. For example, if yeast cells are broken up under pressure and extracted, an enzyme is obtained. This catalyses the fermentation of solutions of *d*-glucose to alcohol. *l*-glucose, however, is not affected by the enzyme, although chemically it is almost identical with *d*-glucose.

Another enzyme obtained from yeast will catalyse the decomposition of hydrogen peroxide solutions. Its action is entirely similar in this respect to that of finely divided platinum.

A very large number of enzymes are known, and they are of great importance in biological processes.

Since enzymes are colloidal in nature, they are easily coagulated, and are thus very sensitive to the action of added substances. Further, at increased temperatures they are coagulated, and lose their activity. There is thus in general an optimum temperature at which their catalytic efficiency is a maximum.

Photochemical Reactions.—It follows from the discussion in the preceding pages that the fundamental requisite for reaction is the acquisition of sufficient energy by the reactant molecule. In thermal reactions this energy is acquired by a series of collisions such that a certain molecule obtains energy greater than that of the average molecule of the reactant. There are, however, other methods by which a molecule of the reactant may acquire the activation energy necessary for it to react. One of such methods of acquiring energy is by the absorption of light, and the subject of photochemistry deals with such processes.

Since the fundamental process in a photochemical reaction is the input of energy to the reactant molecule, it follows that only light which is absorbed by the reaction system can be effective in causing photochemical change. This idea is known as the Grotthus-Draper law.

Soon after the development of modern ideas regarding the absorption and emission of light, Einstein pointed out that the reaction process must consist of the absorption of one quantum of light, followed by reaction, and hence in a photochemical reaction we would expect one molecule of the reactant to undergo change for each quantum of light of the effective wave length absorbed by the system. This statement is known as the Einstein law of photochemical equivalence.

In the application of Einstein's law, however, it is necessary to differentiate clearly between the original process in which light is absorbed (the *primary process*) and possible subsequent secondary reactions of the substances produced in the primary process. It is now generally conceded that Einstein's law is strictly applicable to the primary process, but not to the overall reaction consisting of the primary process and subsequent secondary processes. Thus, for example, in the decomposition of hydrogen iodide by ultraviolet light, we have

$$\begin{array}{rl}
\mathrm{HI} + (\text{1 light quantum}) \rightarrow \mathrm{H} + \mathrm{I} & \text{Primary process} \\
\left.\begin{array}{r}\mathrm{H} + \mathrm{HI} \rightarrow \mathrm{H_2} + \mathrm{I} \\ 2\mathrm{I} \rightarrow \mathrm{I_2}\end{array}\right\} & \text{Secondary processes} \\
\hline
2\mathrm{HI} + (\text{1 light quantum}) \rightarrow \mathrm{H_2} + \mathrm{I_2} & \text{Overall reaction}
\end{array}$$

As a result of the secondary reactions involving hydrogen and iodine atoms, two molecules of hydrogen iodide disappear for each quantum of light absorbed. The reaction is therefore said to have a *quantum yield* of two.

A large number of photochemical reactions have quantum yields varying from small values to 5 or 10, and when sufficient information is available it is possible to draw up mechanisms such as the above to account for the quantum yield.

Chain Reactions.—There are a number of very interesting reactions in which exceedingly high values are obtained for the quantum yield. The classical example of this sort is the photochemical synthesis of hydrogen chloride from hydrogen and chlorine. In this reaction the primary process is the absorption of light by chlorine,

$$\mathrm{Cl_2} + (\text{1 light quantum}) \rightarrow 2\,\mathrm{Cl}.$$

The quantum yield is very high, under appropriate conditions reaching 10^6. The main secondary reactions which follow are

$$\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H}$$

$$\mathrm{H} + \mathrm{Cl_2} \rightarrow \mathrm{HCl} + \mathrm{Cl}.$$

It will be seen that the occurrence of this pair of secondary reactions results in the formation of two molecules of HCl, and the *regeneration of the chlorine atom* consumed in the first reaction. As a result this pair of reactions can repeat over and over again thousands of times, and a high quantum yield follows. Reactions of this sort are known as *chain reactions.*

QUESTIONS AND PROBLEMS

1. The partial pressure of azomethane in a bulb at 298° C. was found to fall from 37.18 cm. to 31.36 cm. in 10 minutes, as the azomethane decomposed. The reaction is unimolecular. Calculate the velocity constant. *Ans.* 0.01698 min.^{-1}

2. Using the velocity constant calculated in question 1, find the partial pressure of azomethane 1 hour from the start. *Ans.* 13.40 cm.

3. The decomposition of gaseous diazomethane is second order. At 162° C. the partial pressure of diazomethane fell from 155 mm. to 124 mm. in 358 seconds. Calculate the rate constant. *Ans.* $4.5 \times 10^{-6}\ \text{mm.}^{-1}\ \text{sec.}^{-1}$

4. Using the value of k obtained in question 3, calculate the partial pressure of diazomethane 15 minutes later. *Ans.* 82.4 mm.

5. Discuss the order and mechanism of reactions.

6. Show how the order of a reaction may be determined.

7. Define the time to one-half value, and discuss its dependence on the concentration of the reactants.
8. Discuss the mechanism of activation in bimolecular reactions.
9. Distinguish clearly between the heat of a reaction and the activation energy.
10. Discuss the mechanism of activation in unimolecular reactions.
11. What is meant by catalysis?
12. Give examples of homogeneous catalysis.
13. Discuss catalytic poisons.
14. Discuss the mechanism of heterogeneous catalysis, giving examples.
15. Discuss enzyme reactions.
16. State the Grotthus-Draper law.
17. State Einstein's law of photochemical equivalence.
18. What is the "quantum yield" of a photochemical reaction?
19. Discuss the photochemical synthesis of hydrogen chloride.

CHAPTER XVI

ELECTROLYTIC DISSOCIATION

For a number of years after van't Hoff had put forward his theory of solutions, certain experimental discrepancies were cited against the theory. These discrepancies occurred with aqueous solutions of acids, bases, and salts. One type of anomaly is observed when the molecular weight of such a dissolved substance in very dilute solution is calculated from the lowering of the freezing point. The calculated molecular weight under these circumstances was found to be a fraction, for example, 1/2, 1/3, etc., of the theoretical molecular weight of the solute. This points to an osmotic pressure which is a simple multiple, 2, 3, etc., of the osmotic pressure calculated from

$$P = \frac{nRT}{V}.$$

Measurements of the lowering of vapour pressure and the rise in the boiling point of such solutions gave results in harmony with those obtained by the freezing-point method.

Unfortunately, it has proved impossible to find a satisfactory semi-permeable membrane for the direct measurement of the osmotic pressures of solutions of acids, bases, and salts. Any membrane which has been used invariably allows some of the solute to leak through. In some cases, however, it has been possible to obtain rough measurements, which have indicated that the osmotic pressures of such solutions are much higher than that calculated from $P = \frac{nRT}{V}$. The natural conclusion is that such solutes are dissociated into two or more parts in solution.

One great difficulty arises, however, if such an assumption is made. In the case of a substance such as hydrogen chloride, the lowering of the freezing point indicates that in dilute solution the HCl molecule is dissociated into two parts. The only possible dissociation would therefore seem to be $HCl \rightarrow H + Cl$.

A solution of hydrogen chloride, however, shows no indications of the presence of hydrogen or chlorine, the first of which is practically insoluble in water, while the second has properties such as colour, odour, etc., which are absent in a solution of hydrogen chloride.

It was noticed that solutions of acids, bases, and salts, which show such anomalies, also possess one other property in common, namely, the ability to conduct the electric current. This property is absent in solutions which conform to the van't Hoff theory of solutions. The conduction of electricity by a solution is accompanied by a number of physical and chemical changes. This phenomenon of conduction is called electrolysis, and the solutes which give rise to it are called electrolytes.

Arrhenius succeeded in explaining both the abnormal molecular weights of electrolytes, and the conduction of the electric current, by means of the theory of electrolytic dissociation.

The Theory of Electrolytic Dissociation.—Arrhenius postulated that when an electrolyte is dissolved to form a dilute solution it is dissociated, not into normal atoms or groups of atoms, but into atoms or groups of atoms which are electrically charged. Such charged particles are called ions, and their properties are quite different from those of the corresponding uncharged particles. Modern work on the structure of the atom has strongly confirmed the idea that an electric charge may alter the properties of an atom.

The Mechanism of Conduction.—It is found that a solution of an electrolyte is electrically neutral as a whole, i.e., it shows no sign of being charged when it is placed in an electroscope. In consequence, the dissociation into charged atoms must be such that some are positively charged and others negatively charged, the total amounts of positive charge and negative charge being equal. The state of such a solution can therefore be represented diagrammatically by a number of positive and negative charges chaotically distributed throughout the solution.

The ions are free to move, and uniformity of electric distribution will thus be maintained by diffusion, just as homogeneity of composition is maintained. This uniformity of electric distribution is also favoured by another factor, viz., the electric forces due to the charges on the particles, which prevent the accumulation of particles of one sign in any portion of the solution. The condition of the solution may thus be represented by Fig. 86 (*a*).

The mechanism of the conduction of electricity follows immediately. The ions are free to move, and consequently, if placed in an electric field, the positive ions will move in one direction and the negative ions in the other, as shown in Fig. 86 (*b*). If the electric field is caused by two metallic plates immersed in the solution and connected to a battery, ions will be attracted to the plates, where their charge will be neutralized and their ordinary properties as uncharged atoms will be resumed.

Two factors tend to slow up the movement of the ions in an electric field. In the first place, the solvent molecules by means of collisions slow up the rate of diffusion enormously. In the second place, the tendency to maintain uniformity of electric distribution prevents the free motion of the ions to the charged plates. In consequence the ions do not move rapidly to the charged metal plate, or electrode, in a body, but slowly diffuse, the positive ions going to the negative electrode, and *vice versa.* If the charge on the electrodes is maintained by a battery, there will thus be a continuous flow of electricity through the solution.

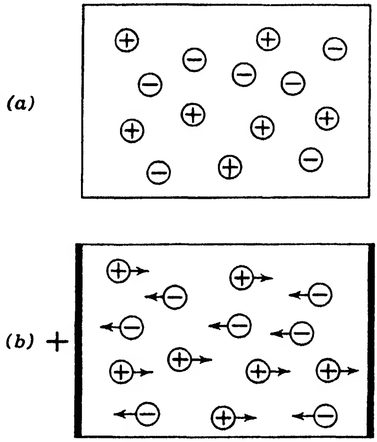


FIG. 86.

Electrolysis.—When the ions come into contact with the electrodes they give up their charges and revert to their ordinary chemical nature. It is therefore at these electrodes that information can be obtained regarding the nature of the carriers of electricity, or ions.

A number of special terms have come into use in connection with the passage of an electric current through a solution. As previously mentioned, chemical or physical changes occur owing to the passage of the current. The net change which takes place is called electrolysis, and this can usually be represented by a chemical equation which sums up the various changes which have taken place. The points at which the current enters the solution are called electrodes, the positive electrode being referred to as the anode, and the negative one as the cathode. The ions that are discharged at the cathode, and which must therefore have been positively charged, are called cations, and similarly the negatively charged ions liberated at the anode are called anions.

A few simple cases of electrolysis will now be described. When a current is sent through a solution of hydrogen chloride, for example, experiment shows that hydrogen alone is liberated at the cathode, and chlorine alone at the anode. According to molecular weight determinations, the hydrogen chloride molecule is presumably dissociated into two parts in solution. Hence, presumably we have hydrogen ions with a positive charge and chlorine ions with a negative charge. The dissociation can thus be represented by

$$HCl \rightarrow H^+ + Cl^-,$$

the plus and minus signs representing the nature of the charge, without for the moment having any reference to its magnitude.

The above results are obtained when the electrodes are made of platinum. When a hydrogen ion is discharged, it reverts at the moment of contact with the platinum into a hydrogen atom. Since no compound is formed between platinum and hydrogen, hydrogen atoms accumulate on the platinum surface. These combine readily with one another to form hydrogen molecules, which are given off in the form of a series of gas bubbles. At the anode the newly formed chlorine atoms also combine with one another, and gaseous chlorine is given off. We may therefore represent all the changes which occur as follows:

$$\begin{array}{l}
2HCl \rightarrow 2H^+ + 2Cl^- \\
2H^+ \rightarrow 2H \quad - 2e^* \\
2H \rightarrow H_2 \\
2Cl^- \rightarrow 2Cl + 2e \\
2Cl \rightarrow Cl_2 \\
\hline
2HCl \rightarrow H_2 + Cl_2,
\end{array}$$

the total electrolysis being given by the final equation.

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* In these equations *e* represents an electron.

It is possible to predict what will occur if other electrodes are used. Thus suppose a solution of hydrogen chloride is electrolysed with zinc electrodes. As atoms of hydrogen are formed, there is no tendency to react with zinc and they are therefore given off as hydrogen gas. The newly formed chlorine atoms come into existence in contact with the other zinc plate, and consequently have the opportunity of reacting with it before they can combine to form molecules. Since zinc and chlorine combine readily, zinc chloride is formed and dissolves in the solution, of course in the form of ions. All the changes can therefore be represented by

$$\begin{aligned} 2HCl &\rightarrow 2H^+ + 2Cl^- \text{ *} \\ 2H^+ &\rightarrow 2H - 2e \\ 2H &\rightarrow H_2 \\ 2Cl^- &\rightarrow 2Cl + 2e \\ 2Cl + Zn &\rightarrow ZnCl_2 \\ \hline 2HCl + Zn &\rightarrow ZnCl_2 + H_2 \end{aligned}$$

The total electrolysis therefore involves the material of one of the electrodes. These predictions have been confirmed experimentally.

Extensive experiments in electrolysis have enabled the following generalizations to be made. In solution all acids are dissociated into positively charged hydrogen ions, the remainder of the molecule, i.e., the halogen or acid group, giving rise to a negatively charged ion. In a solution of a base, the hydroxyl ion is negatively charged, the rest of the molecule forming an ion with a positive charge. In salts, the metal forms the positive ion and the remainder of the molecule the negative ion.

The result of any experiment in electrolysis can now be predicted by taking into account three factors: (*a*) the products of ionization and their signs; (*b*) the chemical nature of the discharged ions; (*c*) the fact that the electrode has the first chance of reacting with the discharged ion, since the latter

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* On this and the next three pages examples of electrolysis are discussed. The simple mechanisms given lead to correct conclusions regarding the products of the reactions and are therefore very useful. Actually, however, as we shall see later, (p. 360), the situation is more complicated than is represented here owing to factors connected with the voltage.

remains protected by its electric charge until it is actually in contact with the electrode.

A few examples of such experiments in electrolysis are given below. The various events which occur can be fully represented by a series of chemical equations, the sum of which gives the total net result, i.e., the total electrolysis. In each case the first equation represents the dissociation of the solute, which takes place when it is brought into solution. It should be emphasized that this occurs *on solution,* and is not in any way caused by the passage of the current. The final products of the electrolysis are, for convenience, represented in their undissociated form.

*Copper Bromide with Platinum Electrodes.**

$$\begin{array}{r} CuBr_2 \rightarrow Cu^{++} + 2Br^- \\ Cu^{++} \rightarrow Cu - 2e \\ 2Br^- \rightarrow 2Br + 2e \\ 2Br \rightarrow Br_2 \\ \hline CuBr_2 \rightarrow Cu + Br_2 \end{array}$$

Sulphuric Acid with Platinum Electrodes.

$$\begin{array}{r} H_2SO_4 \rightarrow 2H^+ + SO_4^= \\ 2H^+ \rightarrow 2H - 2e \\ 2H \rightarrow H_2 \\ SO_4^= \rightarrow SO_4 + 2e \\ SO_4 \rightarrow SO_3 + \frac{1}{2}O_2 \\ SO_3 + H_2O \rightarrow H_2SO_4 \\ \hline H_2O \rightarrow H_2 + \frac{1}{2}O_2 \end{array}$$

It should also be noticed that, although the ions formed by the dissociation of sulphuric acid take part in the electrolysis,

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* In this, and in one or two other examples, the SO_4 or other ions are shown with two plus or minus signs. The reason for writing the ions in this way will be shown in the next section. They are given here in this form merely to follow conventional usage.

and are liberated at the electrodes, subsequent reactions result in the reformation of sulphuric acid whose concentration thus remains constant. The resultant electrolysis is therefore that of water.

Copper Sulphate with Copper Electrodes.

$$\begin{array}{c}
\mathrm{CuSO_4} \rightarrow \mathrm{Cu^{++}} + \mathrm{SO_4^{=}} \\
\mathrm{Cu^{++}} \rightarrow \mathrm{Cu} - 2e \\
\mathrm{SO_4^{=}} \rightarrow \mathrm{SO_4} + 2e \\
\mathrm{Cu} + \mathrm{SO_4} \rightarrow \mathrm{CuSO_4} \\
\hline
\text{——} \quad \rightarrow \quad \text{——}
\end{array}$$

The above example illustrates a type of electrolysis in which no resultant chemical change occurs. A physical change occurs, however, inasmuch as metallic copper is dissolved at the anode and deposited on the cathode. This type of electrolysis is of importance in electroplating, and in the refining of metals.

It is worthy of note that the passage of an electric current through a solution of an electrolyte is always accompanied by a material change in the system. This type of conduction differs, therefore, from ordinary metallic conduction in which the conductor is left unchanged after the passage of the current.

Faraday's Laws of Electrolysis and the Charge on an Ion.—Experiments in electrolysis have shown that the sign of the charge on an ion is always the same for the same ion, irrespective of the compound from which it was formed. The next question is the magnitudes of the relative charges on various ions, either of the same or of different types. This can be approached by the measurement of the quantity of an element deposited at an electrode, when a definite quantity of electricity passes through the solution. Faraday was the first to perform systematic experiments of this kind.

In these experiments a known amount of electricity was sent through a solution, and the amount of substance deposited at each electrode was measured. For example, when a current is sent through a solution of silver sulphate with platinum electrodes, silver is deposited at the cathode and oxygen at the anode. The changes which occur may be represented by the following equations:

$$\begin{aligned} Ag_2SO_4 &\rightarrow 2Ag^+ + SO_4^= \\ 2Ag^+ &\rightarrow 2Ag - 2e \\ SO_4^= &\rightarrow SO_4 + 2e \\ SO_4 &\rightarrow SO_3 + \tfrac{1}{2}O_2 \\ SO_3 + H_2O &\rightarrow H_2SO_4 \\ \hline Ag_2SO_4 + H_2O &\rightarrow H_2SO_4 + 2Ag + \tfrac{1}{2}O_2 \end{aligned}$$

The silver deposited may be determined by weighing the electrode before and after the experiment, the oxygen by collection in a eudiometer. The current which passes through the solution is measured by an ammeter in series with the electrodes, and the time during which the current flows is noted. The results obtained in experiments of this kind may be summed up in what are called Faraday's laws of electrolysis. These are two in number, viz.:

First Law.—The amount of electrolysis is proportional to the current, and to the time during which it flows, i.e., to the quantity of electricity passing through the solution.

Second Law.—The amount of electrolysis of different substances by the same quantity of electricity is proportional to the equivalent weight of the element liberated.

These laws can be summed up by the equation

$$W = KEIt,$$

where W is the weight of substance deposited in grams;
I is the current in amperes;
t is the time of flow of the current in seconds;
E is the equivalent weight of the element concerned, and
K is a constant which has been found to have the numerical value 0.00001036.

Since the quantity of electricity conveyed by one ampere in one second is one coulomb, the above equation may be written

$$W = 0.00001036EQ,$$

where Q is the number of coulombs which passed through the solution.

It follows from the above that the quantity of electricity which will liberate the equivalent weight of any element is

$$\frac{1}{0.00001036} = 96{,}500 \text{ coulombs.}$$

Consider the case of hydrogen ions. The amount deposited is dependent solely on the quantity of electricity which is passed through the solution, irrespective of the voltage, the compound from which the hydrogen ions have been formed, or the concentration of the solution. It follows that the number of hydrogen ions deposited by 96,500 coulombs is always the same, i.e., one gram. Hence, if e is the average charge on one hydrogen ion, and N the number of ions in one gram, then

$$Ne = 96{,}500,$$

since each ion deposited neutralizes an amount of electricity equal to e. Hence

$$e = \frac{96{,}500}{N} \text{ coulombs} = \text{constant.}$$

At first sight this does not appear to prove that the charge is the same for all hydrogen ions, but merely that the average charge on any experimentally observable number of ions is a constant. The fact that Faraday's laws hold, irrespective of the duration of the flow of current, proves that all the charges must be the same, since otherwise the ions with high charges would move faster and would therefore be deposited at the electrodes first.

The same behaviour is found with any one species of ion, and hence it may be concluded that the charges on the ions of any one species are all identical.

According to Faraday's second law, equivalent weights of different elements are deposited by the same quantity of electricity. It follows that the total charge on the equivalent weight of any ion must be constant and equal to 96,500 coulombs.

We may define the equivalent weight of an element as the atomic weight divided by the valence. The atomic weights of all the elements contain equal numbers of atoms, say N. The equivalent weight of an element therefore contains N/v atoms, where v is its valence. The number of ions of an element deposited by 96,500 coulombs of electricity is therefore N/v, or, in other words, N/v ions have a total charge of 96,500 coulombs. Or, if e is the charge on one ion, we have

$$e = \frac{96{,}500}{N/v}$$

$$\frac{e}{v} = \frac{96{,}500}{N} = \text{constant.}$$

That is, the charge on an ion divided by its valence is a constant.

The electric charges on ions are therefore whole-number multiples of the charge on a monovalent ion. To determine the charge on an ion such as the sulphate ion, which is not liberated at the electrode as such, all that is necessary is to consider the intermediate reactions which take place during electrolysis. Thus with silver sulphate one SO_4 ion is deposited for every two silver ions. The charge on the sulphate ion must therefore be twice that on a silver ion. The following list gives some typical examples of ions of different valences. In each case the number of positive or negative signs attached gives the magnitude of the charge, in terms of the charge on the hydrogen ion as unity.

Monovalent

H^+, Ag^+, Na^+, Cl^-, Br^-, OH^-, NO^-_3.

Divalent

$SO_4{}^{--}$, $SO_3{}^{--}$, Ca^{++}, Zn^{++}.

Trivalent

Al^{+++}, $PO_4{}^{---}$.

Tetravalent

Ti^{++++}, $Fe(CN)_6{}^{----}$.

The facts that the charge on an ion is a whole-number multiple of a definite quantity, and that fractions of this quantity are never observed on any ion in any solution, led Faraday to the conclusion that atoms must contain in their structure electrical charges which are indivisible, and correspond to some elementary unit charge. Electricity can thus be looked upon as being " atomic " in nature. These speculations of Faraday are in close agreement with prevailing ideas regarding the structure of the atom. The fundamental unit of electricity in all phenomena seems to be the same as the charge on a hydrogen ion.

Ionic Movement.—When a current of electricity passes through a solution it is carried by the ions; the amount of current carried in unit time, i.e., the current, will therefore be dependent upon the velocities of the ions. After the passage of a current the solution shows no sign of having acquired a resultant electric charge, and equal quantities of electricity must therefore have been discharged at both electrodes. It would, in consequence, appear at first sight that a pair of monovalent ions, such as H^+ and Cl^- derived from HCl, must move with the same velocity, since they carry the same amount of current in unit time. It might also be expected that a divalent ion, which carries twice as much charge, must move half as fast as a monovalent ion. We will now show that this is not necessarily the case.

That ions will move with a definite velocity may be seen from the following considerations. The force on the ion is given by the product of the charge and the electric field between the electrodes. Acceleration is prevented, however, by the friction suffered by the ion due to collisions with the molecules of the solvent. This friction is balanced by the electric force, and a steady state is reached in which the ions move with constant velocity. This velocity is dependent on the strength of the electric field, i.e., the voltage, and is usually expressed in terms of centimetres per second, when the potential difference between the electrodes is one volt per centimetre.

When the ions are coloured, or when they cause a colour change in the solution as they travel through it, it is possible to observe their motion visually, and hence their velocity may be measured directly. This direct method has been applied to the measurement of the velocities of the hydrogen and hydroxyl ions, by placing an indicator in the solution.

The apparatus is illustrated diagrammatically in Fig. 87. The tube on the left-hand side of the capillary is filled with a solution of hydrochloric acid. The capillary and right-hand tube contain a slightly alkaline solution of sodium chloride which is coloured pink by phenolphthalein. The electrodes are connected to a source of current as shown, and current flows through the solution. The hydrogen ions from the hydrochloric acid move towards the right-hand electrode and decolourize the phenolphthalein as they go. The rate at which the hydrogen ions travel may be observed by watching the rate at which the line of junction between the pink and colourless solutions moves along the capillary tube. A capillary is used to cut down ordinary diffusion as much as possible.

The velocities of the ions found in this way are extremely small. The hydrogen ion moves about 11.8 cm. per hour, and the hydroxyl ion 6.5 cm. per hour, under a potential difference of one volt per centimetre.

The above method is, of course, very limited in its applicability. It has been found to be possible to determine the relative velocities of the ions formed by the dissociation of an electrolyte, by measuring the concentration changes which occur when a current is sent through the solution. Before considering the experimental details, we will discuss the principle involved, and the subject of ionic velocities in general.

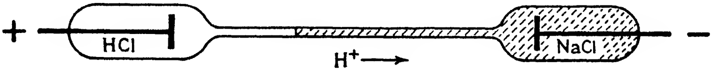

FIG. 87.

Consider a solution of an electrolyte MX, which dissociates as represented by the equation

$$MX \rightarrow M^+ + X^-.$$

Suppose that the two ions, M^+ and X^-, move with equal velocities. Let 20 equivalents of this solution be placed in a cell, in which the anode and cathode compartments are separated by a capillary tube to prevent ordinary molecular diffusion. The distribution of positive and negative ions may be diagrammatically represented by Fig. 88. This representation overlooks the chaotic distribution that actually exists, but it is used to indicate the uniform distribution of material and of electric charge which must prevail throughout the solution.

Suppose that we now pass 4 × 96,500 coulombs (or 4 faradays) of electricity through the solution. Four equivalents of the cation M^+ will separate at the cathode, and 4 equivalents of the anion X^- at the anode. Since the velocities of the ions are the same, they will share the carrying of the current equally, i.e., 2 faradays will be carried by each kind of ion. Hence 2 equivalents of the cation will move into the cathode compartment from the anode compartment, and 2 equivalents of the anion will move into the anode compartment from the cathode compartment. The distribution of ions will now be as represented in Fig. 89, the letters M and X outside the apparatus representing the number of equivalents of M^+ and X^- which have been discharged at the electrodes.

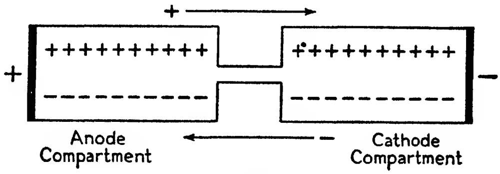

FIG. 88.

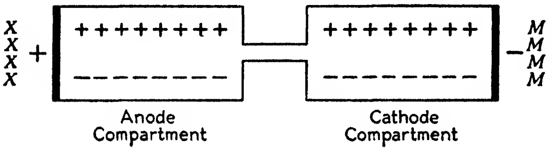

FIG. 89.

The changes which have taken place in the solution may be summarized thus:

The Anode Compartment.

Cations present at the start = 10
Cations lost by migration to the cathode compartment = 2

Cations left at the end 8

Anions present at the start = 10
Anions gained by migration from the cathode compartment = 2
Anions lost by being discharged at the anode = 4

Anions left at the end 8

Decrease in concentration of MX in the anode compartment
= 10 − 8 = 2 equivalents.

The Cathode Compartment.

Cations present at the start = 10
Cations gained by migration from the anode compartment = 2
Cations lost by being discharged at the cathode 4

Cations left at the end = 8

Anions present at the start = 10
Anions lost by migration to the anode compartment = 2

Anions left at the end = 8

Decrease in concentration of MX in the cathode compartment
$= 10 - 8 = 2$ equivalents.

Thus a total of 4 equivalents of MX have been lost, and 4 equivalents of M have separated at the cathode, and 4 equivalents of X at the anode.

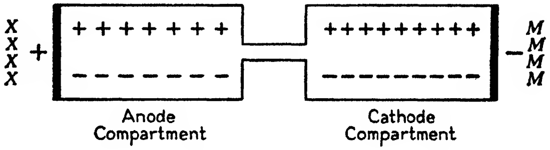

FIG. 90.

Suppose we now consider the same system as before, but assume in this case that the cation M^+ moves three times as fast as the anion X^-. Again let 4 faradays of electricity flow through the solution. As before, 4 equivalents of each ion will separate at the electrodes. Since the cation travels 3 times as fast as the anion, 3 faradays will be carried by the cation and 1 faraday by the anion. Hence, 3 equivalents of the cation will migrate to the cathode compartment, and one equivalent of the anion will migrate to the anode compartment. The distribution of ions will now be as represented in Fig. 90. As before we may summarize the changes which have occurred:

The Anode Compartment.

Cations present at the start = 10
Cations lost by migration to the cathode compartment = 3

Cations left at the end = 7

Anions present at the start = 10
Anions gained by migration from the cathode compartment = 1
Anions lost by being discharged at the anode = 4

Anions left at the end 7

Decrease in concentration of MX in the anode compartment
$= 10 - 7 = 3$ equivalents.

The Cathode Compartment.

Cations present at the start	=10
Cations gained by migration from the anode compartment	= 3
Cations lost by being discharged at the cathode	= 4
Cations left at the end	= 9

Anions present at the start	=10
Anions lost by migration to the anode compartment	= 1
Anions left at the end	= 9

Decrease in concentration of MX in the cathode compartment $= 10 - 9 = 1$ equivalent.

Hence we have

$$\frac{\text{Decrease in concentration in the anode compartment}}{\text{Decrease in concentration in the cathode compartment}} = \frac{3}{1} = \frac{\text{velocity of the cation}}{\text{velocity of the anion}}.$$

We can thus determine the relative velocities of two ions in a solution by analysing the solution in the neighbourhood of the electrodes after a current has passed through. This can be carried out conveniently by means of the apparatus shown in Fig. 91. A solution which is, say, tenth normal with respect to an electrolyte MX is placed in the apparatus. The two electrodes are in compartments, which are separated from one another by a fine capillary to cut down diffusion. A current is passed through the solution for some time. The tap in the capillary tube is then shut, and samples are drawn off from each side of the apparatus and analysed. Suppose that the concentration of MX in the neighbourhood of the anode is now 0.095 N, and in the neighbourhood of the cathode is 0.085 N. The drop in concentration around the anode is $0.100 - 0.095 = 0.005$. The decrease around the cathode is $0.100 - 0.085 = 0.015$. Then we have

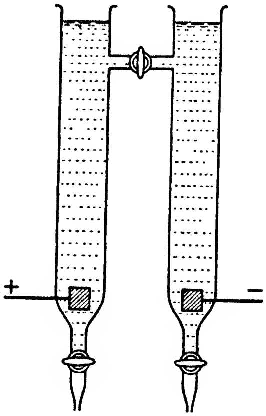

FIG. 91.

$$\frac{0.005}{0.015} = \frac{\text{velocity of cation}}{\text{velocity of anion}} = \frac{1}{3},$$

i.e., in this case the anion moves three times as fast as the cation.

Since the relative velocities of a pair of ions may be measured in this way, and since the absolute velocities of a few ions, such as H^+, are known, it follows that the absolute velocity of any ion may be computed. In the following table the absolute velocities of a number of different ions are given for a temperature of 20° C.

H^+ = 0.00329 cm./sec./volt/cm.
Cl^- = 0.00068
OH^- = 0.00182
$SO_4^{=}$ = 0.00071
Cu^{++} = 0.00048

It should be noted that the proportion of the current carried by an ion in a binary electrolyte is dependent upon the relative velocities of the ions. If u and v are the absolute velocities of the cation and anion, respectively, the fraction of the current carried by each will be

$$\frac{u}{u+v} \text{ for the cation, and}$$

$$\frac{v}{u+v} \text{ for the anion.}$$

These fractions are called transport numbers, and are often convenient for purposes of calculation, since they are independent of the applied voltage.

The Hydration of Ions.—It has been found experimentally that the velocities of ions increase with increasing temperature. The temperature coefficients for almost all monovalent ions are found to lie near 0.025. The temperature coefficient of the viscosity of water is 0.025. It therefore looks as if the rate at which the ions move was determined merely by the friction introduced by the water in the solution.

The absolute velocities of different ions vary over a wide range. The velocity is in no way dependent upon the " molecular " weight of the ion, as is the case in the diffusion of gas molecules. Thus the potassium ion moves about 50 per cent faster than the sodium ion, although the atomic weight of potassium is nearly twice that of sodium.

In order to explain the slow velocities of ions, the temperature coefficients, and the lack of parallelism between ionic velocity and weight, it has been assumed that ions are hydrated. If each ion in the solution is surrounded by a large number of attached water molecules, their velocities will be small, since the total molecular weight of the aggregate will be very large; and the relative velocities will be dependent not on the molecular weight of the simple ions, but upon the degree of hydration. The resistance to motion will be virtually that of water flowing through water, and consequently the temperature coefficient will be merely that of the viscosity of water.

It has been possible to prove experimentally that this hydration exists. Suppose that we have an aqueous solution which contains both sodium chloride and sugar. The sugar is not ionized, and all the current will be carried by the ions derived from sodium chloride. The sodium and chlorine ions move to the electrodes and carry their aggregated water with them. At the electrodes the ions are discharged, and the water is given back to the solution. As a result, there will be a flow of water from the middle of the solution to the electrodes. Sugar molecules, however, will not be carried to the electrodes by the ions. In consequence the sugar solution will be diluted around the electrodes, and concentrated in the region between them. The number of water molecules associated with an ion may be calculated from experiments of this kind.

The Electrical Conductivity of Solutions.—The specific electrical resistance of a substance is defined as the resistance in ohms between the opposite faces of a cube of the material having an edge one centimetre long. The reciprocal of this quantity is known as the specific conductance, i.e., if c is the specific conductance and r the specific resistance, then $c = 1/r$. In the case of a solution, the measurements may be made by determining the resistance between two electrodes of one square centimetre area, one centimetre apart, the intervening space being filled with the solution. The resistance of such a cell is then determined by means of a Wheatstone bridge. A cell of this type is represented diagrammatically in Fig. 92.

The passage of an electric current through a solution causes electrolysis, which not only changes the composition of the solution, but also causes the deposition of the products at the electrodes, where they may give rise to disturbing effects. The conductivity of such a solution cannot, therefore, be measured with any accuracy unless electrolysis can be prevented.

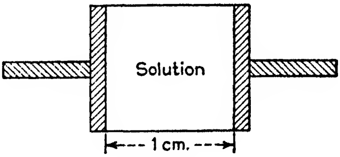

FIG. 92.

When a quantity of electricity is sent through a solution, an appreciable time is required in order that the products of the electrolysis can enter into new combinations. If, therefore, the same quantity of electricity can be sent through the solution in the opposite direction within a short enough time, combination will take place between the two deposits, so that there will be no resultant change in the composition of the system. Thus in the case of a solution of hydrochloric acid, hydrogen ions are deposited on the cathode and form atoms. If the current is reversed rapidly this electrode becomes the anode, and chlorine ions are liberated. These form chlorine atoms, which combine with the previously formed hydrogen atoms to regenerate hydrochloric acid. There has thus been no resultant change in the solution.

In order that such recombination may take place efficiently there are certain essential conditions which must be fulfilled. In the first place, the quantities of electricity passing through the solution in opposite directions must be exactly equal, in order that equivalent quantities of each substance may be deposited at each electrode, leaving no surplus of one or the other. Again, the alternations in the current must be so rapid that the deposited substances cannot react to form stable molecules, or escape from the electrodes. This depends also upon the existence of a large electrode area over which the deposit occurs, thus decreasing the chance of combination between deposited atoms. Finally, since the electrodes always have the first chance of reacting with the deposited substance, they must be constructed of some inert material such as platinum.

In practice an alternating current of about 1000 cycles per second is used. Most galvanometers will not register an alternating current, and a telephone receiver is used to indicate the passage of a current, the Wheatstone bridge being adjusted until the sound in the telephone is a minimum. The alternating current employed must be such that the total quantity of electricity in each direction in unit time is exactly the same.

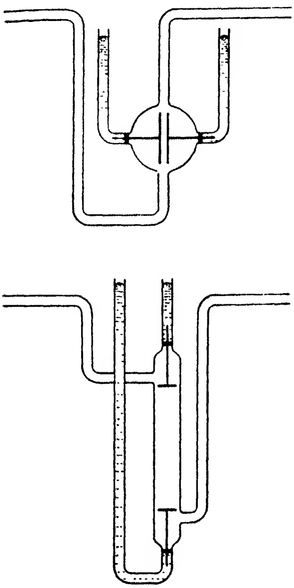

FIG. 93.

It is generally impractical to use a very large electrode. Instead of this, small platinum electrodes are used, upon which platinum black has been deposited. Owing to the porosity of this substance, the actual surface of the electrodes is increased many thousand times without increasing their dimensions.

For solutions which have a high resistance, it is usually advantageous to have large electrodes which are close together; whereas for solutions of low resistance small, widely separated electrodes are used. In this way the actual resistance to be measured may be adjusted to a convenient value. Some cells of the type designed by Washburn are shown in Fig. 93.

It is impossible to calculate the dimensions of such a cell with much accuracy and they are calibrated by means of potassium chloride solutions, whose specific resistances have been measured with great accuracy in cells of standard dimensions. It is therefore possible to calculate the specific resistance of a potassium chloride solution if its concentration is known. Such a solution is placed in a cell of the type illustrated above, and its resistance, R, is measured The specific conductance of the potassium chloride solution, c, is then given by $c = K/R$, where K is a constant which depends upon the dimensions of the cell. Since c is known from the concentration of the solution, K, the "cell constant," can be calculated. This constant is dependent solely on the dimensions of the cell, and will therefore remain the same for any other solution.

The complete apparatus ordinarily employed in measurements of the conductivity of solutions is shown in Fig. 94. The ordinary type of Wheatstone bridge is usually replaced by a slide-wire bridge, as shown. The resistance is then calculated from the relation

$$\frac{X}{R} = \frac{l_1}{l_2}, \text{ in the usual manner.}$$

The specific conductance of a solution of an electrolyte is dependent upon the velocities of the ions, their charges, and their number. Let Q be the quantity of electricity which passes through the solution in t seconds, I be the current flowing, and E the voltage. Suppose that u and v are the velocities of the cation and anion under a potential gradient of 1 volt per centimetre, n is the number of ions per cubic centimetre, and e is the charge on each ion. Then the average velocity of the ions is given by

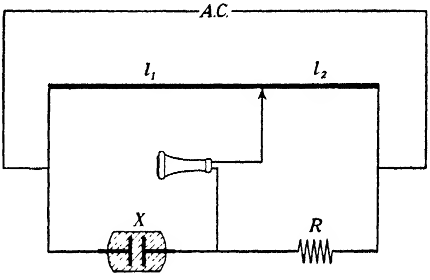

FIG. 94.

$$\frac{uE + vE}{2}.$$

Hence we have

$$Q \propto \frac{uE + vE}{2} net,$$

or

$$\frac{Q}{t} = KE(u + v)n,$$

where K is a constant for any particular solution and includes e the charge on the ions. But

$$\frac{Q}{t} = I = \frac{E}{R}.$$

Hence

$$c = \frac{1}{R} = Kn(u + v).$$

Since u and v are supposedly independent of the concentration of the solution, it might be expected that the specific conductance would be directly proportional to *n*, the number of ions per cubic centimetre, and hence to the concentration of the solution. That this is not the case is shown by the following table.

CONDUCTIVITIES OF POTASSIUM CHLORIDE SOLUTIONS AT 20° C.

Concentration in Gram Molecules per Litre	Specific Conductance	$\frac{\text{Specific Conductance}}{\text{Concentration}}$
1.000	0.0983	0.0983
0.500	0.0512	0.1024
0.100	0.0112	0.1120
0.0500	0.00579	0.1158
0.0100	0.00122	0.1224
0.00200	0.000252	0.1263
0.00100	0.000127	0.1273
0.000200	0.0000256	0.1288
0.000100	0.0000129	0.1290
0.0000100	0.00000130	0.1300

It will be seen from the above table that the specific conductance is proportional to the concentration only at very low concentrations. Thus, if we have a solution which contains 1 gram molecule of sodium chloride in 1 litre, and this is diluted to 2 litres, we would expect the specific conductance to fall from 0.0983 to 0.0491, since there are presumably only half as many ions per cubic centimetre. Actually the specific conductance is found to be greater than this, viz., 0.0512. Presumably then there are more ions in 2 litres of the dilute solution than in 1 litre of the concentrated solution. This was explained by assuming that the dissociation of sodium chloride into ions is not complete, i.e., that an equilibrium exists:

$$\text{NaCl} \rightleftarrows \text{Na}^+ + \text{Cl}^+.^*$$

The equilibrium is presumably shifted from left to right on diluting the solution.

Suppose that α_x represents the fraction of an electrolyte which is dissociated when the concentration is x. Then 1 gram

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* The discrepancy could also be explained on the assumption that the number of ions does not vary, but that the mobilities vary with the concentration. As we shall see later this latter explanation is the true one in many cases. However, it is convenient for our purpose to develop the argument in its historical order.

molecule of the solute will give rise to $2N\alpha_x$ ions in the case of a binary electrolyte, where N represents the number of molecules of solute in 1 equivalent weight before dissociation into ions occurred, and is of course a constant which is independent of the nature of the electrolyte. The number of ions per cubic centimetre of solution will then be $\frac{2N\alpha_x}{V}$, where V is the number of cubic centimetres which contain 1 equivalent of the solute. Hence, if c_x is the specific conductance at concentration x, we have

$$c_x = \text{constant}\cdot\frac{2N\alpha_x}{V}(u + v).$$

Or

$$c_x V = \text{constant}\cdot 2N\alpha_x (u + v).$$

The product $c_x V$, i.e., the specific conductance multiplied by the volume in cubic centimetres which contains 1 gram molecule, is usually called the equivalent conductance. If we denote this by λ_x we have

$$\lambda_x = K\alpha_x(u + v),$$

where K is a constant.

In the table below the equivalent conductances are given in the second column for sodium chloride solutions of various concentrations.

SODIUM CHLORIDE SOLUTIONS AT 18° C.

Concentration, Gram Molecules per Litre	Equivalent Conductance (λ)	α from Conductivity Measurements	α from the Lowering of the Freezing Point
1.000	74.31	0.682	
0.500	80.9	0.773	0.824
0.200	87.7	0.818	0.850
0.100	92.0	0.852	0.875
0.0500	95.7	0.882	0.892
0.0200	99.6	0.916	0.922
0.0100	101.9	0.936	0.938
0.00500	103.7	0.953	0.953
0.00100	106.4	0.977	
0.000500	107.1	0.984	
0.000100	108.0	0.992	
0.000000	108.9	1.000	1.000

It will be seen that the equivalent conductance increases with increasing dilution, and finally reaches a maximum value in very dilute solutions; this maximum value is for convenience called the equivalent conductance at infinite dilution, and may be denoted by λ_∞.

According to the relationship given above, this increase in equivalent conductance with dilution must mean that α increases as the solution becomes more dilute, and finally reaches a maximum value. In other words, it may be assumed that the amount of dissociation into ions increases with dilution until finally complete dissociation occurs. Complete dissociation means that $\alpha = 1$. Hence we have

$$\lambda_\infty = K(u + v).$$

Whence

$$\frac{\lambda_x}{\lambda_\infty} = \frac{K\alpha_x(u + v)}{K(u + v)} = \alpha_x.$$

We can thus calculate α_x if we know the equivalent conductance at infinite dilution and at concentration x. These values are given in the third column of the above table.

We have seen previously that in the case of a binary electrolyte* the molecular weight, calculated from the lowering of the freezing point and extrapolated to infinite dilution, is exactly one-half the theoretical molecular weight. The values obtained at higher concentrations lie between the theoretical value and one-half the theoretical value, the divergence from the latter being much greater than the expected aberrations from the laws of ideal solutions. This is in accord with the results of equivalent conductance measurements, and a quantitative comparison of the two is possible. Since the observed molecular weight is inversely proportional to the number of particles in the solution, we have

$$\text{Observed molecular weight} = M_0 = \frac{K}{(1 - \alpha)N + 2\alpha N},$$

$$= \frac{K}{(1 + \alpha)N},$$

since $(1 - \alpha)N$ particles are left undissociated, and $2\alpha N$ ions are

---

* A binary electrolyte is one in which each molecule gives two ions on dissociation, for example, NaCl.

formed. The theoretical molecular weight, M_T, is inversely proportional to the number of undissociated molecules, i.e.,

$$M_T = \frac{K}{N}.$$

Whence

$$\alpha = \frac{M_T - M_0}{M_0}.$$

The fourth column in the above table gives values of α calculated from measurements of the lowering of the freezing point in this way. The agreement with the values of α calculated from conductivity measurements is excellent except at high concentrations, where appreciable deviations occur.

It seems to be established, therefore, that an equilibrium exists between an undissociated electrolyte and its ions, the amount of dissociation increasing as the solution is diluted. There is good agreement between the results of conductivity and osmotic pressure determinations, except at high concentrations. The reason for the discrepancies with concentrated solutions will be discussed later.

We have seen that $$\lambda_\infty = K(u + v).$$

This may be written $$\lambda_\infty = Ku + Kv.$$

The value of u or v is constant for any particular ion, independent of the salt from which it was formed. Hence, by measuring λ_∞ for a number of salts having common ions, the Ku and Kv values of each can be estimated, provided that we know the relative values of u and v for any one pair of ions. The Ku or Kv value is known as the equivalent conductance at infinite dilution of the ion concerned. These values can be used additively to give the equivalent conductance at infinite dilution of any solute, since each ion contributes its share to the conductivity independently. The following table gives the values of Ku or Kv for some typical ions at 18° C.

EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

H^+	315.0	OH^-	174.0
K^+	64.6	NO_3^-	61.7
Na^+	43.5	ClO_3^-	55.0
Ag^+	54.3	Cl^-	65.5

As an example, we may calculate the equivalent conductance of silver nitrate at infinite dilution:

$$\begin{aligned} AgNO_3 &= Ag^+ + NO_3^- \\ &= 54.3 + 61.7 \\ &= 116.0 \end{aligned}$$

This type of calculation has given results which are in excellent agreement with experiment. It should be emphasized that conductivities can be calculated in this way only for infinite dilution. This furnishes a further confirmation of the hypothesis of complete dissociation at infinite dilution. The above relationship is of considerable importance, because with weakly dissociated electrolytes complete dissociation occurs at concentrations which are far too low to be investigated experimentally. The values of the equivalent conductance at infinite dilution for such electrolytes can, however, be calculated in the manner illustrated above.

Ostwald's Dilution Law.—It was pointed out by Ostwald that the increase in dissociation with increasing dilution follows immediately, if we assume that there is an equilibrium between undissociated molecules and ions to which the law of mass action can be applied.

Suppose that 1 gram molecule of a binary electrolyte MX is dissolved in V litres of solution. Let α be the fraction dissociated into ions. Then we have

$$MX \rightleftarrows M^+ + X^-.$$

Hence, from the law of mass action

$$\frac{[MX]}{[X^-][M^+]} = K.$$

But

$$[MX] = \frac{1 - \alpha}{V}$$

and

$$[X^-] = [M^+] = \frac{\alpha}{V}.$$

Whence by substitution

$$\frac{(1-\alpha)V}{\alpha^2}=K_1,$$

or, as it is usually written,

$$\frac{\alpha^2}{(1-\alpha)V}=K.$$

This is known as Ostwald's dilution law.

From this relationship it obviously follows that with increasing dilution, i.e., an increase in V, α increases. Also when $V=\infty$, $\alpha=1$.

By substituting for α the values calculated from equivalent conductances or freezing-point lowerings, the value of the dissociation constant K in the above equation can be calculated at various dilutions. The following table for acetic acid solutions shows a satisfactory constancy of K.

Acetic Acid Solution at 25° C.

Volume in Litres Containing 1 Gram Molecule	α Calculated from Equivalent Conductances	K
0.99	0.0037	14.1×10^{-6}
1.98	0.0057	16.5
3.95	0.0083	17.6
7.91	0.0119	18.1
15.8	0.0169	18.4
31.6	0.0238	18.5
63.3	0.0336	18.5
126.5	0.0472	18.5
253.0	0.0660	18.4
506.0	0.092	18.4
1012.0	0.128	18.4
2024.0	0.176	18.5
∞	(1.000)	

In the case of sodium chloride, K is by no means constant, and varies greatly at the higher concentrations as shown on page 336.

Aberrations from Ostwald's Dilution Law.—In the preceding section it was shown that the general trend of the variation of conductivity with dilution is a logical consequence of the assumption that an equilibrium exists between the undissociated molecules of an electrolyte and its ions. The question now arises why, in the case of acetic acid, there is an excellent quantitative agreement between theory and experiment, except at high concentrations, whereas with sodium chloride solutions there is no such agreement at any dilution. If we consider tenth molal solutions of these two substances, the equivalent conductance shows that acetic acid is dissociated only to the extent of 1.35 per cent, whereas sodium chloride is 85.2 per cent dissociated. In other words, acetic acid is far less dissociated than sodium chloride at corresponding concentrations. Electrolytes may be roughly divided into two classes. Those like acetic acid, which are only slightly dissociated at ordinary concentrations, are called "weak" electrolytes; substances like sodium chloride, which are highly dissociated under such conditions, are called "strong" electrolytes. Experiments with a large number of substances have shown that weak electrolytes conform closely to Ostwald's dilution law except at high concentrations. All strong electrolytes, on the other hand, show very large discrepancies.

SODIUM CHLORIDE SOLUTIONS AT 18° C.

Volume in Litres Containing 1 Gram Molecule	α Calculated from Equivalent Conductances	K
1	0.741	2.120
2	0.777	1.353
5	0.818	0.735
10	0.852	0.491
20	0.882	0.330
50	0.916	0.200
100	0.936	0.137
200	0.953	0.0967
500	0.969	0.0606
1000	0.977	0.0415
∞	(1.000)	

The next question for consideration is the reason for the inapplicability of Ostwald's dilution law to strong electrolytes.

Ostwald's dilution law is based on the application of the law of mass action to the process of dissociation. The law of mass action, in turn, is based on the assumption of a purely chaotic distribution of the structural units of the reactants, and of purely chance collisions between them. These assumptions are true enough when the forces of molecular attraction come into play only at the time of collision. Ions, however, owing to their electric charges, repel or attract one another with a force which falls off comparatively slowly (as the square of the distance between the ions), and the electric forces are thus effective over relatively large distances. There will therefore be a tendency for negative ions to gather round a positive ion and *vice versa*. As a result the solution will contain a somewhat ordered arrangement of ions rather than a purely chaotic distribution. The larger the number of ions per unit volume, the closer will they be to one another, and hence the greater will be the extent to which such an ordered arrangement occurs. The effect will thus be much greater with strong electrolytes than with weak at the same concentration, since the strong electrolytes contain more ions. In the case of very weak electrolytes, the distances between the ions may be so large that the electric forces come into play over only a very small amount of the distance which the ion travels between collisions. The postulate upon which the mass law is based is invalid in the case of strong electrolytes, and in consequence Ostwald's dilution law is inapplicable.

The Debye-Hückel Theory.—Various attempts have been made to obtain a modified mass law expression of the Ostwald dilution law type for strong electrolytes, but all of these have been strikingly unsuccessful. There now appears to be no doubt that for *weak* electrolytes the basic postulates of the Arrhenius theory are sound, and that the Ostwald dilution law is a close approximation to the truth, especially for dilute solutions. For *strong* electrolytes, however, it is now certain that the idea of an equilibrium between ions and undissociated electrolytes is false, and that strong electrolytes are to be regarded as completely dissociated at virtually all concentrations.

The discrepancy between this point of view and that of Ostwald is not as great as would appear at first sight. When two ions approach one another, it is difficult to say at what moment they are to be considered to have combined to form an undissociated molecule, unless actual neutralisation of their charges occurs. The modern theory of the structure of the atom indicates that this neutralisation of charge does not necessarily occur at all, since it appears that even in the pure solid state a substance such as sodium chloride consists of charged atoms which are held together by electrical forces.

The most successful attempt to describe the properties of strong electrolytes is that of Debye and Hückel. They start from the premise that strong electrolytes are completely dissociated at all concentrations. If this is so, then there are two main facts for which the theory must provide an explanation. (*a*) If the number of ions in the solution is directly proportional to the concentration, how is it that the osmotic pressure decreases with dilution more slowly than would be expected from the decrease in concentration? (*b*) If the number of ions in the solution is directly proportional to the concentration, how is it that the equivalent conductance increases with dilution?

Debye and Hückel answer the first question as follows. It is possible to account thermodynamically for the colligative properties of solutions of non-electrolytes, such as the freezing-point lowering, osmotic pressure, etc., by considering the work which must be done in transferring a solute molecule from a solution which is infinitely dilute to the given solution. We may call this the "osmotic work." Now with strong electrolytes we may similarly calculate the osmotic work required to transfer an ion from an infinitely dilute solution to the given solution. Actually, however, when an ion is introduced into the given solution there will be a tendency for ions of opposite sign to collect around the given ion on account of electrostatic forces. Of course this "atmosphere" is a dynamic one. Ions of both signs come and go, but on the average there will be a tendency for ions of opposite sign to congregate around the given ion. As a result of the presence of the ionic atmosphere, when an ion is transferred from an infinitely dilute solution to the given solution, work will have to be done against electrical forces. As a result the total work done is the sum of the osmotic and the electrical work.

Debye and Hückel calculate the electrical work done in bringing up the ion. When this is added as a correction to the ordinary osmotic work, results are obtained for the osmotic pressure as a function of the concentration which are in excellent agreement with experiment for solutions up to about 0.01 *M* in concentration. For still more concentrated solutions aberrations occur, as a result of approximations in the treatment which are no longer valid with concentrated solutions. However, in principle the problem may be regarded as solved, and the first of the above two questions is therefore satisfactorily answered.

It remains to explain the variation of the equivalent conductance of solutions of strong electrolytes with concentration. It was pointed out before that there are two alternative possibilities: (*a*) It is assumed that the number of ions varies, while the mobilities remain constant. This was the classical explanation, but as we have seen above it cannot now be maintained for strong electrolytes, although it is true for weak electrolytes. (*b*) It is assumed that the number of ions remains constant, but that the mobilities vary with concentration. This is now the accepted explanation for strong electrolytes.

As pointed out above, an ion in solution is surrounded by an atmosphere of ions of opposite sign, and this atmosphere is dynamic in nature. Now suppose that electrodes are placed in the solution and a potential is applied. Let the given ion be a positive one. Then it will start to move towards the negative electrode. As it moves under the action of the applied electromotive force it will leave behind it the negative ions which constituted its atmosphere, and other negative ions will take their place. Hence the actual ions constituting the atmosphere will be continually changing. Now a certain time will be required for the replacement of ions lost from the atmosphere, and hence the ionic atmosphere will lag behind the ion as it moves along, as shown by Fig. 95. When the positive ion is surrounded by a spherically symmetrical atmosphere of negative ions, the centre of gravity of the negative atmosphere coincides exactly with the position of the ion, and hence the ion is in no way affected by the atmosphere in so far as its motion is concerned. When, however, the atmosphere lags behind, the centre of gravity of the atmosphere is now at A, which no longer coincides with the position of the ion itself. The result is as if all the negative ions in the atmosphere were concentrated at A. Hence the given positive ion is attracted towards A by the atmosphere, and this attraction partially offsets the action of the applied E.M.F. Hence the mobility of the ion is diminished by the presence of the ion atmosphere. As the solution becomes more dilute, the effect of the ionic atmosphere diminishes, and hence the mobility of the ion increases with increasing dilution. This is the explanation of the increase in the equivalent conductance of solutions of strong electrolytes with increasing dilution.

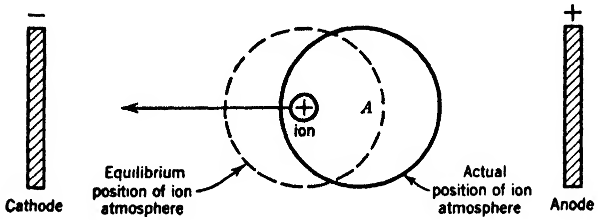

FIG. 95.

Non-Aqueous Solutions.—It has been found that when an electrolyte is dissolved in solvents other than water, an electrically conducting solution is obtained, electrolysis takes place, and all the phenomena due to electrolytic dissociation are evidenced. There is, however, a wide variation in the electrical conductivity of solutions of the same electrolyte in different solvents. The conductivity of a solution depends on the mobility of the ions and upon the extent to which the solute is dissociated. Various factors tend to show that the latter factor is by far the more important in governing the magnitude of the conductivity. We can therefore use the conductivity as a qualitative indication of the extent to which an electrolyte is dissociated in various solvents. The following table gives a qualitative idea of the extent of dissociation of electrolytes in various solvents. In the last column the dielectric constants of the solvents at 0° C. are tabulated. These are found to increase as the dissociating power of the solvent increases.

Solvent	Dissociation of Dissolved Salts	Dielectric Constant
Benzene	almost nil	2.3
Ether	distinctly measurable	4.68
Alcohol	fairly strong	28.4
Formic acid	strong	59.5
Water	very strong	88.0
Hydrogen peroxide	very strong	95.0
Hydrogen cyanide	very strong	96.0

The relation between the dielectric constant and the dissociating power of the solvent throws considerable light upon the mechanism of dissociation. The extent to which a weak electrolyte MX is dissociated depends upon the relative rates of the two opposing reactions

$$\mathrm{MX} \rightleftarrows \mathrm{M}^+ + \mathrm{X}^-.$$

The reaction in which the ions recombine is governed by the forces between them. If these are electrical in nature, they will be given by Coulomb's law, viz.:

$$F = \frac{e_1e_2}{Dr^2},$$

where e_1 and e_2 are the charges on the ions, r is the distance between them, and D is the dielectric constant of the medium. It follows that the force tending to cause the recombination of the ions varies inversely as the dielectric constant.

Suppose that we compare solutions of an electrolyte in benzene and in water. The force tending to cause recombination of the ions is about 35 times stronger in benzene than in water. The amount of dissociation will therefore be much greater in water than it is in benzene.

Other factors come into play, such as the solvation of the ions, etc., and in consequence there is no exact relationship between the dielectric constant and the dissociating power of a solvent. The dielectric constant is, however, the major factor in determining the extent to which an electrolyte is dissociated in a solvent.

QUESTIONS AND PROBLEMS

1. Write out in full the equations representing the total electrolysis of a solution of cupric chloride: (*a*) with platinum electrodes; (*b*) with copper electrodes; (*c*) with zinc electrodes.

2. Write out the equations representing the total electrolysis when a current is sent through a solution of cupric bromide: (*a*) with a copper anode and a platinum cathode; (*b*) with a copper cathode and a platinum anode.

3. Calculate the amount of copper deposited from a solution of copper sulphate by a current of 1.2 amperes flowing for 5 minutes. *Ans.* 0.1184 gram.

4. Ten grams of silver are deposited when a current flows through a solution of a silver salt for 4 hours. Find the strength of the current. *Ans.* 0.6224 amp.

5. Sixteen equivalents of a binary electrolyte MX are placed in each of the compartments of an apparatus similar to that illustrated in Figs. 88 to 90. The transport number of the anion is twice that of the cation. Six faradays are sent through the system. Summarise the concentration changes which occur in the manner given on pages 322 to 325.

6. The specific conductivity of a 0.1 molar solution of a salt is 0.00920. Calculate the equivalent conductance and the amount of dissociation, given that the equivalent conductance is 108.9 at infinite dilution. *Ans.* 92.0, 84.5 per cent.

7. The lowering of the freezing point of a 0.2 molar solution of a salt is 0.691° C. Calculate the extent to which it is dissociated at this concentration. The density of the solution is 0.990. *Ans.* $\alpha = 0.817$.

8. One gram of sodium nitrate is dissolved in 10,000 litres of water. Assuming complete dissociation, calculate the specific conductivity of the solution from the data given in the table of equivalent conductances at infinite dilution on page 333. *Ans.* 1.24×10^{-7}.

9. The Ostwald dilution law constant for ammonia solutions is 17×10^{-6}. Calculate the amount of dissociation in a 0.1 *M* solution of ammonia. *Ans.* $\alpha = 0.0130$.

10. The equivalent conductance at infinite dilution of the ammonium ion is 64.3. That of the hydroxyl ion is 174.0. Calculate the specific conductivity of the solution mentioned in question 9. *Ans.* 3.10×10^{-4}.

11. Calculate the lowering of the freezing point of the solution given in questions 9 and 10, assuming the density of a 0.1 *M* solution of ammonia to be 1.00. *Ans.* 0.189° C.

12. A 0.01 *M* solution of a monobasic organic acid is found to be 5 per cent dissociated into ions. Calculate the Ostwald dilution law constant. *Ans.* 2.63×10^{-5}.

13. Calculate the amount of dissociation in a 0.1 *M* solution of the acid referred to in question 12. *Ans.* 1.61 per cent.

14. From the data given in question 6 calculate the Ostwald dilution law constant for a 0.1 *M* solution of the salt. *Ans.* 0.4606.

15. Describe the experimental evidence for electrolytic dissociation.

16. Show that the theory of electrolytic dissociation offers an explanation of the conductivity of solutions, and of anomalous osmotic phenomena.

17. Define electrolysis, and give examples.

18. State Faraday's laws of electrolysis, and describe the experimental evidence on which they are based.

19. Show that the charge on an ion divided by its valence is a constant.

20. Show how conduction occurs in a solution when the anion and the cation have different mobilities.

21. Describe experimental methods of measuring ionic mobilities.

22. Discuss the evidence for the hydration of ions.

23. Discuss the measurement of the conductivities of solutions.

24. Derive an expression for the conductance of a solution as a function of the number of ions and their mobilities.

25. Discuss the relationship between conductance and concentration.

26. Show how the molecular weight of an electrolyte, as determined by the lowering of the freezing point, may be used to determine the amount of dissociation.

27. Discuss aberrations from Ostwald's dilution law, and the reasons for such aberrations.

28. Discuss the evidence for the complete dissociation of strong electrolytes, and the Debye-Hückel theory.

29. Derive Ostwald's dilution law.

30. On the basis of the Debye-Hückel theory, explain the variation of the equivalent conductance of strong electrolytes with concentration.

31. Discuss non-aqueous solutions of electrolytes, and the influence of the dielectric constant of the solvent on the amount of dissociation.

CHAPTER XVII

APPLICATIONS OF THE IONIC HYPOTHESIS

The Electrolytic Dissociation of Water.—The specific conductance of even the best-conducting electrolyte solutions is far less than that of ordinary metals. Thus a 15 per cent solution of sulphuric acid has a specific conductance of 0.54 compared to 6×10^5 for copper. As such a solution is diluted, its conductivity decreases and becomes extremely small in very dilute solutions, but never actually reaches zero.

Ordinary tap water has a specific conductance of about 10^{-4}, while water distilled in an ordinary still has a value of about 10^{-5}. The difference between the two values is due to the presence of electrolytes in tap water, which are removed by distillation. The apparatus in which a distillation is carried out is generally made of material which is somewhat soluble in water. Thus freshly distilled water, which is stored in a glass container, is found to have a conductivity which slowly increases with time by reason of the solution of the glass. Furthermore, the distillation of water does not remove volatile impurities such as carbon dioxide and ammonia, which in solution give rise to ions. It may be inferred therefore that most, if not all, the conductivity of ordinary water is due to the presence of dissolved electrolytes.

An investigation was carried out by Kohlrausch to determine the extent to which water could be purified in relation to its conductivity. The water was first treated chemically to remove volatile impurities, and was then subjected to an elaborate fractional distillation in vacuo in a platinum apparatus. In this way he obtained a product with a specific conductance of 0.040×10^{-6} at 18° C. At first sight it might appear that this small residual conductivity was due to the presence of dissolved impurities. However, the fact that virtually the same end value was reached in every case, even under altered conditions of purification, leads to the conclusion that there is a limiting conductivity which can be assigned to an inherent conducting power of pure water. The final estimate made by Kohlrausch was that the specific conductance of pure water is about 0.036×10^{-6} at 18° C. and 0.054×10^{-6} at 25° C.

That this residual conductivity is ionic in nature is shown by the fact that it is necessary to use an alternating current in its measurement. If a direct current is used, inconsistent results are obtained, presumably on account of the deposition of electrolytic decomposition products on the electrodes. If no impurities are present, the ions which conduct the current must be derived from water itself. The only possible ions are H^+, OH^-, and $O^=$. The latter ion, however, is never found in aqueous solutions, whereas the two former are very common. It may therefore be assumed that the dissociation of water can be represented as

$$H_2O \rightleftarrows H^+ + OH^-.$$

Further confirmation of this representation will be given in the succeeding sections.

Since the specific conductance is given by the expression

$$C = Kn(u + v)$$

it is possible to estimate the number of ions in unit volume of the solution, provided that the mobilities of the ions are known. The number of ions in the solution is most conveniently expressed in terms of gram equivalents per litre. In this way it may be calculated that at 25° C. we have

$$[H^+] = [OH^-] = 1.1 \times 10^{-7}$$

gram equivalents per litre. From the law of mass action we have

$$[H^+]\,[OH^-] = K[H_2O].$$

The concentration of the water is not appreciably altered by the very small amount of dissociation, and hence may be taken as constant. We therefore have

$$\begin{aligned}[H^+]\,[OH^-] &= K = (1.1 \times 10^{-7})^2 \\ &= \text{approximately } 10^{-14}.\end{aligned}$$

This relationship is of great importance, because it follows that in the presence of water the product of the concentrations of the hydrogen and hydroxyl ions must always be constant, and independent of the presence of other ions, provided that the concentration of any other solute is not great enough to alter the concentration of the water to an appreciable extent.

It has been found that all acids form hydrogen ions when dissolved in water, and all bases form hydroxyl ions. Hydrochloric acid in a tenth normal solution is almost completely dissociated, and hence

$$[H^+] = 10^{-1}.$$

Since the hydrogen ions formed from the water are negligible compared to this, we may say that the total hydrogen-ion concentration of the solution is 10^{-1}. It follows that in the above solution the hydroxyl-ion concentration is given by

$$[OH^-]\,(10^{-1}) = 10^{-14},$$

whence

$$[OH^-] = 10^{-13}.$$

In an acid solution, therefore, there are still hydroxyl ions present. Their concentration, however, is far less than that of the hydroxyl ions in pure water. Similarly, in an alkaline solution, hydrogen ions are still present, but hydroxyl ions predominate. This makes possible an exact definition of acidity and alkalinity in aqueous solutions. An acid solution is one in which $[H^+]$ is greater than $[OH^-]$; an alkaline solution is one in which $[H^+]$ is less than $[OH^-]$; and in a neutral solution $[H^+] = [OH^-]$.

A special nomenclature has come into use in connection with the hydrogen-ion concentration, or acidity, of solutions. It is always possible to express the hydrogen-ion concentration of a solution in terms of 10 raised to some power, i.e., as

$$[H^+] = 10^x.$$

This index with its sign changed, i.e., $-x$ in the above example, is called the *p*H of the solution. For example, suppose that we have at 25° C. a 0.002 normal solution of some acid which is completely dissociated. Then

$$[\mathrm{H}^+] = 0.002 \text{ gram equivalents per litre,}$$

$$= 10^{-2.7} \text{ gram equivalents per litre;}$$

the *p*H of the solution is therefore 2.7.*

In a neutral solution $[\mathrm{H}^+] = [\mathrm{OH}^-] = 10^{-7}$ at 25° C. The *p*H of a neutral solution at this temperature is therefore 7. In an acid solution $[\mathrm{H}^+]$ is greater than 10^{-7}, and hence the *p*H will be *less* than 7. In an alkaline solution $[\mathrm{H}^+]$ is less than 10^{-7}, and the *p*H is therefore *greater* than 7. As an example consider a one-hundredth normal solution of a base which is completely dissociated. Then $[\mathrm{OH}^-] = 0.01 = 10^{-2}$. $[\mathrm{H}^+]$ is therefore 10^{-12}, and hence the *p*H of the solution is 12.

Further evidence for the dissociation of water will be given in the following sections. Other methods of calculating the extent to which water is dissociated are known, and these give results which are in substantial agreement with those given above.

Acids and Bases.—It has long been possible to classify certain substances as acids or bases, on account of a number of properties which are common to all members of each class. It has been customary to grade acids or bases according to their "strength," i.e., their ability to liberate other acids or bases from their salts. Thus sulphuric acid is said to be a very strong acid, since we have the reaction

$$\mathrm{H_2SO_4} + 2\mathrm{NaCl} \rightarrow 2\mathrm{HCl} + \mathrm{Na_2SO_4}.$$

The hydrogen chloride can be driven off, and liberated completely from its salts.

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* Suppose that $[\mathrm{H}^+] = 10^{x}$.

Then $\log\,[\mathrm{H}^+] = x$

$-\log\,[\mathrm{H}^+] = -x =$ the *p*H of the solution.

It follows that the *p*H of a solution may be calculated by taking the logarithm of the hydrogen-ion concentration and changing its sign.

It has already been emphasized, however, that a reaction such as the above does not really go to completion in a closed system, but an equilibrium will be reached so that

$$\frac{[H_2SO_4]\,[NaCl]^2}{[HCl]^2\,[Na_2SO_4]} = K.$$

If the reaction is carried out in an open vessel, hydrogen chloride is completely driven off because it is the only volatile reactant, and as it is removed the reaction continually goes from left to right. The apparent strength of sulphuric acid is therefore due in part to its low volatility, and there is no justification for the use of a reaction in which one of the participants can escape as a measure of the "chemical driving force," or strength, of an acid. This was realized after the discovery of the law of mass action and its theoretical basis. The definition of the strengths of acids was therefore modified to the following: When equivalent amounts of one acid and a neutral salt of another are brought together in aqueous solution, the relative strengths of the two are given by the inverse ratio of their concentrations at equilibrium. For example, if equivalent amounts of hydrochloric acid and sodium acetate are brought together in a closed system we have

$$HCl + Na \cdot C_2H_3O_2 \rightleftarrows NaCl + H \cdot C_2H_3O_2.$$

The relative strengths of the two acids are given by

$$\frac{\text{strength of HCl}}{\text{strength of } H \cdot C_2H_3O_2} = \frac{[H \cdot C_2H_3O_2]}{[HCl]}.$$

At equilibrium $[H \cdot C_2H_3O_2]$ is very much greater than $[HCl]$, and hence hydrochloric acid is said to be much stronger than acetic acid.

With the development of the theory of electrolytic dissociation, it was soon realized that the fundamental property of an acid is its ability to dissociate in aqueous solution so as to give a larger concentration of hydrogen ions than that which exists in pure water at the same temperature. It is obvious that there must therefore be some connection between the strengths of acids and their ability to form hydrogen ions in solution. It is possible to show from the law of mass action that a base will distribute itself between two acids which are competing for it in a manner which depends on the extent to which the acids are dissociated into ions. This leads to the conclusion that the strength of an acid is proportional to the extent to which it is ionized.

The quantitative derivation of this relationship from the law of mass action is complicated, and is of necessity only approximate, since the mass law can be applied accurately only to dilute solutions of weak electrolytes. It is possible, however, to give a qualitative indication of the manner in which the strength of an acid is dependent on the ease with which it ionizes. Suppose that we consider the ions derived from a molecule of hydrochloric acid, and those from a molecule of sodium acetate, to be brought into juxtaposition as indicated in Fig. 96. If the force by which the hydrogen ion is attracted to the acetate ion is greater than that with which it is attracted to the chloride ion, then the reaction may be written

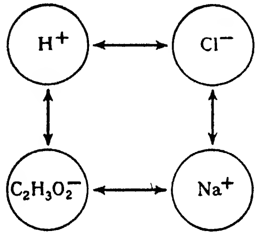

FIG. 96.

$$H^+ + Cl^- + C_2H_3O_2^- + Na^+ \rightarrow HC_2H_3O_2 + Na^+ + Cl^-.$$

There is therefore a greater tendency to recombine to form undissociated acetic acid than there is to recombine to form undissociated hydrochloric acid, as represented by

$$H^+ + Cl^- + C_2H_3O_2^- + Na^+ \rightarrow HCl + C_2H_3O_2^- + Na^+.$$

The relative strengths of the two acids are therefore dependent on the tendency of their ions to recombine, i.e., on the extents to which they are dissociated into ions.

The electrolytic dissociation, or conductivity, is thus a measure of the strengths of acids. If we call hydrochloric acid the standard, with a strength of 100, the strengths of other acids have been found to have the values given below.

Acid	Strength by Physicochemical Methods	Strength by Conductivity Methods
Hydrochloric	100.0	100.0
Oxalic	17.0	20.0
Orthophosphoric	6.0	7.3
Monochloracetic	4.5	4.9
Tartaric	2.3	2.3
Acetic	0.35	0.4

The second column in the above table gives the strengths of the acids as determined from the measurement of the equilibrium concentrations when they are competing for a base. The last column gives the relative extents to which the acids are dissociated in solution. It will be seen that there is a good general agreement throughout, though not an exact quantitative one. The values given above are for normal solutions of the acids concerned. It is obvious that these values, but not their sequence, will alter with dilution. Since the dissociation of all the weak acids increases with dilution, their strengths will become more nearly equal to that of the strong acids; and at infinite dilution, where they are all completely dissociated, they will all be equally strong.

The properties of bases are dependent upon the formation of hydroxyl ions, and the relative strengths of bases are dependent upon the extent to which they are dissociated to form such ions. The relative strengths of some common bases are given below.

Base	Strength Relative to Lithium Hydroxide as 100
Lithium hydroxide	100
Tetraethylammonium hydroxide	75
Triethylammonium hydroxide	14
Ammonia	2

The Hydrolysis of Salts.—According to the definition previously given, an aqueous solution is acidic, neutral, or basic depending on whether $[H^+]$ is greater than, equal to, or less than $[OH^-]$. It would therefore be expected that a solution of a neutral salt, which yields neither hydrogen nor hydroxyl ions, would be neutral. Experiment shows, however, that when such salts are dissolved in water the ratio $[H^+]/[OH^-]$ is altered. Thus a solution of Na_2CO_3 is alkaline, and one of $AlCl_3$ is acid. This furnishes an additional confirmation of the dissociation of water, since in these cases the hydrogen or hydroxyl ions which cause acidity or basicity can have been derived only from the solvent.

Consider, for example, a solution of sodium acetate. When this is dissolved, sodium and acetate ions are formed. Since hydrogen and hydroxyl ions derived from the water are also present, the formation of sodium hydroxide and acetic acid is possible. The complete behaviour of such a system can therefore be represented qualitatively as follows:

$$\begin{array}{ccccc}
Na\cdot C_2H_3O_2 & \rightleftarrows & Na^+ & + & C_2H_3O_2^- \\
 & & + & & + \\
H_2O & \rightleftarrows & OH^- & + & H^+ \\
 & & \downarrow\uparrow & & \downarrow\uparrow \\
 & & NaOH & & H\cdot C_2H_3O_2.
\end{array}$$

At the start $[Na^+]$ must be equal to $[C_2H_3O_2^-]$, and $[OH^-]$ must be equal to $[H^+]$. If, however, the products NaOH and $H\cdot C_2H_3O_2$ are not dissociated to the same extent, the above equalities must be upset before equilibrium can be reached. In the present example $H\cdot C_2H_3O_2$ is only very slightly dissociated, while NaOH is completely dissociated, so that hydrogen ions are removed from the solution to form undissociated products while the hydroxyl ions remain. The relationship

$$[H^+]\,[OH^-] = K$$

must be maintained, however, and consequently more water must dissociate, and $[OH^-]$ must be increased sufficiently to offset the decrease in $[H^+]$. The solution is therefore alkaline, since $[OH^-]$ is greater than $[H^+]$. If, as in this case, the resulting acid is only very slightly dissociated, practically all its ions will combine with hydrogen ions to form undissociated acid. The process may therefore be represented as

$$Na^+ + C_2H_3O_2^- + H^+ + OH^- \rightarrow Na^+ + OH^- + H\cdot C_2H_3O_2.$$

This phenomenon is called hydrolysis.

When we have a salt of a strong base and a weak acid, as in the above example, the solution is always alkaline. With a salt of a strong acid and a weak base, the solution will be acid, for example, $AlCl_3$. When the salt is derived from a weak base and a weak acid, both hydrogen and hydroxyl ions are removed to form practically undissociated products. Thus with ferric acetate we have

$$Fe^{+++} + 3C_2H_3O_2^- + 3H^+ + 3OH^- \rightarrow Fe(OH)_3 + 3H \cdot C_2H_3O_2,$$

the reaction going almost to completion in the direction indicated. With a salt of a strong acid and a strong base, practically no hydrolysis occurs, since both products are practically completely dissociated. Thus in a solution of sodium chloride we have

$$Na^+ + Cl^- + H^+ + OH^- \rightarrow Na^+ + OH^- + H^+ + Cl^-.$$

The Dissociation of Weak Acids and Bases, and Indicators.—For weak acids and bases we have seen that Ostwald's dilution law holds accurately, and it is therefore possible to calculate the $[H^+]$ of a solution of a weak acid or base if the concentration of the solution is known. With acetic acid, for example, we have

$$\frac{\alpha^2}{(1 - \alpha)V} = 1.8 \times 10^{-5}.$$

The dissociation α is small compared to 1, and hence $1 - \alpha$ is approximately equal to unity. We therefore have

$$\alpha^2 = 1.8 \times 10^{-5}\ V.$$

For a tenth normal solution, V is 10, and we have

$$\alpha^2 = 1.8 \times 10^{-4},$$

or

$$\alpha = 1.3 \times 10^{-2}.$$

Whence, since

$$[H^+] = \frac{\alpha}{V},$$

$$[H^+] = \frac{1.3 \times 10^{-2}}{10} = 1.3 \times 10^{-3}.$$

In the case of carbonic acid, the dissociation constant is still less, viz., 3×10^{-8}. Calculation shows that, even in a saturated solution of this acid, the hydrogen-ion concentration is never greater than 10^{-6}.

It has long been known that certain organic dyes change colour reversibly upon the addition of acids or bases, i.e., with change in hydrogen-ion concentration. These substances are useful in indicating changes in the hydrogen-ion concentration of a solution. Two common "indicators" are phenolphthalein and methyl orange, the latter of which changes from red to yellow at a pH of between 4 and 5, and the former from colourless to red at a pH of about 8.

It has been suggested that such substances may be regarded as similar to weak acids or bases. It may be assumed that the undissociated indicator has a different colour from its ions. Thus if we represent methyl orange as MH, we have

$$\underset{\text{Red}}{\mathrm{MH}} \rightleftarrows \underset{\text{Yellow}}{\mathrm{M}^{-}} + \mathrm{H}^{+}.$$

From the law of mass action

$$\frac{[\mathrm{M}^{-}][\mathrm{H}^{+}]}{[\mathrm{MH}]} = K.$$

An increase in $[\mathrm{H}^{+}]$ will shift the equilibrium from right to left, and will therefore cause the red to predominate. An increase in $[\mathrm{OH}^{-}]$ will cause a decrease in $[\mathrm{H}^{+}]$, and hence the equilibrium will be shifted from left to right and yellow will predominate.

Since the constant K for methyl orange is less than that of acetic acid, the presence of acetic acid will cause the predomination of the red colour. On the other hand, since K for carbonic acid is far less than that for methyl orange, its presence or absence will not affect the hydrogen-ion concentration of the solution sufficiently to disturb the colour of methyl orange. It is possible therefore to titrate a solution of acetic acid in the presence of carbonic acid, with methyl orange as indicator.

Phenolphthalein, however, is far less dissociated than methyl orange. Its dissociation constant is therefore much less than that of carbonic acid, and its colour is therefore affected by the presence of hydrogen ions arising from the carbonic acid.

In the above hypothesis it has been assumed that indicators behave like weak acids or bases. In some cases at least this assumption requires modification. It has also been assumed that in certain cases the colour change is due to an internal rearrangement of the indicator molecule. This rearrangement, however, is dependent on the hydrogen-ion concentration of the solution. No very fundamental change in the above reasoning is therefore necessary.

It has been possible to find indicators which will change colour in almost any desired hydrogen-ion concentration range. A series of such substances can therefore be employed to determine the pH of any solution. This method is somewhat simpler than the E.M.F. method, which is described later, but is much less accurate, since indicators do not change colour in an absolutely sharp manner, and the change is spread over a range of hydrogen-ion concentration.

Voltaic Cells.—When a chemical reaction proceeds, heat is given out or absorbed, and if there is a volume change work is done by or against the external forces. We may therefore say that when a chemical reaction proceeds chemical energy is converted into mechanical energy and heat energy. Under appropriate circumstances it is possible to have the chemical energy transformed into electrical energy rather than mechanical or heat energy. Such an arrangement is called a voltaic cell. Thus in the well-known Daniell cell the chemical reaction which occurs is

$$Zn + CuSO_4 = ZnSO_4 + Cu,$$

or, more accurately,

$$Zn + Cu^{++} = Zn^{++} + Cu.$$

A suitable arrangement by means of which electrical energy may be obtained from this reaction consists of a zinc rod dipping into a normal solution of zinc sulphate and a copper rod dipping into a normal solution of copper sulphate, the two solutions being in contact with one another. In practice one solution is placed inside a porous porcelain pot and the other outside; this serves to bring the solutions into contact through the pores of the pot, but prevents too much diffusion of one solution into the other. This system may be conventionally represented as

$$- \mathrm{Zn} \mid N \cdot \mathrm{ZnSO_4} \parallel N \cdot \mathrm{CuSO_4} \mid \mathrm{Cu} +.$$

If now the two electrodes are connected by a wire, zinc is dissolved from the zinc rod to form zinc ions, copper ions deposit on the copper rod forming unionized copper, and positive electricity flows through the cell from left to right, i.e., the zinc electrode becomes negative and the copper electrode positive.

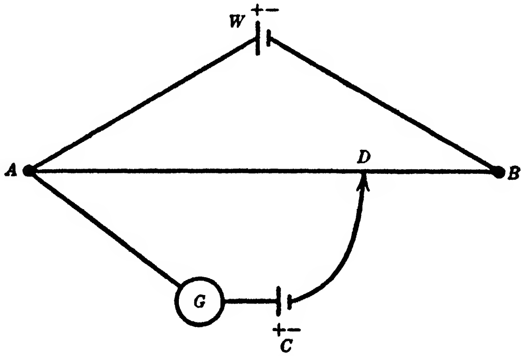

FIG. 97.

The Measurement of the Electromotive Force of a Cell.—When the poles of a cell are joined by a wire, current flows, the amount depending on the resistance in the circuit and the E.M.F. of the cell. The E.M.F. is most conveniently and accurately measured by means of a potentiometer. In this arrangement the potential due to the cell is balanced by a potential applied from another cell, called the working cell. The arrangement is shown diagrammatically in Fig. 97. AB is a wire of uniform resistance. Across the ends of this a potential is applied by the working cell, W. The cell whose E.M.F. is to be determined, C, is connected through a galvanometer, G, to A, and the other side of C is connected to the wire AB by a sliding contact, D. The contact, D, is moved along the wire until the galvanometer indicates that no current is flowing.

When this occurs the fall in potential along the wire from A to D is the same as the fall in potential from A to D through the galvanometer and cell, i.e., it is the same as the potential of the cell. If the potential of the working cell is known, we know the total drop in potential from A to B. Since the wire is of uniform resistance the potential drop from A to D is given by

$$\frac{\text{Potential drop from } A \text{ to } D}{\text{Potential drop from } A \text{ to } B} = \frac{\text{length of wire } AD}{\text{length of wire } AB}.$$

In practice the potential drop from A to B due to the working cell is determined by means of a *standard cell*, the potential of which is very accurately known. This is interposed in place of the cell C, and the position of the contact D is noted: C is then substituted and the position of balance is again noted. We then have

$$\frac{\text{Length of wire with standard cell}}{\text{Length of wire with cell } C} = \frac{\text{potential of standard cell}}{\text{potential of cell } C}.$$

Standard Cells.—Certain cells have been found which have a very accurately reproducible E.M.F., and these are known as standard cells. In general, a standard cell will only maintain a constant and reproducible potential provided that very little current is drawn from it. For this reason the main source of current in a potentiometer is a working cell, usually a storage battery, and the standard cell is interposed only with a high resistance in series, or near the position of exact balance, so that very little current is drawn from it.

The standard cell which is almost always used in potentiometric measurements is the Weston cell. This consists of

−cadmium amalgam	saturated solution of cadmium sulphate in contact with solid cadmium sulphate	saturated solution of mercurous sulphate in contact with sold mercurous sulphate	Hg +.

This cell has a potential of 1.01827 volts at 20° C. It has a very small temperature coefficient, and provided that it is properly made the potential is accurately reproducible to within a few millionths of a volt.

Single Electrode Potentials.—The potential of a cell such as the Daniell cell is made up of three separate parts: (*a*) the potential difference between the zinc electrode and the solution of zinc sulphate; (*b*) the potential difference between the copper electrode and the solution of copper sulphate; (*c*) the potential difference at the point of contact between the zinc sulphate solution and the copper sulphate solution.

The factor (*c*) is usually small compared to (*a*) and (*b*), and for our purposes may be neglected. We may therefore consider the potential of the Daniell cell to be the sum of two *single electrode potentials*, due to

$$\text{Zn} \mid \text{ZnSO}_4 \quad \text{and to} \quad \text{Cu} \mid \text{CuSO}_4.$$

If all single electrode potentials of this type could be determined, it would then be possible to calculate the potentials of all conceivable cells by the mere addition of the single electrode potentials of their component parts.

Actually, however, it is by no means easy to determine the absolute values of such single electrode potentials. Suppose, for example, that a copper rod dips into a normal solution of copper sulphate, and that we wish to determine the potential difference between the copper and the solution, i.e., the single electrode potential $\text{Cu} \mid \text{CuSO}_4$. The obvious way to determine this potential would be to connect the copper to one side of a potentiometer and the solution to the other side. It is easy to connect the copper rod to one terminal of a potentiometer, since if we use a copper wire for the connection we can be sure that there will be no potential produced at the point of contact of the wire and the rod. However, the problem is to make electrical contact between the copper sulphate solution and the other terminal of the potentiometer. Suppose that a copper rod is used to make this contact. We will then have the system

$$\overset{+}{\text{Cu}} \,\Big|\, \overset{-}{\text{CuSO}_4} \,\Big\|\, \overset{-}{\text{CuSO}_4} \,\Big|\, \overset{+}{\text{Cu}},$$

the two $\text{Cu} \mid \text{CuSO}_4$ potentials will cancel one another, and we will have no potential difference across the cell. In other words we are not measuring the single electrode potential of the system Cu | $CuSo_4$, but the algebraic sum of two such single electrode potentials working against one another. Suppose that the attempt is made to avoid this difficulty by using a zinc rod as the other terminal, i.e.,

$$Cu \mid CuSO_4 \mid Zn.$$

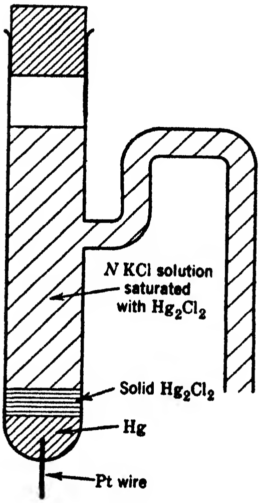

Fig. 98.
Calomel Electrode

Under these circumstances a small amount of zinc will go into solution as Zn^{++}, some copper ions will come out of solution, and deposit on the Zn rod, plating it over with copper, and the system will become

$$Cu \mid CuSO_4 \mid Cu.$$

The resulting E.M.F. will therefore be zero as before.

Actually, by indirect means, it is possible in certain cases to determine single electrode potentials. Once one single electrode potential is known all others can be determined by combining the known electrode system, or half-cell, with another, determining the total E.M.F. of the combination, and finding the unknown single electrode potential by subtraction. One of the two following *standard electrodes* is usually employed for this purpose.

(*a*) *The Normal Calomel Electrode.*—This consists of

Hg | saturated solution of Hg_2Cl_2 in normal KCl, in contact with
solid Hg_2Cl_2

and has been found indirectly to have a potential of 0.5648 volt at 25° C. The form of electrode usually used is shown in Fig. 98.

Actually, however, the value of this potential is not very certain, and, since we are almost always interested only in the sum or difference of *two* single electrode potentials, it has become customary arbitrarily to call the potential of the calomel electrode zero, and to refer all other potentials to it. For example, suppose that it is desired to determine the electrode potential of a metal M in contact with a normal solution of MSO_4, i.e., the potential of the system $M \mid MSO_4$. This electrode is combined with a calomel electrode and the potential of the system

$$\text{normal calomel electrode} \parallel MSO_4 \mid M$$

is measured. This potential will be the single electrode potential of the system $M \mid MSO_4$, referred to the normal calomel electrode as zero.

(*b*) *The Hydrogen Electrode.*—Another standard electrode which is often employed is the hydrogen electrode. This consists of hydrogen at atmospheric pressure in contact with a normal solution of hydrogen ions. We will discuss the form of the electrode in more detail later.

It is found that at 25° C. the E.M.F. of the cell

$$- \ H_2 \mid N \cdot H^+ \parallel \text{normal calomel electrode} \ +,$$

is 0.2805 volt. Hence the potential of the normal hydrogen electrode referred to the normal calomel electrode as zero is -0.2805 volt. Or, the potential of the normal calomel electrode referred to the normal hydrogen electrode as zero is $+0.2805$ volt.

In practice both these standard electrodes are widely used, and all other single electrode potentials are usually referred to one or other of them. The following table gives some typical normal electrode potentials, i.e., those of an electrode in contact with a normal solution of its salt, referred to both the calomel and the hydrogen electrodes as standards. It will be noted that the order in which the elements appear in the table is that of the so-called "electromotive series."

The Mechanism of Electrolysis.—It is now possible to give a more exact discussion of electrolysis. In electrolysis the reaction at the cathode is always a consumption of electrons, i.e.,

$$M^+ + e = M,$$

while at the anode electrons are deposited,

$$X^- = X + e.$$

When there are several different ions of the same sign in the solution, there will be several different possible electrode reac-

NORMAL ELECTRODE POTENTIALS AT 25° C.

Electrode	Potential Referred to the Normal Calomel Electrode, Volts	Potential Referred to the Normal Hydrogen Electrode, Volts
$K \mid K^+$	−3.204	−2.924
$Ca \mid Ca^{++}$	−3.0	−2.7
$Zn \mid Zn^{++}$	−1.038	−0.758
$Fe \mid Fe^{++}$	−0.7207	−0.4402
$Co \mid Co^{++}$	−0.549	−0.268
$Ni \mid Ni^{++}$	−0.511	−0.231
$Sn \mid Sn^{++}$	−0.41	−0.13
$Pb \mid Pb^{++}$	−0.40	−0.12
$H_2 \mid H^+$	−0.2805	0.000
$Cu \mid Cu^{++}$	+0.063	+0.344
$Ag \mid Ag^+$	+0.5173	+0.7978
$Hg \mid Hg^{++}$	+0.620	+0.901
$Br_2 \mid Br^-$	+0.784	+1.064
$Cl_2 \mid Cl^-$	+1.0778	+1.3583
$Au \mid Au^{+++}$	+2.57	+2.85

tions of the above type. Actually, the process which occurs will be that which requires the least energy, i.e., the process which occurs at the lowest potential.

Thus the electrolysis of a solution of sulphuric acid has already been discussed on page 315, in an approximate way. The real mechanism of this reaction is as follows. We have in the solution before the passage of the current

$$H_2SO_4 = 2H^+ + SO_4^{--}$$

$$H_2O = H^+ + OH^-.$$

At the cathode hydrogen ions discharge and hydrogen is given off,

$$2H^+ + e = 2H$$

$$2H = H_2.$$

At the anode there are two possibilities,

$$SO_4^{--} = SO_4 + 2e$$

and

$$OH^- = OH + e.$$

It requires a much lower potential to discharge OH^- than to discharge SO_4^{--}, and hence sulphate ions are not discharged at all. The anode process is therefore

$$OH^- = OH + e$$

$$2OH = H_2O + \tfrac{1}{2}O_2.$$

The complete mechanism of the electrolysis is therefore

$$\begin{aligned}
2H_2O &= 2H^+ + 2OH^- \\
2H^+ + 2e &= 2H \\
2H &= H_2 \\
2OH^- &= 2OH + 2e \\
2OH &= H_2O + \tfrac{1}{2}O_2 \\
\hline
H_2O &= H_2 + \tfrac{1}{2}O_2
\end{aligned}$$

The overall result is thus the same as that given in the previous discussion.

Other cases of electrolysis can be worked out in a similar manner, but since there are a number of complications we will not discuss the matter further.

The Origin of the E.M.F. at Metal-Solution Interfaces.—Nernst has suggested an explanation of the origin of electrode potentials, and his hypothesis has been exceedingly fruitful in stimulating investigations in electrochemistry. The electromotive force is obviously dependent on ions of the substance of which the electrode is made. Some equilibrium must therefore be looked for in which these ions and the electrode both participate. Nernst supposes that in the electrode itself some ions already exist, i.e., in zinc, for example, there are some positively charged zinc atoms at all times. Such an assumption is in agreement with modern ideas of the structure of the atom, and of metallic conduction.

When a metal is immersed in water, the metal atoms are usually almost insoluble. The ions, however, are soluble, since they exist in solution when an electrolyte is dissolved. We can therefore regard the ions in the metal as having a tendency to go into solution. It would therefore be expected that they would dissolve until the saturation concentration of the solution was reached. The ions, however, carry with them a positive charge when they dissolve, and leave the originally neutral electrode with a negative charge. The charge which is thus set up opposes the solution of any further ions. It is therefore increasingly difficult for each successive ion to enter the solution, and an equilibrium E.M.F. is eventually attained, long before the saturation concentration of the solution is reached.

If the concentration of the ions in the solution is increased by the addition of an electrolyte which gives rise to them, the tendency for ions from the electrode to enter the solution will be correspondingly diminished. When the concentration in the solution reaches the "saturation concentration" of the ions contained in the metal, a dynamic equilibrium will result, and the number of ions leaving the metal in unit time will be equal to the number returning to it from the solution. There will now be no resultant tendency for ions from the metal to enter the solution, and hence no charge on either the electrode or the solution. If the ion concentration of the solution is still further increased by the addition of electrolyte, the solution becomes supersaturated as far as the ion-electrode equilibrium is concerned. Ions therefore deposit out on the metal, taking with them their positive charge. The solution becomes negatively charged, since the removal of cations leaves the anions in excess. As before, an electric field is set up which prevents the deposition of many ions, and hence equilibrium with the electrode is not reached. The electrode acquires a greater and greater positive charge as the ion concentration is still further increased.

The Nernst hypothesis thus gives a plausible explanation of the observed facts. It is also possible to derive from it a quantitative relationship between the electromotive force and the ion concentration of the solution. The expression is

$$E = E_0 + \frac{0.0591}{V} \log_{10} C,$$

where E is the E.M.F. in volts at 25° C. between the electrode and a solution of concentration C of an ion of valence V, and E_0 is a constant which depends on the material composing the electrode. This relationship has been found to be in excellent agreement with experimental results.

In order to avoid confusion a convention may be adopted for the *sign of electrode potentials* based on the above discussion. If, in contact with a solution of its own ions, a metal tends to go into solution, thus furnishing positive ions to the solution and becoming negatively charged itself, it will be referred to as the negative electrode. On the other hand, if ions tend to come out on the electrode and impart to it a positive charge, it will be referred to as positive. Thus in the discussion of the Daniell cell in the next section, we will write

$$- \text{Zn} \mid \text{ZnSO}_4 \parallel \text{CuSO}_4 \mid \text{Cu} +.$$

The Mechanism of the Daniell Cell.—As an illustration of the application of the Nernst theory consider the mechanism of the Daniell cell. If we have

$$- \text{Zn} \mid N\cdot\text{ZnSO}_4 \parallel N\cdot\text{CuSO}_4 \mid \text{Cu} +,$$

then according to the Nernst theory the solution in contact with the zinc electrode is highly "unsaturated" with respect to zinc ions, whereas the copper sulphate solution is highly "supersaturated" with respect to copper ions. As a result there is a tendency for zinc to go into solution to form zinc ions, and for copper ions to come out of the solution as metallic copper. The situation is therefore that represented in Fig. 99. If now the two electrodes are connected by a wire, zinc ions will go into solution, copper ions will come out, and a current will flow through the wire.

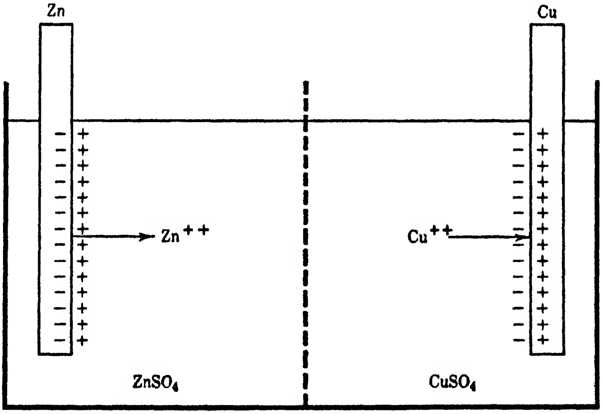

FIG. 99.

Concentration Cells.—Let us consider the cell

$$\mathrm{Cu} \mid \mathrm{Cu}^{++}\ \text{(dilute)} \parallel \mathrm{Cu}^{++}\ \text{(concen.)} \mid \mathrm{Cu}.$$

On the basis of the Nernst theory, it is obvious that the potential of the half-cell, $\mathrm{Cu} \mid \mathrm{Cu}^{++}$ (dilute), will not be the same as that of the half-cell, $\mathrm{Cu} \mid \mathrm{Cu}^{++}$ (concentrated). Hence the above "concentration cell" will possess an E.M.F. owing to the fact that the two solutions are not of the same concentration. The origin of the electrical work which can be derived from such a cell is the tendency of the two solutions of Cu^{++} to become of equal concentration by diffusion.

It is found that in general for cells of this type it is not legitimate to assume that the potential of the cell is merely the algebraic sum of those of the two half-cells, and to neglect the potential difference at the liquid-liquid junction

$$\mathrm{Cu}^{++}\ \text{(dilute)} \mid \mathrm{Cu}^{++}\ \text{(concen.)}.$$

Thus consider a concentration cell containing an electrolyte MA which dissociates to give M^+ and A^- ions, i.e.,

$$\mathrm{M} \mid \mathrm{MA}\ \text{(dilute)} \mid \mathrm{MA}\ \text{(concen.)} \mid \mathrm{M}.$$

Diffusion will tend to make both cations and anions travel from right to left, viz.,

dilute	concentrated
M^+	$\leftarrow \mathrm{M}^+$
A^-	$\leftarrow \mathrm{A}$

The result of the diffusion of cations from right to left will be to leave the right-hand side negatively charged, and to impart a positive charge to the left-hand side. The diffusion of anions from right to left will produce the opposite effect. As a result, if the cations and anions have equal velocities, their effects will compensate, and no potential difference will arise at the liquid-liquid junction. If, however, the cation diffuses faster than the anion, then the effect of the diffusion of cations will outweigh that of the anions, and the right-hand side will become negatively charged and the left-hand side positively charged. In other words, an electrical double layer will be set up at the liquid-liquid junction, i.e.,

$$\begin{array}{cc:cc} \text{dilute} & & & \text{concentrated} \\ & + & - & \\ M^{+} & + & - & M^{+} \\ & + & - & \\ A^{-} & + & - & A^{-} \\ & + & - & \end{array}$$

The potential difference thus produced will tend to prevent further diffusion of cations, and to increase the diffusion of anions, and a steady state will be reached in which we have potential differences at the three junctions,

$$\begin{array}{ccccccc} \text{M} & | & \text{MA (dilute)} & | & \text{MA (concen.)} & | & \text{M.} \\ & E_1 & & E_3 & & E_2 & \end{array}$$

The E.M.F. of the cell as a whole will then be $E_1 - E_2 - E_3$. It follows, therefore, that if cations and anions have different velocities, the liquid-liquid junction potential cannot be neglected.

The Hydrogen Electrode.—If a platinum electrode is coated with finely divided platinum (platinum black) so as to obtain a large surface, and is then saturated with hydrogen, it has been found that in contact with a solution of hydrogen ions it will behave as though it were a plate of metallic hydrogen. It is thus possible to determine the single electrode potential of the system $H_2 \mid H^+$. One form of hydrogen electrode is shown in Fig. 100. Hydrogen is run in slowly through the side tube and is allowed to bubble out of the bottom of the tube over the platinum electrode.

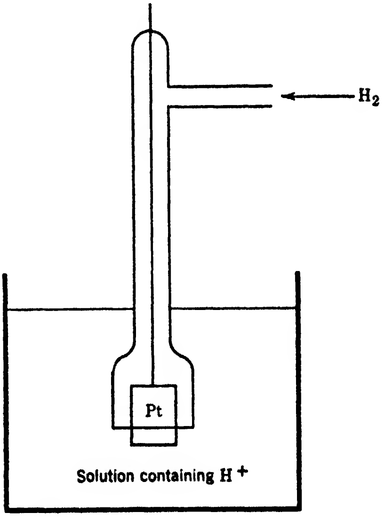

FIG. 100.—Hydrogen Electrode

The potential of such an electrode, like that of any other electrode, depends on the concentration of the pertinent ions in the solution. Hence if we have a solution of unknown hydrogen-ion concentration, it is possible to determine this concentration by dipping into the solution a hydrogen electrode, making connection with some other suitable half-cell, and measuring the potential of the system. Thus if we determine the potential of

$$H_2 \mid H^+ \parallel \text{normal calomel electrode},$$

it is possible to calculate the concentration of hydrogen ions in the solution. This method is widely employed for the determination of the *p*H of solutions, and has many biological applications.

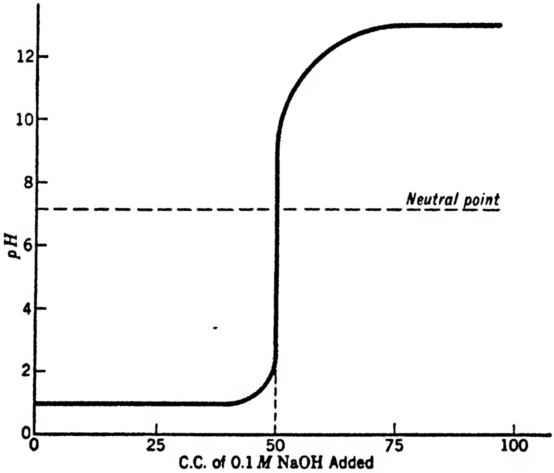

FIG. 101.

Potentiometric Titrations.—Since the neutralization of an acid by a base involves a change in the hydrogen-ion concentration from a high value to 10^{-7} molar, it is obviously possible to follow the process by means of a hydrogen electrode. Titrations may therefore be carried out in which the hydrogen electrode takes the place of an indicator. Thus suppose that an acid of unknown strength is to be titrated by means of 0.1 *M* sodium hydroxide. We may take, say, 100 c.c. of the acid and into it dip a hydrogen electrode and the side tube of a calomel electrode. Sodium hydroxide is then run into the solution in definite amounts from a burette, and the potential is determined after each addition. From this potential the hydrogen-ion concentration or the *p*H of the solution may be calculated.

A curve of the type given in Fig. 101 is thus obtained. In this case 50 c.c. of base are required to titrate 100 c.c. of acid, and the acid is therefore 0.05 *M*. It will be noticed that the "break" in the curve at the neutral point is very sharp, and the neutral point can therefore be determined very accurately.

The method has many applications, and is particularly useful for turbid solutions, and for the automatic recording of the variations in acidity in a system. By the use of suitable electrodes the method may be adapted for use in titrations other than those involving neutralization.

QUESTIONS AND PROBLEMS

1. A 0.001*M* solution of hydrochloric acid is completely dissociated. Calculate the hydrogen- and hydroxyl-ion concentrations of such a solution.

Ans. 10^{-3} and 10^{-11} mole per litre, respectively.

2. The hydrogen-ion concentration of a solution is 1.7×10^{-5} mole per litre. Calculate the *p*H. *Ans.* 4.8.

3. The *p*H of a solution is 9.6. Calculate the hydrogen- and hydroxyl-ion concentrations.

Ans. 2.5×10^{-10} and 4.0×10^{-5} mole per litre, respectively.

4. From the data given in the tables on page 350 state whether the following solutions are acid or alkaline:

(*a*) ammonium oxalate,
(*b*) sodium tartrate,
(*c*) lithium acetate.

5. In the manner indicated on page 352 calculate the hydrogen-ion concentration and *p*H of a 0.001 *M* ammonium hydroxide solution. The Ostwald dilution law constant for ammonium hydroxide is 17×10^{-6}.

Ans. $[H^+] = 0.77 \times 10^{-10}$, $pH = 10.11$.

6. Discuss the electrolytic dissociation of water.

7. Define acidity, alkalinity, *p*H.

8. Show how the relative strength of acids and bases is dependent on the extent to which they are dissociated.

9. Discuss the hydrolysis of salts.

10. Discuss the action of voltaic cells.

11. Show how potentials may be measured.

12. Describe the Weston cell.

13. Discuss single electrode potentials and the difficulties involved in their determination.

14. Describe the normal calomel and the normal hydrogen electrodes.

15. Discuss the Nernst theory of the origin of the electromotive force at metal-solution interfaces.

16. Discuss the mechanism of the Daniell cell.

17. Discuss potentiometric titrations.

CHAPTER XVIII

THERMOCHEMISTRY

A LARGE number of physical changes such as evaporation, fusion, etc., are accompanied by a flow of heat into or out of the system. It has been seen that these changes are the result of disturbing a dynamic equilibrium between molecules in different states of aggregation. It is therefore to be expected that heat changes will occur in any system which is not in molecular equilibrium, but in which such equilibrium is in the process of establishment.

In the case of a chemical reaction, the accompanying heat change is called the heat of reaction. In a quantitative sense it refers to the number of calories which are absorbed or given out when gram-molecular quantities of the substances concerned react. Thus the reaction

$$2H_2 + O_2 \rightarrow 2H_2O$$

is accompanied by the evolution of 137000 calories, when 4 grams of hydrogen react with 32 grams of oxygen to form 36 grams of water.

When a vapour condenses to form a liquid, the latent heat of condensation is given out. The amount of heat absorbed when the reverse change occurs is exactly the same. We can therefore represent these changes as

$$\text{Vapour} \rightarrow \text{Liquid} + h$$

and

$$\text{Liquid} + h \rightarrow \text{Vapour}$$

or

$$\text{Liquid} \rightarrow \text{Vapour} - h.$$

By convention the heat given out is represented as positive, and that absorbed as negative.

When heat is evolved in a process, the process is said to be exothermic, and when heat is absorbed it is called endothermic. In the above example we can represent the condition of equilibrium between a liquid and its vapour by

$$\text{Vapour} \rightleftarrows \text{Liquid} + h$$

or

$$\text{Liquid} \rightleftarrows \text{Vapour} - h.$$

The heat, *h*, refers to the amount required to change 1 gram molecule of the substance completely from the liquid to the vapour state or *vice versa*. It follows that every reversible process must be exothermic in one direction and endothermic in the other. At equilibrium the amount of change in one direction in unit time is exactly equal to the amount of change in the other direction. The accompanying heat changes are therefore also exactly equal, and there is no resultant heat change while the system remains in equilibrium.

Reactions are often classified as exothermic or endothermic, according to the heat change which accompanies the reaction when it proceeds in the direction in which we are usually interested. Some examples are given below:

Exothermic

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 24000 \text{ calories.}$$

$$H_2 + Cl_2 \rightleftarrows 2HCl + 44000 \text{ calories.}$$

Endothermic

$$N_2 + O_2 \rightleftarrows 2NO - 42000 \text{ calories.}$$

$$H_2 + I_2 \rightleftarrows 2HI - 12000 \text{ calories.}$$

At first sight it might appear that there would be some difficulty in measuring the heat of reaction in cases where an equilibrium is reached, such as the reaction

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

In this case equilibrium is reached when the reaction has proceeded only $\frac{2}{3}$ to completion. Since the position of equilibrium is known, however, we can calculate the amounts of the substances which have actually reacted, measure the heat change, and hence calculate the heat change which would have occurred if gram-molecular quantities had reacted.

The Law of Constant Heat Summation.—If in any closed system changes take place involving the absorption or evolution of heat, then from the first law of thermodynamics it follows that the heat change must be independent of the rate or nature of the process, and must depend solely on the initial and final conditions of the system. Hence, as long as the initial and final conditions of a system are the same in a series of experiments, the amount of heat absorbed or evolved will be the same, independent of the intermediate stages through which the system may have passed. This principle was applied by Hess to the heat changes which accompany chemical reactions, and is known as the law of constant heat summation. The amount of heat absorbed or evolved in a chemical reaction is thus independent of the course of the reaction, which may, for example, have occurred directly or in a series of intermediate steps. In any case the total heat change depends solely on the reactants and the products, and upon their condition.

The complete oxidation of carbon, for example, may occur in either of the following ways:

$$C + O_2 \rightarrow CO_2,$$

or

$$C + \tfrac{1}{2}O_2 \rightarrow CO$$

followed by

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2.$$

When 12 grams of carbon are oxidized as shown in the first equation above, 94300 calories are evolved. In the second case, 26000 calories are evolved in the first step, and 68000 in the second. Within the experimental error, the first amount is equal to the sum of the other two, i.e., when 12 grams of carbon are oxidized to carbon dioxide the amount of heat evolved is independent of whether the process is direct or indirect.

It will be seen from the above that by the addition of a series of chemical equations we can obtain not only the resultant products of the series of reactions, but also the net heat effect, thus

$$\begin{array}{r}
C + \tfrac{1}{2}O_2 \rightarrow CO \;\; + 26000 \text{ calories} \\
CO + \tfrac{1}{2}O_2 \rightarrow CO_2 + 68000 \text{ calories} \\
\hline
C + O_2 \rightarrow CO_2 + 94000 \text{ calories.}
\end{array}$$

Another example of the law of constant heat summation is furnished by the formation of sodium hydroxide from metallic sodium. This process may be carried out in two ways, either by combination of sodium and oxygen, and subsequent solution of the oxide in water, or by direct solution of the metal in water, and the simultaneous oxidation of the hydrogen evolved. The heats of all these reactions have been measured and are given below.

$$\begin{array}{ll}
(a) & 2Na + \tfrac{1}{2}O_2 \rightarrow Na_2O \quad + 100000 \text{ calories} \\
 & Na_2O + H_2O \rightarrow 2NaOH + \ \ 56000 \text{ calories} \\
\hline
 & 2Na + H_2O + \tfrac{1}{2}O_2 \rightarrow 2NaOH + 156000 \text{ calories.}
\end{array}$$

$$\begin{array}{ll}
(b) & 2Na + 2H_2O \rightarrow 2NaOH + H_2 + \ \ 88000 \text{ calories} \\
 & H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad\qquad + \ \ 68500 \text{ calories} \\
\hline
 & 2Na + H_2O + \tfrac{1}{2}O_2 \rightarrow 2NaOH \qquad + 156500 \text{ calories.}
\end{array}$$

It will be seen that, within the experimental error, the net heat change is the same in the two processes.

We are now in a position to define the heat of a chemical reaction in a more precise manner. Since the heat of reaction depends on the initial and final conditions of the system, its value will obviously be dependent on the physical state, etc., of the reactants and products. The condition of the substances concerned must therefore be explicitly defined when the heat of a reaction is stated. This condition is usually indicated by attaching a subscript to the formulae of the substances in the chemical equation which represents the reaction. Thus the equation previously given for the oxidation of carbon would be written

$$C_{(solid)} + O_{2(gas)} \rightarrow CO_{2(gas)} + 94300 \text{ calories}$$

It is often possible to estimate the heat of reaction when the substances are in one state of aggregation from that when they are in another, provided that the energy changes which accompany the change of state are known. Thus it has been found experimentally that

$$H_{2(gas)} + \tfrac{1}{2}O_{2(gas)} \rightarrow H_2O_{(gas)} \ \ + 58000 \text{ calories.}$$

$$H_{2(gas)} + \tfrac{1}{2}O_{2(gas)} \rightarrow H_2O_{(liquid)} + 68500 \text{ calories.}$$

The difference between the two heats of reaction, 10,500 calories, is equal to the latent heat of evaporation of a gram molecule of water, i.e., to the energy change which accompanies the process

$$H_2O_{(gas)} \rightarrow H_2O_{(liquid)}.$$

Similar considerations can be applied to all chemical changes. One measurement of the heat of a reaction can therefore be used as a basis for the calculation of the heat change when the substances concerned are in different states of aggregation, crystalline forms, etc.

As in the case of the heat changes which accompany the change in the temperature of a gas, i.e., the specific heat, the heat of a chemical reaction depends upon whether the reaction is carried out at constant volume or at constant pressure. If the reaction takes place at constant pressure, the experimental measurements involve energy changes due to the performance of work. By convention, therefore, the heat of a reaction is usually referred to the condition of constant pressure, since most measurements are made under these conditions. As in the case of specific heats, it is possible to calculate the heat of reaction at constant pressure from that at constant volume and *vice versa*.

Heats of Solution and Dilution.—Heat changes also take place when a substance is dissolved in a solvent, or when the concentration of a solution is altered by the addition of further solvent. The heat of solution is therefore dependent upon the amount of solvent in which the solute is dissolved. It is defined as the amount of heat absorbed or evolved when 1 gram molecule of a substance is dissolved in a specified amount of solvent. It is convenient to use the subscript (aq.) to denote that the substance indicated is in aqueous solution, thus $NaCl_{(aq.)}$. The formula $NaCl_{(100\ aq.)}$ is similarly used to denote the fact that 1 gram molecule of sodium chloride is dissolved in 100 gram molecules of water.

The heat of dilution is defined as the amount of heat given out or absorbed when a solution containing 1 gram molecule of a solute is diluted with further solvent, the initial and final concentrations being specified. It follows from the law of constant heat summation that, if the heat of solution is known at one concentration, and the heat of dilution is also known, we can calculate the heat of solution at other concentrations. Thus with sodium chloride solutions we have

$$NaCl_{(\text{solid})} + 10H_2O_{(\text{liquid})} \rightarrow NaCl_{(10\ \text{aq.})} + h_1$$
$$NaCl_{(\text{solid})} + 100H_2O_{(\text{liquid})} \rightarrow NaCl_{(100\ \text{aq.})} + h_2.$$

whence, combining the two equations,

$$NaCl_{(10\ \text{aq.})} + 90H_2O_{(\text{liquid})} \rightarrow NaCl_{(100\ \text{aq.})} + (h_2 - h_1),$$

i.e., the heat of dilution is the difference between the two heats of solution. The experimentally determined values at 25° C. are

$$h_1 = -\ 457 \text{ calories}$$

$$h_2 = -\ 970 \text{ calories},$$

whence

$$h_2 - h_1 \text{ (by difference)} = -\ 513 \text{ calories},$$

which agrees with the experimentally found value.

In practice it is sometimes convenient to refer to the heat of solution as the value obtained when 1 gram molecule of the solute is dissolved in an infinite amount of solvent. These values, of course, are obtained by the extrapolation of experimental results.

Heats of Formation and Combustion.—The heat of formation may be defined as the heat evolved or absorbed during the formation of 1 gram molecule of a compound from its elements. For example, 24000 calories are evolved when 1 gram molecule of ferrous sulphide is formed from its elements, i.e.,

$$Fe + S \rightarrow FeS + 24000 \text{ calories}.$$

Sometimes the heat of formation of a compound is not equal to the heat of the reaction in which it is formed, but is a fraction of the heat of reaction. Thus the formation of hydrogen chloride may be represented by

$$H_2 + Cl_2 \rightarrow 2HCl + 44000 \text{ calories}.$$

The heat of reaction is 44000 calories. Two gram molecules of hydrogen chloride are formed in the reaction, and hence the heat of formation of hydrogen chloride is

$$\frac{44000}{2}, \text{ or 22000 calories per gram molecule.}$$

If the heats of formation of all the compounds which participate in a reaction are known, it is possible to calculate the heat of the reaction. As an example consider the reaction

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O + h_1,$$

where h_1, is the heat of the reaction. If h_2, h_3, h_4, and h_5 are the heats of formation of the substances involved, we have

$$h_2 + ZnO \rightarrow Zn + \tfrac{1}{2}O_2$$

$$2h_3 + 2HCl \rightarrow H_2 + Cl_2$$

$$Zn + Cl_2 \rightarrow ZnCl_2 + h_4$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + h_5.$$

On adding up both the substances and the heat changes in these four reactions, we obtain

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O + h_4 + h_5 - h_2 - 2h_3.$$

It follows therefore from the law of constant heat summation that

$$h_1 = h_4 + h_5 - h_2 - 2h_3.$$

In other words, the heat of the reaction is equal to the sum of the heats of formation of the products, minus the sum of the heats of formation of the reactants. In a reaction in which an element participates, its heat of formation is, of course, zero.

It is evident that a knowledge of the heats of formation of compounds is of considerable practical value. In many cases the heat of formation of a compound cannot be determined directly, and must be calculated from the heat of some reaction which involves the compound in question. Especially in the case of organic compounds, the direct determination of the heats of formation is difficult, since these compounds are seldom formed directly from their elements, or in quantitative yield.

With organic compounds, therefore, use is made of what is called the heat of combustion of the compound. This is the heat given out when 1 gram molecule of the compound is oxidized completely by gaseous oxygen to carbon dioxide and water. These heats of combustion can be experimentally determined with considerable accuracy. The following will serve as an example.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 212000 \text{ calories.}$$

Now the heats of formation of carbon dioxide and water are known, i.e.,

$$CO_2 + 94300 \text{ calories} \rightarrow C + O_2$$

$$2H_2O + 2 \times 68500 \text{ calories} \rightarrow 2H_2 + O_2.$$

Hence, adding up the three equations,

$$CH_4 \rightarrow C + 2H_2 - 19300 \text{ calories,}$$

or

$$C + 2H_2 \rightarrow CH_4 + 19300 \text{ calories.}$$

As another example we may consider ethyl alcohol. We have

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O + 330000 \text{ calories}$$

$$2CO_2 + 2 \times 94300 \text{ calories} \rightarrow 2C + 2O_2$$

$$3H_2O + 3 \times 68500 \text{ calories} \rightarrow 3H_2 + 1\tfrac{1}{2}O_2.$$

Hence, by addition,

$$C_2H_5OH \rightarrow 2C + 3H_2 + \tfrac{1}{2}O_2 - 64100 \text{ calories}$$

or

$$2C + 3H_2 + \tfrac{1}{2}O_2 \rightarrow C_2H_5OH + 64100 \text{ calories.}$$

Heats of Neutralization.—The heat of neutralization may be defined as the heat evolved when an aqueous solution which contains one equivalent of an acid is neutralized by the addition of a solution containing one equivalent of a base. Long before the development of the theory of electrolytic dissociation, an important generalization had been made concerning heats of neutralization. The heats of ordinary chemical reactions vary widely from reaction to reaction. It was found, however, that when one equivalent of a strong acid was neutralized by a strong base in dilute solution, 13700 calories were evolved, no matter what acid or base was employed. If such reactions are represented by the ordinary chemical equations, it is difficult to see why, for example,

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

and

$$HCl + KOH \rightarrow KCl + H_2O$$

should both be accompanied by the same energy change, since the heats of formation of the various compounds involved are entirely different.

According to the theory of electrolytic dissociation, however, the above reactions should be written

$$Na^+ + OH^- + H^+ + NO^-_3 \rightarrow H_2O + Na^+ + NO^-_3$$

and

$$K^+ + OH^- + H^+ + Cl^- \rightarrow H_2O + K^+ + Cl^-.$$

In other words, the only change which occurs in either reaction is

$$H^+ + OH^- \rightarrow H_2O + 13700 \text{ calories.*}$$

With strong acids and bases dissociation into ions is complete. The salt formed is also completely dissociated, whereas water is virtually undissociated. In every case, therefore, the only reaction occurring is the formation of water from its ions. The constancy of the heats of neutralization is therefore a striking confirmation of the postulates of the theory of electrolytic dissociation. In the tables below, some of the observed values of heats of neutralization of strong acids and bases are given.

Acids Neutralized by NaOH at 18° C.

Acid	Heat of Neutralization, Calories
Hydrochloric	13700
Nitric	13700
Hydrobromic	13700
Hydriodic	13700
Chloric	13800
Bromic	13800

---

* The heat of formation of water from hydrogen and hydroxyl ions is, of course, quite different from the heat of formation from its elements, viz.,

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + 68500 \text{ calories.}$$

Bases Neutralized by HCl at 18° C.

Base	Heat of Neutralization, Calories
Sodium hydroxide	13700
Potassium hydroxide	13750
Lithium hydroxide	13850
Calcium hydroxide	13900
Strontium hydroxide	13800
Barium hydroxide	13900
Thallium hydroxide	13750

Obviously, if the dissociation of an electrolyte is incomplete, the measured heat of neutralization must involve the heat change which accompanies the dissociation of the electrolyte into ions. Also, since the salt formed will be that of weak acid or base, hydrolysis will be a complicating factor. In the case of weak acids or bases, therefore, the heat of dissociation into ions can be estimated from the observed heat of neutralization. Some examples of the heats of neutralization of weak acids and bases follow.

Heats of Neutralization of Weak Acids and Bases

Substance	Heat of Neutralization, Calories
Ammonia by hydrochloric acid	12270
Ammonia by nitric acid	12300
Hydrocyanic acid by sodium hydroxide	2770
Sulphuric acid by sodium hydroxide	15700
Carbonic acid by sodium hydroxide	10000
Ferrous hydroxide by hydrochloric acid	10700

In the case of ammonia neutralized by hydrochloric acid, for example, since ammonia is only very slightly dissociated, the reaction may be written

$$NH_4OH + H^+ + Cl^- \rightarrow NH_4^+ + Cl^- + H_2O + h_1.$$

This reaction is really the combination of the two stages,

$$NH_4OH \rightarrow NH_4^+ + OH^- + h_2$$

and

$$H^+ + OH^- + Cl^- \rightarrow H_2O + Cl^- + 13700 \text{ calories.}$$

$$\overline{\begin{aligned}NH_4OH + H^+ + Cl^- \rightarrow NH_4^+ + Cl^- + H_2O + h_2 \\ + 13700 \text{ calories.}\end{aligned}}$$

Hence from the law of constant heat summation,

$$h_2 = h_1 - 13700 \text{ calories.}$$

The heat of neutralization, as measured, is h_1, and has the value 12200 calories. h_2, the heat of dissociation of ammonium hydroxide into ions, is therefore equal to -1500 calories, i.e., 1500 calories are absorbed when 1 gram molecule of ammonium hydroxide is dissociated into its ions.

The Effect of Temperature on Chemical Reactions.—When a change in the temperature of the environment occurs, a chemical reaction is affected in a number of ways. In the first place, the velocity of the reaction is altered and the time required for the attainment of equilibrium is decreased as the temperature rises. The equilibrium concentrations of the participating substances, as indicated by the mass law constant, also vary with the temperature of the system. In most cases the heat of the reaction also varies with change in temperature.

The effect of temperature on the heat of the reaction may be explained on the basis of the law of constant heat summation. Consider the reaction

$$A + B \rightleftarrows C + D.$$

This may be carried out in two different ways as indicated by Fig. 102. In the first case, 1 gram molecule of A and of B react at a temperature T_1 to give C and D. Let h_1 be the heat of reaction at this temperature. In the second case suppose that we start with A and B at T_1 as before. They are then heated to T_2. This involves an absorption of $(C_A + C_B)(T_2 - T_1)$ calories, where C_A and C_B are the molecular heats of A and B, respectively. The reaction is allowed to proceed at T_2, C and D are formed, and h_2, the heat of the reaction at this temperature, is evolved. The products C and D are then cooled to T_1, with an evolution of $(C_C + C_D)(T_2 - T_1)$ calories, where C_C and C_D are the molecular heats of the products of the reaction C and D. Since the

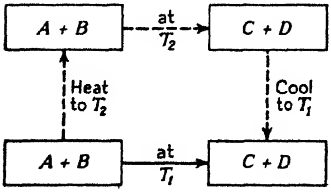

FIG. 102.

initial and final conditions are the same in both processes, the heat changes must be identical, i.e.:

$$h_1 = -(C_A + C_B)(T_2 - T_1) + h_2 + (C_C + C_D)(T_2 - T_1),$$

or

$$\frac{h_1 - h_2}{T_2 - T_1} = C_C + C_D - C_A - C_B.$$

The variation of the heat of the reaction with the temperature is thus dependent upon the difference between the molecular heats of the products and the reactants. It follows that, if the heat of reaction is known at one temperature, and the specific heats of the compounds involved are known, the heat of the reaction can be calculated at any other temperature.

The effect of a temperature change upon a chemical equilibrium depends on the nature of the heat change which accompanies the reaction. When the temperature is raised the equilibrium will always shift in such a direction that heat is absorbed. This is another application of the principle of Le Châtelier that when a factor which governs the equilibrium of a system is altered the system will change in such a way as to diminish the effect of the alteration. Thus, in this case, when heat is added to a system the equilibrium shifts, heat is absorbed, and hence the addition of heat to the system is partly neutralized, and the rise in temperature is less than would normally have occurred. As an example we may consider the reaction between hydrogen and oxygen to form water,

$$2H_2 + O_2 \rightleftarrows 2H_2O + 137000 \text{ calories.}$$

Since this is exothermic a rise in temperature causes the equilibrium to shift to the left. The dissociation of water into its elements is therefore increased with rise in temperature. On the other hand the reaction

$$H_2 + I_2 \rightleftarrows 2HI - 12000 \text{ calories}$$

is endothermic, and a rise in temperature causes the equilibrium to shift to the right, so that the dissociation of hydrogen iodide into its elements decreases as the temperature rises.

The same remarks apply to physical equilibria also. Thus consider the equilibrium

$$H_2O_{\text{(liquid)}} \rightleftarrows H_2O_{\text{(vapour)}} - L,$$

where L is the latent heat of evaporation. A rise in temperature shifts the equilibrium to the right, water evaporates, and the vapour pressure rises.

The relationship between the heat of the reaction and the equilibrium concentrations of the substances involved may be obtained quantitatively as well as qualitatively. It can be shown that, over a range of temperature where the heat of reaction may be assumed to be constant, we have

$$\log \frac{K_{T_1}}{K_{T_2}} = \frac{H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where K_{T_1} and K_{T_2} are the mass law constants at T_1 and T_2, respectively, R is the gas constant, and H is the heat of reaction.

The effect of temperature on the velocity of a chemical reaction has already been indicated. In all cases a rise in temperature causes an increase in the rate of a reaction. In the case of an exothermic reaction, the heat evolved may not be dissipated to the environment quickly enough to make the change an isothermal process. The temperature will therefore rise, the rise will cause an increased reaction velocity, this will cause a still more rapid rise in temperature, and the reaction will continually accelerate. As a result, what is called an explosion occurs.

In this connection it is of interest to point out that so-called endothermic compounds, i.e., those with negative heats of formation, very often have explosive properties. Acetylene is a good example of such a compound. From its heat of combustion, it can be calculated that its heat of formation is −53000 calories. We thus have the reaction

$$H_2 + 2C \rightleftarrows C_2H_2 - 53000 \text{ calories.}$$

A rise in temperature therefore favours the formation of acetylene, and it exists at low temperatures merely because the velocity of its decomposition, i.e., of the reaction from right to left, is exceedingly slow at such temperatures. Acetylene is thus unstable at room temperature. If the decomposition is initiated, the substance heats up rapidly since its decomposition is exothermic, and an explosion results. Hydrogen peroxide is another example of an endothermic compound. It breaks down into water and oxygen with the evolution of heat, and in consequence may explode with great violence. Every endothermic compound is thus a potential explosive. Some compounds of this type, however, such as nitric oxide, are not explosive under ordinary conditions because a very high temperature is necessary for their decomposition to occur at a measurable rate.

The Fixation of Atmospheric Nitrogen.—It is of interest to apply the ideas which have been discussed above to some reaction which is of practical importance, in order to show the way in which the theoretical knowledge of reactions may be used. For the fixation of atmospheric nitrogen two reactions have been employed, viz.,

$$N_2 + O_2 \rightleftarrows 2NO - h_1$$

and

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + h_2.$$

The object of these reactions in practice is to obtain as large a yield of fixed nitrogen as possible, i.e., to shift the equilibria to the nitric oxide or ammonia side. We will therefore discuss the various factors which may influence these equilibria, and the resulting yield of fixed nitrogen.

The nitric oxide reaction is endothermic, as indicated by the above equation. Since an increase in temperature will shift the equilibrium in the direction of absorption of heat, as high a temperature as possible should be used in order to obtain a large yield of nitric oxide. If the specific heats of the substances concerned are known, and the equilibrium concentrations and heat of reaction are known at one temperature, it is possible to calculate the yield of nitric oxide at any other temperature.

A rise in temperature also increases the rate at which equilibrium is attained. To obtain nitric oxide from the equilibrium mixture, it is necessary to cool the system at a rate which is greater than that at which the equilibrium can shift, until a temperature is reached at which the velocity of decomposition is immeasurably small. It is therefore useless to heat the reaction mixture above a certain temperature, since, although the equilibrium amount would be increased, the rate of decomposition on cooling would be faster than any practical rate of cooling.

Since the most important consideration in carrying out the reaction is to slow down the attainment of equilibrium during cooling, it is obvious that the presence of catalysts must be avoided. As mentioned previously, the fact that there is no volume change during the reaction means that the pressure will not influence the position of equilibrium.

The ammonia reaction differs from the nitric oxide reaction in that it is exothermic. The yield of ammonia is consequently decreased by raising the temperature. As in the nitric oxide reaction, the effect of temperature on the yield can be calculated from the heat of reaction, specific heat data, etc. The maximum yield will be obtained at very low temperatures, but there the velocity of reaction will be immeasurably slow. Thus no reaction can be detected between nitrogen and hydrogen at room temperature. The optimum temperature is therefore the lowest temperature at which the reaction proceeds at a practical rate. As a result, catalysts are of great value since they permit the use of lower temperatures, and an increased yield is obtained. The success of the process from a commercial point of view has depended upon the discovery of suitable catalysts.

Since there is a decrease in volume during the formation of ammonia, an increase in pressure will cause the equilibrium to shift, and an increased yield will be obtained. A high pressure is therefore used in this reaction.

The above examples will illustrate the manner in which the principles of physical chemistry can be employed to indicate the most advantageous conditions under which a chemical reaction may be carried out. The effect of physical factors upon chemical reactions may thus be predicted, and, with more advanced knowledge, quantitative calculations may be made.

QUESTIONS AND PROBLEMS

1. One and one-half grams of zinc are dissolved in a solution of hydrochloric acid; 694 calories are evolved. Calculate the heat of the reaction

$$Zn + 2HCl \rightleftarrows ZnCl_2 + H_2. \qquad \textit{Ans.}\ 30200 \text{ cals.}$$

2. The following reactions are accompanied by the heat changes indicated:

$$H_2 + \tfrac{1}{2}O_2 \rightleftarrows H_2O + 68500 \text{ calories.}$$
$$Fe + \tfrac{1}{2}O_2 \rightleftarrows FeO + 65700 \text{ calories.}$$

Using the law of constant heat summation, calculate the heat of the reaction

$$Fe + H_2O \rightleftarrows FeO + H_2. \qquad \textit{Ans.}\ -2800 \text{ cals.}$$

3. In 180 grams of water, 7.46 grams of potassium chloride are dissolved; 439 calories are absorbed. On the addition of a further 180 grams of water to the solution 50 calories are absorbed. Calculate the heat of solution of potassium chloride at the second concentration. *Ans.* − 4890 cals.

4. Calculate the heat of formation of hydrogen iodide, given the following information:

$$\begin{aligned} Na_2O + 2HI &\rightleftarrows 2NaI + H_2O + 120300 \text{ calories} \\ 2Na + \tfrac{1}{2}O_2 &\rightleftarrows Na_2O + 100000 \text{ calories} \\ Na + \tfrac{1}{2}I_2 &\rightleftarrows NaI + 69000 \text{ calories} \\ H_2 + \tfrac{1}{2}O_2 &\rightleftarrows H_2O + 68500 \text{ calories.} \end{aligned}$$

Ans. −6900 cals.

5. Calculate the heat of the reaction $PbO + H_2SO_4 \rightleftarrows PbSO_4 + H_2O$ from the following data:

$$\begin{aligned} Pb + O &\rightleftarrows PbO + 50000 \text{ calories.} \\ H_2 + \tfrac{1}{2}O_2 &\rightleftarrows H_2O + 68500 \text{ calories.} \\ Pb + S + 2O_2 &\rightleftarrows PbSO_4 + 216000 \text{ calories.} \\ H_2 + S + 2O_2 &\rightleftarrows H_2SO_4 + 200000 \text{ calories.} \end{aligned}$$

Ans. 34500 cals.

6. Calculate the heat of formation of naphthalene, $C_{10}H_8$, from the following:

heat of combustion = 1228800 calories.
heat of formation of water = 68500 calories.
heat of formation of carbon dioxide = 94000 calories.

Ans. −14800 cals.

7. The heat of formation of zinc sulphate is 230000 calories. The heat of formation of copper sulphate is 181000 calories. Calculate the heat of the reaction

$$Zn + CuSO_4 \rightleftarrows ZnSO_4 + Cu. \qquad \textit{Ans.}\ 49000 \text{ cals.}$$

8. The heat of formation of acetylene, C_2H_2, is −53000 calories. Calculate its heat of combustion using the values of the heats of formation of water and carbon dioxide given above. *Ans.* 309500 cals.

9. The heat of combustion of ethyl alcohol is 325100 calories; that of acetic acid is 209500 calories. Calculate the heat of the reaction

$$C_2H_5OH + O_2 \rightleftarrows CH_3COOH + H_2O. \qquad \textit{Ans.}\ 115600 \text{ cals.}$$

10. The heat of neutralization of hydrocyanic acid by sodium hydroxide is 2770 calories. Calculate the heat of dissociation of HCN into its ions.

Ans. −10930 cals.

11. It is stated that the heat of combustion of amorphous carbon is 97340 calories, and that of diamond is 94000 calories. From these values calculate the heat of the allotropic change

Amorphous carbon $\rightleftarrows$ diamond. *Ans.* 3340 cals.

12. At 20° C. we have

$$Zn + \tfrac{1}{2}O_2 \rightleftarrows ZnO + 85000 \text{ calories.}$$

If the specific heat of zinc is 0.0935 calorie, the specific heat of zinc oxide is 0.1248 calorie, and the molecular heat of oxygen is 4.98 calories, over the temperature range 20° C. to 220° C., calculate the heat of the above reaction at 220° C.

Ans. 84690 cals.

13. In the reaction

$$N_2 + O_2 \rightleftarrows 2NO - 43000 \text{ calories,}$$

the mass law constant is 9800 at 1900° C. Assuming that the heat of the reaction does not change as the temperature changes, calculate the volume percentage of nitric oxide in air at 4000° C., using the relationship $\log_e \frac{K_{T_1}}{K_{T_2}} = \frac{H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Ans. 2.3 per cent.

14. Calcium carbonate may be prepared by means of the reaction:

$$CaO + CO_2 \rightleftarrows CaCO_3 + 43000 \text{ calories}$$

Discuss the effect of temperature, pressure, and the presence of a catalyst on the yield of calcium carbonate.

15. Define heat of reaction, heat of solution, heat of combustion, heat of neutralization.

16. State the law of constant heat summation, and illustrate its application by means of an example.

17. Discuss heats of neutralization from the point of view of the theory of electrolytic dissociation.

18. Discuss the effect of temperature on chemical reactions.

19. Discuss the fixation of atmospheric nitrogen from the point of view of temperature, pressure, concentration, and the presence or absence of a catalyst.

APPENDIX I

INTERNATIONAL ATOMIC WEIGHTS, 1938

	Symbol	Atomic Weight		Symbol	Atomic Weight
Aluminum	Al	26.97	Molybdenum	Mo	95.95
Antimony	Sb	121.76	Neodymium	Nd	144.27
Argon	A	39.944	Neon	Ne	20.183
Arsenic	As	74.91	Nickel	Ni	58.69
Barium	Ba	137.36	Nitrogen	N	14.008
Beryllium	Be	9.02	Osmium	Os	190.2
Bismuth	Bi	209.00	Oxygen	O	16.0000
Boron	B	10.82	Palladium	Pd	106.7
Bromine	Br	79.916	Phosphorus	P	31.02
Cadmium	Cd	112.41	Platinum	Pt	195.23
Calcium	Ca	40.08	Potassium	K	39.096
Carbon	C	12.010	Praseodymium	Pr	140.92
Cerium	Ce	140.13	Protactinium	Pa	231
Cesium	Cs	132.91	Radium	Ra	226.05
Chlorine	Cl	35.457	Radon	Rn	222
Chromium	Cr	52.01	Rhenium	Re	186.31
Cobalt	Co	58.94	Rhodium	Rh	102.91
Columbium	Cb	92.91	Rubidium	Rb	85.48
Copper	Cu	63.57	Ruthenium	Ru	101.7
Dysprosium	Dy	162.46	Samarium	Sm	150.43
Erbium	Er	167.2	Scandium	Sc	45.10
Europium	Eu	152.0	Selenium	Se	78.96
Fluorine	F	19.00	Silicon	Si	28.06
Gadolinium	Gd	156.9	Silver	Ag	107.880
Gallium	Ga	69.72	Sodium	Na	22.997
Germanium	Ge	72.60	Strontium	Sr	87.63
Gold	Au	197.2	Sulphur	S	32.06
Hafnium	Hf	178.6	Tantalum	Ta	180.88
Helium	He	4.003	Tellurium	Te	127.61
Holmium	Ho	163.5	Terbium	Tb	159.2
Hydrogen	H	1.0081	Thallium	Tl	204.39
Indium	In	114.76	Thorium	Th	232.12
Iodine	I	126.92	Thulium	Tm	169.4
Iridium	Ir	193.1	Tin	Sn	118.70
Iron	Fe	55.84	Titanium	Ti	47.90
Krypton	Kr	83.7	Tungsten	W	183.92
Lanthanum	La	138.92	Uranium	U	238.07
Lead	Pb	207.21	Vanadium	V	50.95
Lithium	Li	6.940	Xenon	Xe	131.3
Lutecium	Lu	175.0	Ytterbium	Yb	173.04
Magnesium	Mg	24.32	Yttrium	Y	88.92
Manganese	Mn	54.93	Zinc	Zn	65.38
Mercury	Hg	200.61	Zirconium	Zr	91.22

APPENDIX II

Derivation of Equations for First- and Second-Order Reactions.—*First-Order Reactions.*—Let the initial concentration of the reactant be a, and the amount reacted after t seconds be x. Then at time t the concentration of the reactant will be $a - x$. Now the rate at time t is proportional to the concentration of the reactant, hence

$$\frac{dx}{dt} = k(a - x).$$

Or

$$\frac{dx}{a - x} = k\,dt,$$

$$-\frac{d(a - x)}{a - x} = k\,dt.$$

Intergrating

$$-\log_e(a - x) = kt + I,$$

where I is a constant of integration. Now when $t = 0$, $x = 0$, hence

$$I = -\log_e a.$$

Substituting for I,

$$\log_e \frac{a}{a - x} = kt.$$

Second-Order Reactions.—Consider the reaction $2\,\mathrm{A} \rightarrow$ (Products). Then using the same symbols as before, we have

$$\frac{dx}{dt} = k(a - x)^2.$$

Hence

$$\frac{dx}{(a - x)^2} = k\,dt,$$

or

$$-\frac{d(a - x)}{(a - x)^2} = k\,dt.$$

Integrating

$$\frac{1}{a - x} = kt + I.$$

When $t = 0$, $x = 0$, hence

$$I = \frac{1}{a}.$$

Substituting for I,

$$\frac{1}{a - x} - \frac{1}{a} = kt,$$

$$\frac{a - (a - x)}{a(a - x)} = kt,$$

$$\frac{x}{a(a - x)} = kt.$$

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