TEXTBOOK OF

PHYSICAL CHEMISTRY

BY

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PREFACE

THIS textbook is intended primarily for the use of classes beginning the subject of Physical Chemistry. In the preparation of the text I have endeavored to keep in mind that the presentation is to students who meet the subject matter for the first time, and that they are to acquire a broad foundation for their subsequent work. As some time intervenes between the elementary courses in which the fundamental ideas of chemistry are presented and the time at which the work in Physical Chemistry is given, it is found that a short review of these fundamental concepts is necessary in order to have the student properly oriented as to the relationship of his elementary work and that which is usually incorporated in a course in Physical Chemistry. That this is absolutely necessary is the experience of most teachers, and the result can be attained more quickly by briefly restating this fundamental matter in a form in which it can subsequently be utilized. Hence, there is given a résumé of some of the information which the student is assumed to have in order to place him in a position to correlate the new material with that which he already possesses.

The order of topics usually follows the logical development of the subject matter in that the experimental data are first presented with the statement of the laws, then the explanation of the facts by the formulation of the theory. The limitations are then emphasized by presentation of experimental data which appear to be *abnormal*, with the subsequent modification of the theory to explain these, and in some cases to show that the facts are not in accord with the present theories. The historical setting is illustrated by recording after the names of the men who have been influential in developing the science of chemistry, the date at which each man was actively engaged in the work with which his name is associated. This chronological sequence of the main advances in chemistry is of vital importance in aiding the student to acquire a true perspective of the subject.

The subject matter has been presented by employing only the more elementary mathematics, — arithmetic and algebra, — and in but few cases has use been made of higher mathematics. Where the calculus has been employed, practically all of this matter has been incorporated in such a way that, if desired, it can be omitted without disturbing the order of the presentation of the subject. In the presentation it is recognized that only by many numerical examples can the principles be properly illustrated and emphasized. Therefore, there is incorporated in the Appendix a large number of problems, the data for which are tabulated in such a way that the answers appear as one of the parts of the tabulation. By not expressing the conditions of the problem in words, much space is saved and the instructor may clothe the data in whatever form he desires.

The selection of the subject matter for a textbook of this character resolves itself into the process of exclusion, and the guiding factors in making the selections have been the general information for the student, the fundamental character of the material, and the technical importance of the facts as well as of the theoretical considerations. Special emphasis has been placed upon the equilibrium reactions in gases with technical uses as illustrated by means of problems. The conception of phases has been introduced early in the discussion, and their relation and utilization in explanation of many operations has been emphasized, particularly in the formulation of the Phase Rule, with illustrations of its industrial importance and applications. The theories of solutions have been presented so that the student may become familiar with their experimental basis, the assumptions involved, and their limitations. It is necessary that students beginning the study of theoretical chemistry should acquire a working knowledge of the prevailing theories in order to make the voluminous literature more accessible to them. In order to accomplish this result the discussion has been extended to a consideration of concentrated solutions and nonaqueous solutions. The colloid state of matter is receiving such marked attention from the industrial as well as from the theoretical point of view, that it is becoming of great importance. Hence, colloid chemistry has been presented in considerable detail.

There have been presented a large number of tables of experimental data, most of which have been taken from Landolt, Börnstein, and Roth's *Tabellen*, edition of 1912. With this material directly before the student, the discussion of the principles and facts presented may be more fully carried on, and in this way the subject can be much better presented to the student and he will be in a better position to see the significance of the conclusions. Then these data may be utilized as a valuable source of material from which problems may be formulated.

Free use has been made of the available literature in obtaining the material for this text, and the author desires to express his indebtedness for the same, and particularly to the following, to which the student is referred for further details:

Text Books of Physical Chemistry, edited by Sir William Ramsay, which include *A System of Physical Chemistry* by W. C. McC. Lewis, *The Phase Rule and its Applications* by Alexander Findlay, *Stoichiometry* by Sidney Young, *Stereochemistry* by Alfred W. Stewart, *Metallography* by Cecil H. Desch. *Monographs on Inorganic and Physical Chemistry*,

edited by Alexander Findlay; particularly *The Chemistry of the Radio-Elements* by Frederick Soddy, and *Osmotic Pressure* by Alexander Findlay.

Text Book of Inorganic Chemistry, edited by J. Newton Friend; Vol. I, *An Introduction to Modern Inorganic Chemistry* by J. Newton Friend, H. F. V. Little and W. E. S. Turner; Vol. IV, *Aluminium and its Congeners, Including the Rare Earth Metals* by H. F. V. Little.

Organic Chemistry for Advanced Students by Julius B. Cohen; Vol. II, *Handbook of Colloid Chemistry* by Wolfgang Ostwald, translated by Martin H. Fischer.

On the Physical Aspect of Colloidal Solutions by E. F. Burton, University of Toronto Studies No. 36.

An Introduction to the Physics and Chemistry of Colloids by Emil Hatschek.

The Chemistry of Colloids by W. W. Taylor. *Outlines of Chemistry* by H. J. H. Fenton.

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PHYSICAL CHEMISTRY

CHAPTER I

INTRODUCTION

Units of Measure. — The work in chemistry and physics consists chiefly in making measurements in order to ascertain the quantity of the materials present or the forces acting between these substances. Shortly after the introduction of the balance into the chemical laboratory there began a vigorous campaign to determine the weights of substances as well as of the relative quantities of the constituents of which these were composed and in what ratio various substances combined. It was not only necessary to have a unit of weight but also a unit to represent these combining relations, just as it was necessary to have a unit of length to obtain the dimensions of substances or their distances apart. When an effort was made to measure the various forces, some convenient standard of reference had to be employed in terms of which these forces could be represented. A *unit* for measurement is some convenient quantity of that particular thing which is to be applied as a divisor in order to ascertain how many times this arbitrarily selected quantity is contained in the quantity of the thing *to be measured.* Or in other words, a *unit* is any quantity to which another quantity of the same kind can be compared for the purposes of measurement and for expressing the magnitude of the same. The measure of this unit quantity is represented by the number 1. The *fundamental units* are selected arbitrarily, and the *derived units* are defined in terms of the fundamental units.

The method of measurement is the comparison of the quantity to be measured with our unit. This may be accomplished (1) *by applying the unit* directly to the quantity to be measured, as that of a foot rule to a floor to find its dimensions, a graduated vessel to the liquid to be measured; or (2) by the effect the particular quantity to be measured has as compared to the effect that unit quantity has, as in determining the strength of an alkali by titrating it against a standard acid which has been expressed in terms of our unit alkali, or any of our quantitative methods for determining the quantity of a particular substance present, as by determining the refractivity of a liquid, the electrical conductance, etc.

The knowledge of the phenomena occurring about us has been obtained by accurate measurements, and the *fundamental units* in which these have been expressed are the units of *time*, *space*, and *mass*. The scientific *unit* of *time*, the *second*, is the 86,400th part of a *mean solar day*, which is the average interval (or period) that elapses between successive transits of the sun across the meridian at any place during the whole year.

Owing to the fact that the speed of the rotation of the earth is decreasing, resulting in the corresponding increase in the length of the second, it has been suggested that the time of vibration of the atom of some element be selected as our unit of time, as this seems to be invariable and unalterable.

Our conception of position is that of relative positions only, and the location of one object is expressed in relation to some other object. The change of the position of a body with respect to another is termed motion, *i.e. motion is the change of position*. The change of position in unit time is the *speed*, while the rate of change of position in a specified direction is the *velocity*. If this velocity is not constant during successive intervals of time, the amount of change in the velocity during the interval of unit time is designated the *acceleration*, *i.e.* $\frac{v_2 - v_1}{t} = a$, where the change of velocity has been from v_1 to v_2 in the time t, giving an acceleration represented by a.

Matter. — Being familiar with handling various substances, such as iron, sodium chloride, water, etc., we are able to distinguish them by certain individual characteristics that we call properties. These properties are always constant and persistent and are not detachable from the body. The embodiment of these properties is that something which is familiarly known as *matter*. Closely associated with these properties are manifestations of what we designate *energy*, and in our experiences we have not been able to separate energy from matter. Yet it is through these manifestations that we know of the existence of that which we designate *matter*.

The quantity of matter is measured by means of the balance, and its measure is expressed in terms of weight. This measure is the attraction of the earth for the particular quantity of the material substance or matter. Since the attraction of the earth varies with the distance from the center of the earth, a body would not have the same weight on all parts of the earth's surface. The quantity of matter does not change, and the *mass*, as it is termed, remains constant. Hence in stating the quantity of a substance, it is not sufficient to speak of its having a certain *weight*, but the term *mass* is used to definitely express the quantity of the substance. Masses are compared by comparing their weights.

Units of Mass. — The units of mass are founded on the *kilogram*, which is the metric standard of mass and is defined as the mass of a piece of platinum-iridium deposited at the

International Bureau of Weights and Measures near Paris. This standard of mass, known as the International Prototype Kilogram, is equal to the "*kilogramme des Archives*" made by Borda, which was intended to have the same mass as a cubic decimeter of distilled water at the temperature of 4° C. and 760 mm. Hg pressure, which weighs 1 kilogram and equals actually 1.000027 cu. dm.

The English standard of mass is the *pound* and is the weight of a piece of platinum weighed *in vacuo* at the temperature of 0° C., and which is deposited with the Board of Trade.

Force. — Force is that which changes or tends to change the velocity of a body. It may be measured by the gravitation method, the ordinary spring balance method, or the dynamic method; the first of which is the one generally used by chemists. The unit of force is that force which produces in unit mass unit acceleration. In the C.G.S. system the unit of force is the *dyne* and is defined as that force which acting on a body of unit mass produces an acceleration of one centimeter per second per second. The unit force is called a *poundal* when mass is expressed in pounds, length in feet, and time in seconds. Force may be defined by $F = Ma$, where M is mass and a is the acceleration.

Weight. — The units of force, the dyne and poundal, are designated the *absolute units*, but the so-called gravitational units are more commonly employed, wherein use is made of the force of the attraction of the earth for the body. The unit of force then becomes the attraction of the earth for the unit of mass — one gram or one pound.

The attraction of the earth[1] on one gram causes an acceleration of 981 cm./sec.^{2}. The force of one dyne produces an acceleration of *one* $\frac{\text{cm.}}{\text{sec.}^2}$ when it acts on one gram. Hence the *weight* of one gram is equivalent to 981 dynes.

[1] This has different values at different places.

Pressure. — Pressure is a distributed force. The *intensity* of pressure, *i.e.* the pressure per unit area, is used extensively in science; and in chemistry, particularly, when the term *pressure* is used the *intensity* of pressure is meant.

Density and Specific Gravity. — The mass of a substance in unit volume is termed the *density* of that substance. Density is represented by ρ. Then by definition $\rho = \frac{mass}{V}$. The *specific gravity* of a substance is the ratio of the mass of a given volume of a substance to the mass of an equal volume of another substance taken as a standard. The specific gravity is represented by s. Then $s = \frac{g}{g_s}$, where g is the mass of the substance, and g_s is the mass of an equal volume of the standard substance. It is not always customary to compare the substance at the same temperature. Hence if water at its greatest density (4° C.) is selected as the standard and the other substance compared with it at this temperature, this is usually expressed $\frac{4^\circ}{4^\circ}$, while if the substance is at some other temperature, as 20°, the comparison with water at 4° would be indicated as follows: $\frac{20^\circ}{4^\circ}$, and the expression $\frac{15^\circ}{15^\circ}$ signifies that both the substance and the standard are to be compared at 15°. We should also have $s = \frac{\rho}{\rho_s}$, in which ρ is the density of any substance, and ρ_s is the density of the standard.

CHAPTER II

LAWS OF COMBINATION AND CHEMICAL UNITS

THE uniform occurrence of natural phenomena is observed to take place and the conditions best suited for their reproduction are ascertained by experimentation. The facts gathered by observation and experimentation are classified, and certain particular groups of related facts are then expressed in a generalization which is the so-called law. Or, as Mellor expresses it, " The laws of chemical and physical phenomena are collocations of those circumstances which have been found by experiment and observation to accompany all chemical and physical changes included in the statement of the law." We have as some of the fundamental generalizations of science the following: The Law of the Conservation of Energy; the Law of the Conservation of Matter; Newton's Law of Gravitation; Boyle's Law; etc. We thus see that *a Law of Science is a general statement of what has been found to be true by experiment and observation and of what will probably be true in the future.*

THE LAW OF DEFINITE PROPORTIONS

When magnesium is burned, it is changed to the white oxide, and we have on the one hand metallic magnesium and on the other hand the white oxide, there being no gradation. The amount of the magnesium oxide that can be formed depends upon the quantities of magnesium and oxygen available, and there is a constant relation between the amounts of substances taken and the amount of substance formed. In general this may be stated that when substance *A* changes to substance *B* the ratio of the masses is constant. It was not possible to formulate any such law until the balance was introduced by Lavoisier. It was then demonstrated that 100 parts of zinc always yield 124.5 parts of zinc oxide. By using different amounts of potassium chloride, varying from 44 to 80 grams, the result of seven experiments showed that 100 parts of potassium chloride yield 135.645 parts of potassium nitrate.

If two chemically homogeneous substances, *A* and *B*, react upon each other and yield a third substance, *C*, then the following relations hold:

$$\frac{\text{Mass } A}{\text{Mass } B} = K \text{ (constant)}; \quad \frac{\text{Mass } A}{\text{Mass } C} = K_1; \quad \frac{\text{Mass } B}{\text{Mass } C} = K_2.$$

This may be demonstrated by adding, drop by drop, a solution of potassium bromide to a solution of silver nitrate. It has also been shown that these relations hold under whatever conditions the substances react. For example, the amount of silver chloride formed from a constant given weight of silver is always the same, whatever the method be by means of which it is prepared, as is shown by the following:

1. Burning Ag in Cl gas	100 g. Ag yielded 132.842 g. AgCl.
2. Dissolving Ag in KCl	100 g. Ag yielded 132.847 g. AgCl.
3. Precipitating $AgNO_3$ with HCl aq	100 g. Ag yielded 132.848 g. AgCl.
4. Precipitating $AgNO_3$ with NaCl aq	100 g. Ag yielded 132.842 g. AgCl.

A large number of experiments were made to determine whether the mass formed was equal to the sum of the masses taking part in the reaction. In seven experiments with the formation of silver iodide from silver and iodine, in which quantities of silver varying from 27 to 136 grams were used, the weights of the silver iodide formed did not differ from the sum of the weights of the silver and the iodine taken by more than one part in 20,000 in any case. From this it is seen that there is a definite relation between the substances used and the products formed. This may be expressed in the following form: *The ratio of the mass formed to the constituents is constant and also the ratio of the constituents to the mass formed is constant.* This is termed the *Law of Definite or Constant Proportions.*

While this has been fully demonstrated to the satisfaction of most investigators, there are some who still question whether the mass of a substance always remains constant during its passage through chemical changes. Very recently Landolt[1] published the result of his investigation on the question as to whether chemical changes alter the mass of a particular substance. Of 14 reactions of various types only two gave systematically a change in weight larger than the errors of observation. Each of the experiments, in which 250 to 310 grams were used, has corresponding differences in weights, varying from 0.068 mg. to 0.11 mg. Out of 70 experiments 61 showed losses in weight. Babcock, from his work upon the effect of molecular changes upon weight, states[2] that his experiments indicate that the weight of a body is an inverse function of its energy. While the difference between the weight of the ice and the water resulting from it is always small, the ice was always found to be heavier than the water.

The Law of Multiple Proportions

The mass of a system is not altered by chemical changes that occur in the system, or, as expressed above, the mass of a composite substance is equal to the sum of the masses of its component *elements*. By the term *element* we understand those particular substances which have so far resisted all efforts of the analyst to decompose them into simpler or more elementary constituents.[3] We have already seen that

[1] Landolt, *Jour. de chem. phys.* 6, 625–27 (1908).

[2] In a private communication to the author.

[3] The rare earth elements constitute a group of closely related elements that require peculiar and special methods in order to separate

these elements combine in constant ratios to form chemically homogeneous substances. Such chemically homogeneous substances, whose percentage composition by mass is invariable, are termed *chemical compounds*.

By burning portions of 10 grams of lead in oxygen the following quantities of lead oxide were formed: 10.77, 10.775, 10.78, and 10.75 grams, and Berzelius found as an average of his determinations 10.78 grams of the oxide of lead produced from 10 grams of lead. Taking 10.78 as the value, and expressing the amount of lead oxide produced from 100 grams of lead, we would obtain 107.8 grams of the yellow oxide of lead. It has also been found that 100 grams of lead unite with 11.7 grams of oxygen to form minium (red oxide of lead) and that 100 grams of lead unite with 15.6 grams of oxygen to form brown oxide (peroxide) of lead. These different quantities of oxygen combining with the same

and distinguish them. Certain elements, which include uranium, radium, polonium, actinium, etc., are designated *radioactive* elements and are characterized by giving rise to emanations. The theory of the disintegration of these radioactive elements assumes that the emanations give rise, in some cases, to active deposits which are transformed into another element, and this in turn is transformed into a non-radioactive and stable element. In some radioactive changes, the α particles emitted are charged atoms of helium, as is illustrated in the growth of helium from actinium. Resulting from these emanations there is a group of elements of different atomic weights but which are chemically identical. Such a group of elements is termed *isotopes* and the elements are called *isotopic*. The following members of the actinium series are given by Soddy: *

1. Radioactinium, thorium, radiothorium, ionium, uranium–X.
2. Actinium and mesothorium–2.
3. Actinium–X, radium, mesothorium–1, thorium–X.
4. Actinium emanation and emanations of radium and thorium.
5. Actinium–B, lead, radium–B, thorium–B, radium–D.
6. Actinium–C, bismuth, radium–C, thorium–C, radium–E.
7. Actinium–D, thallium, and thorium–D.

* Soddy, *The Chemistry of the Radio-Elements* (1914), and the *Text-book of Inorganic Chemistry*, Edited by J. Newton Friend, Vol. IV by H. F. V. Little, are sources of additional information and extensive references to the literature.

amount of lead (100 grams) are in the ratio of 7.8 : 11.7 : 15.6, which is the more simple ratio of 2 : 3 : 4; hence a constant quantity of lead combines with different quantities of oxygen in the simple integral ratio 2 : 3 : 4. Similarly it has been found that 100 grams of nitrogen unite with the following quantities of oxygen to form distinct chemical individuals: 57.1; 114.3; 171.4; 228.6; 285.7 grams, which reduces to the following simple ratio: 1 : 2 : 3 : 4 : 5. In the case of hydrogen and oxygen the quantities of oxygen found in combination with the same quantity of hydrogen are in the ratio of 1 : 2. Hence from the above the following general statement may be made:

When an element combines with another element or group of elements to form different compounds, the masses of the first element that combine with a given mass of the other element or group of elements are in some simple ratio to one another.

The Law of Reciprocal Proportions

In the above examples of ratios between the elements lead and oxygen, we expressed the amount of oxygen that combined with 100 parts by weight of lead. We could have expressed the ratio by stating the amount of lead that combined with 1, or 10, or 100 parts of oxygen. The same is true in the case of oxygen and nitrogen; either element might have been selected as the unit of comparison, in any convenient quantity. Further, if the ratio of the two elements, nitrogen and oxygen, is established, and also the ratio of hydrogen and oxygen, the ratio of hydrogen and nitrogen can readily be ascertained by calculation. Again, if the ratio of hydrogen and chlorine be determined and the other two ratios, nitrogen to oxygen and oxygen to hydrogen, then the cross-relation between chlorine and nitrogen can be calculated. This relation can be illustrated in the case of chlorine, iodine, and silver. Let us compare the ratios of the amounts of these elements that combine with equal amounts of silver, say 75.26 parts. In silver chloride we have 24.74 per cent chlorine and 75.26 per cent silver; in silver iodide we have 54.04 per cent iodine and 45.96 per cent silver; in chlorine iodide we have 21.84 per cent chlorine and 78.16 per cent iodine.

Then from the proportion

Iodine : Silver : : Iodine : Silver

we have 54.04 : 45.96 : : x : 75.26.

From which

$$x = \frac{54.04 \times 75.26}{45.96} = 88.49$$

the amount of iodine that would combine with 75.26 parts of silver. Since 24.74 parts of chlorine combine with this same amount of silver, 88.49 parts of iodine would be equivalent to 24.74 parts of chlorine. One part of iodine will be equivalent to $\frac{24.74}{88.49} = 0.279$ part of chlorine. In the direct combination of chlorine and iodine we have the ratio of 21.84 parts of chlorine : 78.16 parts of iodine, or $\frac{21.84}{78.16} = 0.279$ part of chlorine, uniting with one part of iodine, which is the same ratio as above. By a similar method these cross-relations can be calculated between all of the elements, and it is this relation that is known as the *Law of Reciprocal Proportions*, or the *Law of Equivalents*. It may be expressed as follows:

When different elements are combined successively with any other, or with a group of others, the masses of the former that are combined with a given mass of the latter are to one another in the same ratio in which these different elements combine with any other element or group of elements.

From our consideration of the previous laws, and our information concerning chemical compounds, it is evident that we have to distinguish between equal quantities of the constituents of a compound and equal *chemical* quantities of the constituents. In the compounds cited above, silver chloride, for instance, contains 75.26 per cent of silver and 24.74 per cent of chlorine, *i.e.* these quantities of silver and chlorine are equal chemically. In the chemical sense, then, the *equal* quantities of matter are the weights or masses which unite with each other chemically. The amounts of the different substances that unite chemically are chemically equivalent and depend entirely upon the specific nature of the substances.

Units of Chemistry

We employ *symbols* to represent the elements and a combination of symbols in the form of a *formula* to represent the composition of a compound. For example, water is composed of hydrogen and oxygen, and hydrogen peroxide is composed of hydrogen and oxygen. We use H to represent the element hydrogen and O to represent the element oxygen; then the combination HO represents both water and hydrogen peroxide, but not their composition. By analysis we know that water contains 88.85 per cent of oxygen and 11.15 per cent of hydrogen, and hydrogen peroxide 5.91 per cent of hydrogen and 94.09 per cent of oxygen. In water the ratio is 11.15 : 88.85. Then the amount which combines with 94.09 parts of oxygen in the hydrogen peroxide would be $11.15 : 88.85 : : x : 94.09$. Solving for x we have 11.82 parts. The quantities of hydrogen combining with the same quantity of oxygen, 94.09 parts, are 11.82 parts and 5.91 parts, which are in the ratio of 2 : 1. That is, there are two different quantities of hydrogen combining with the same quantity of oxygen to form these two different chemical substances, water and hydrogen peroxide. The hydrogen has two combining weights or equivalents. We could use this weight of oxygen as our unit quantity and represent it by the symbol for oxygen, O, or we could select any other quantity arbitrarily. The quantity that has been selected arbitrarily is 16, and so we shall arbitrarily select as our *symbol weight of oxygen*, 16 grams. Then the equivalent weights of hydrogen would be 2 in the compound water and 1 in the compound hydrogen peroxide. Then the formulæ for these substances could be written respectively H_2O and HO, if we let the symbol H represent the smaller amount of hydrogen combining with the 16 grams of oxygen, thus avoiding a fractional part of the symbol weight were we to select the larger value $H = 2$.

From 34 grams of hydrogen peroxide we can obtain 16 grams of oxygen and 18 grams of water at the same time. This 18 grams of water on decomposition will yield 16 grams of oxygen and 2 grams of hydrogen; that is, the oxygen of hydrogen peroxide can be separated into two equal quantities, but the oxygen in the water cannot be thus separated, for we obtain free hydrogen and free oxygen. From this we assume that the oxygen in water is in the simplest amount possible and is the quantity represented by our symbol weight of oxygen, O, while in the peroxide there is twice this quantity, or O_2.

In the decomposition of hydrogen peroxide we find that all of the hydrogen present remains with one part of the oxygen and is the same as that in the water. Now if we treat water with sodium, we obtain free hydrogen and a compound, sodium hydroxide, which upon analysis gives sodium, oxygen, and hydrogen, — all of the oxygen of the water appearing in this compound and the hydrogen of the water separating into two equal parts, one part appearing free and the other in combination with the oxygen and sodium. The formula for water must show that the hydrogen can be divided; therefore, the formula becomes H_2O. Similarly, the formula for hydrogen peroxide must show that it contains the same amount of hydrogen as in water and also that the oxygen contained can be divided; hence the formula for hydrogen peroxide becomes H_2O_2, instead of HO, which we saw represents the chemical composition as well.

A chemical formula is a combination of symbols wherein each symbol represents that equivalent quantity of the element which we cannot further divide by chemical transformations. These chemical formulæ are the result of experiment and are designated the *empirical* formulæ. If our method is good, only integral multiples of the chemical units represented by symbols enter into and go out of combination. The *symbol weight* of oxygen is defined as 16 grams of oxygen, and the symbol weight of hydrogen is then 1. The sum of the symbol weights is designated the *formula weight.* This is usually called the molecular weight. For example, the formula we derived for the water is H_2O; two symbol weights of H = 2 and one of O = 16 and the sum 18 is the formula weight for water.

The symbol weight of other elements may be determined in a similar manner. Carbon when burned in air forms two oxides which are compounds of oxygen and carbon; by analysis one contains 12 grams of carbon and the other 6 grams of carbon in combination with 16 grams of oxygen. So the formulæ would be C_2O and CO or CO and CO_2 respectively, depending upon whether we select 12 or 6 as the equivalent weight of C. Since carbon has two combining weights, it is necessary for us to have more data in order to decide which we shall select as the symbol weight. Either of the formulæ would represent the chemical composition and would be designated an empirical formula.

In the case of nitrogen, we have five different compounds of nitrogen and oxygen. Expressed in terms of the quantities of nitrogen in combination with 16 grams of oxygen, we have 28, 14, $9\frac{1}{3}$, 7, $5\frac{3}{5}$ grams of nitrogen respectively, *i.e.* we have five different combining weights of nitrogen, and the question arises, which of these equivalent weights shall be selected as the symbol weight of nitrogen?

The answer to this question is obtained by a consideration of the volume relations of gaseous compounds and of the elements entering into the reactions. These volume relations are summed up by *Gay Lussac's Law of Combination by Volume*, which is stated as follows: *When reacting gaseous elements combine, the volumes of the different gases under the same conditions of pressure and temperature are in simple ratio to one another and to the resulting products.*

Taking the volume of 16 grams of oxygen as the unit volume under specified conditions of temperature and pressure, we find experimentally under these same conditions of temperature and pressure the following volume relations between the reacting substances and the resulting product:

Hydrogen	+	Oxygen	=	Water
2 grams		16 grams		18 grams

1. 

2 vols.	+	1 vol.	=	2 vols.

Chlorine	+	Hydrogen	=	Hydrochloric acid
35.5 grams		1 gram		36.5 grams

2. 

1 vol.	+	1 vol.	=	2 vols.

Nitric oxide	+	Oxygen	=	Nitrogen peroxide
30 grams		16 grams		46 grams

3. 

2 vols.	+	1 vol.	=	2 vols.

Hydrogen	+	Nitrous oxide	=	Water	+	Nitrogen
2 grams		44 grams		18 grams		28 grams

4. 

2 vols.	+	2 vols.	=	2 vols.	+	2 vols.

	Nitrogen	+	Hydrogen	=	Ammonia
	14 grams		3 grams		17 grams
5.					
	1 vol.	+	3 vols.	=	2 vols.

In No. 1 we observe that since 16 grams of oxygen is the arbitrarily selected symbol weight and the quantity of hydrogen represents 2 symbol weights of hydrogen the product, 18 grams of water, is represented by the formula H_2O. We notice that the formula weight of water occupies twice the volume of the one symbol weight of oxygen, while two symbol weights of hydrogen occupy the same volume as the formula weight of water or twice the volume of one symbol weight of oxygen. From an examination of the weights of these various compounds used and produced in these five examples, it will be noticed that the volume occupied by the formula weight of water (2 vols.) is the same as that occupied by the formula weights of the other compounds: hydrochloric acid, nitric oxide, nitrogen peroxide, nitrous oxide, and ammonia. That is, *the formula weight of every gaseous compound considered above occupies the same volume.* We can generalize and state that the formula weight of all gaseous compounds occupies the same volume under the same conditions of temperature and pressure. This may be the same as the empirical formula, which is taken as the simplest formula, or it may be some integral multiple of the empirical formula.

Experimentally, it has been found that 16 grams of oxygen at 0° C. and under 760 mm. mercury pressure occupies 11.2 liters. Under these conditions of temperature and pressure 22.4 liters is therefore the volume occupied by the formula weight of the gaseous compounds. This volume is termed the *formula volume.*

The formula of a compound is, then, a combination of symbols that represents the percentage composition of the compound and such that the formula weight in grams of the compound in the gaseous state occupies 22.4 liters of space under standard conditions. A formula is, therefore, *purely an arbitrary affair*, subject to definition. It follows then that we can have a formula of an element; thus O_2 is a combination of two symbol weights of oxygen representing 32 grams of oxygen and occupying 22.4 liters under standard conditions of temperature and pressure. Similarly the formula of hydrogen is H_2, of chlorine Cl_2, of nitrogen N_2.

Rewriting the above reactions, employing formulæ for the reacting substances and products, we have:

1. $2\,H_2 + O_2 = 2\,H_2O$
   2 vols. + 1 vol. = 2 vols.

2. $Cl_2 + H_2 = 2\,HCl$
   1 vol. + 1 vol. = 2 vols.

3. $2\,NO + O_2 = 2\,NO_2$
   2 vols. + 1 vol. = 2 vols.

4. $H_2 + N_2O = H_2O + N_2$
   1 vol. + 1 vol. = 1 vol. + 1 vol.

These chemical equations represent the chemical reaction and the quantities by weight of the reacting substances. The *coefficients* of the formulæ appearing in the equation are the same as the *number of volumes* of the compounds in the gaseous state.

Experimentally, we have developed that *equal volumes of substances in the gaseous state contain the same number of formula weights of the compounds.* (This is Avogadro's Law.)

We have also established the following rule for checking the symbol weight of an element: Determine the weights in grams of the designated element in 22.4 liters, under standard conditions, of the gaseous compounds of that element. The greatest common divisor of all these numbers is the symbol weight of the element.

CHAPTER III

THE GAS LAW

THROUGH whatever chemical change a substance passes, the mass of it remains the same. The same may be said concerning physical transformations as well. If a definite mass of a gas is selected under a specific temperature and pressure, it will occupy a definite volume. If, however, this definite mass be subjected to different pressures and temperatures, the volume which it occupies may vary greatly, and hence the volume which this constant mass occupies depends upon the pressure and temperature; that is, the values for the pressure, p, the temperature, t, and the volume, V, are so related to one another that simultaneous values of any two determine the functional relation. This may be expressed mathematically, $V = f\ (p, t)$. This equation is known as the *Equation of State*. In the functional relation the volume which a given mass occupies depends upon the temperature and pressure. The pressure, p, and the temperature, t, are spoken of as the independent variables, and the volume, V, as the dependent variable, because its value depends upon the values arbitrarily selected for p and t. By keeping one of these independent variables constant it is possible to determine what relation exists between the dependent variable and the other independent variable.

1. Assume a constant mass of gas.

The volume which it occupies depends upon p and t. Then V is a dependent variable.

If we assume t and the mass constant, V depends on p.

Let volume at pressure p be V and the volume at pressure p_1 be V_1.

Now by experiment we find that if 1000 cc. of gas is at 500 mm. pressure, then the volume will be 500 cc. if the pressure is increased to 1000 mm. That is,

1000 cc. : 500 cc. : : 1000 mm. : 500 mm.

or

$$V : V_1 : : p_1 : p.$$

If the temperature is constant, the volumes are inversely proportional to the pressures. This is *Boyle's Law*.

2. Now assume pressure and mass constant and vary the temperature. Gay Lussac found experimentally that if 100 cc. of gas at 0° C. were heated, the volume was 136.65 cc. at 100° C. or an increase of 36.65 cc. for a change of 100° C., or 0.3665 cc. for 1°. The change for 1 cc. is $\frac{1}{100}$ of this, or 0.003665 cc. That is, for every increase of one degree centigrade the volume is increased this proportional amount, or 1 cc. increases 0.003665 cc. per degree C. But 0.003665 = 1/273. Any volume of gas at 0° C. will increase for any number of degrees of change of temperature $\frac{t}{273}$ times the original volume.

Let V_0 = volume of mass of gas at t_0, at pressure p_0.

V = volume of mass of gas at t, and at the same pressure.

Then $V - V_0$ = increase in volume

and $t - t_0$ = change in temperature.

But a gas increases 1/273 of the original volume per degree; then 1/273 times V_0 = increase in volume per degree.

$t - t_0 \times \frac{V_0}{273}$ = increase for change of temperature $t - t_0$ on the centigrade scale.

But the increase in volume is $V - V_0$,

hence $V - V_0 = \frac{t - t_0}{273} \times V_0$ which becomes $\frac{V - V_0}{V_0} = \frac{t - t_0}{273}$.

We are expressing our temperature as temperature differences on the arbitrarily selected centigrade scale.

The equation $\frac{V - V_0}{V_0} = \frac{t - t_0}{273}$ could be simplified mathematically if we were to take $t_0 = 273$ and substitute in the above equation. The zero of the centigrade scale then would become 273 centigrade divisions above the zero point on our new temperature scale. This new point is known as the Absolute Zero and is found to be practically the same as the Absolute Zero on the thermodynamic scale. The readings on the centigrade scale equal $273 + t$ on the Absolute scale, or $T = T_0 + t$. Now having assigned these values, the equation becomes $\frac{V - V_0}{V_0} = \frac{T - T_0}{T_0}$, from which we obtain $\frac{V}{V_0} = \frac{T}{T_0}$ or $V : V_0 : : T : T_0$ which states that the volumes of a given mass of gas under constant pressure are directly proportional to the Absolute temperatures. This is *Charles'* or *Gay Lussac's Law.*

These two laws can be combined into one expression by assuming a constant mass of the gas: and then (1) with the temperature constant, change the pressure; and then (2) with the pressure constant, change the temperature.

Assuming the mass constant and the temperature constant, then let V_0 = the volume of the gas at pressure p_0 and temperature T_0.

V_1 = the volume of the gas at pressure p_1 and temperature T_1.

Then according to Boyle's Law

$$V_0 : V_1 : : p_1 : p_0.$$

Solving for V_1, we have

$$V_1 = \frac{V_0 p_0}{p_1}.$$

Now change the temperature on this new volume keeping the pressure constant, $p_1 = p_2$; we have according to Charles' or Gay Lussac's Law:

$$V_1 : V_2 : : T_1 : T_2 \text{ or } V_1T_2 = V_2T_1.$$

Substituting the value of $V_1 = \frac{V_0p_0}{p_1}$ we have $\frac{V_0p_0T_2}{p_1} = V_2T_1$.

Now eliminate intermediate values and remember $T_0 = T_1$ and $p_1 = p_2$. We have $\frac{V_0p_0T_2}{p_2} = V_2T_0$. Rearranging, we have

$$\frac{V_0p_0}{T_0} = \frac{V_2p_2}{T_2},$$

which is an expression for the combined laws of Gay Lussac and Boyle.

Now it is possible to change these last values to new ones and obtain similarly the same relation. $\frac{V_2p_2}{T_2} = \frac{V_3p_3}{T_3}$, or in general the initial volume multiplied by its corresponding pressure divided by its corresponding temperature, is equal to any other volume times its corresponding pressure divided by its corresponding temperature. $\frac{V_0p_0}{T_0} = \frac{Vp}{T}$, which is constant,

$$\text{or} \qquad \frac{Vp}{T} = \textit{constant}: \; Vp = KT. \qquad \text{(A)}$$

Another Development of the Gas Law Equation

It has been shown experimentally that if we take a definite mass of gas, the volume it occupies will be dependent on its temperature and pressure. That is, keeping the mass constant,

$V = f(p, t)$ or it may be stated that
$p = f(V, t)$ and also, $t = f(V, p)$.

Gay Lussac showed by experiment that when the volume is constant, the change in pressure is directly proportional to the change in temperature. Assuming this to be true for the entire range of temperature and pressure the functional relation $p = f(V, t)$ is expressed by the equation

$$p - p_0 = k(t - t_0) \qquad (1)$$

where k may be a function of the volume.

It will be recalled that

$$y = ax + b$$

is the ordinary equation of a straight line, in which a represents the tangent of the angle which the line makes with the x axis and b represents the intercept on the y axis. Any given point (x', y') on this line must satisfy the equation which gives $y' = ax' + b$.

Eliminating b we get

$$y - y' = a(x - x'). \qquad (2)$$

This is the equation of a straight line through the point (x', y') making an angle, whose tangent is a, with the x axis.

Equation (1) is the same form as equation (2). Therefore the equation

$$p - p_0 = k(t - t_0)$$

represents a straight line through a given point (t_0, p_0) making an angle with the temperature axis whose tangent is k.

Since we may arbitrarily select (t_0, p_0), let us assume it to be the melting point of ice under atmospheric pressure. This is the zero on the ordinary centigrade scale. That is, $t = 0$ and $p =$ the pressure of one atmosphere. Substituting $t_0 = 0$ in equation (1) we get

$$p - p_0 = kt. \qquad (3)$$

In Fig. 1 let the melting point of ice (t_0, p_0), on the pressure axis and some distance above the temperature axis, be represented by A. Now we know by experiment that, when the temperature is raised, the pressure is increased. Therefore, any other point representing a greater pressure will be to the right and above the point A, as point B (p_1, t_1). Then the straight line AB through these two points will be the locus of equation (3).

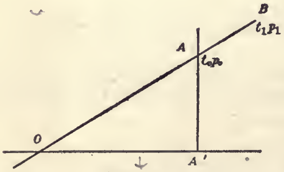


FIG. 1.

The value of p_0 is taken as one atmosphere above absolute zero pressure, as we selected the melting point at the pressure of one atmosphere, but the value of t_0 was assumed without reference to any absolute zero of temperature. Therefore, where the locus cuts the temperature axis is represented the absolute zero of pressure, and it is of some advantage to us, to take the origin of the coördinants at this point O. If we do this, all values of pressures remain the same, but the value of each temperature will be increased by the distance between this point O and the point A', the origin of our old system of axes, *i.e.* the distance OA', which we will designate T_0. So if we refer the temperatures to our new coördinate axis by T, then

$$T = T_0 + t \text{ or } t = T - T_0.$$

Substituting this value in equation (3) we get

$$p - p_0 = k(T - T_0). \qquad (4)$$

Equation (4) may be written

$$p - kT = p_0 - kT_0. \qquad (4')$$

Since the locus of this equation passes through the origin, the coōrdinates (O, O) of the origin must satisfy it.

Substituting, we have

$$o - ko = p_0 - kT_0 \text{ or } p_0 - kT_0 = o.$$

Substituting this value back in equation (4′) it then becomes $p - kT = o$ or

$$p = kT. \qquad (5)$$

This is a simple form of the equation (4) representing the same locus.

Now, equation (4) was developed directly from Gay Lussac's generalization, which, as he showed experimentally, is true for any gas assuming the mass and volume constant. Therefore, equation (5) is true for any gas.

Solving this equation for k, we have

$$k = \frac{p}{T}. \qquad (5')$$

Now Boyle's generalization is, that keeping the mass and temperature constant, the pressures are inversely proportional to the volume; or as we saw, $V : V_1 :: p_1 : p$ which becomes $Vp = V_1p_1$, or keeping the mass and temperature constant the product of the volume and pressure is a constant, *i.e.* $pV = K_1$, or $p = \frac{K_1}{V}$, the pressure is inversely proportional to the volume.

Applying this generalization to (5′) we have $k = \frac{\frac{K_1}{V}}{T}$, and remembering that T is constant we then have $k = \frac{K_1}{V}$. This means that k is constant only when the mass and volume are constant; but that when the volume is increased, k is decreased.

Substituting this value of k in equation (5), we have $p = \frac{K_1}{V} T$ or

$$pV = K_1 T. \tag{6}$$

Discussion of the Constant of The Gas Law

Equation (A) is developed from Boyle's and Gay Lussac's generalization, assuming a constant mass. This is true, however, only in the case of a true gas, which is a hypothetically perfect gas, wherein the internal energy is dependent on the temperature only. Oxygen, hydrogen, air, and nitrogen so nearly conform to perfect gases that for practical purposes they may be considered as ideally perfect and obeying the laws of perfect gases.

The equation

$$K = \frac{pV}{T} \tag{1}$$

means that if the volume of a given mass of gas is changed, the pressure or the temperature, or both temperature and pressure, must change so that the pressure multiplied by the volume divided by the absolute temperature shall always be the same.

By experiment we find that keeping the pressure and temperature constant, the volumes of different masses of the same gas are directly proportional to the masses, *i.e.* $V : V_1 : : M : M_1$, where V is the volume of mass M, and V_1 is the volume of mass M_1. So, different masses of the same gas have different values of K. Also, by experiment, we know that equal masses of different gases have different volumes under the same conditions of temperature and pressure. In general, then, we must use different values of K for equal masses of the different gases.

The value of K for unit mass of a given gas is denoted by r. Let us denote the volume of unit mass of a gas by v, then equation (1) becomes

$$pv = rT. \tag{2}$$

Since r has different values for different gases, the gas must be specified when using equation (2), and r is called the *specific gas constant*.

It follows, then, that K for any mass M is equal to Mr or

$$K = Mr. \tag{3}$$

If we choose the masses of the different gases so as to give the same volumes at the same temperature and pressure, K has the same value for every gas, according to equation (1). By experiment we find that the molecular weight of every chemical compound in the gaseous state occupies the same volume at a definite pressure and temperature.

If the molecular weight of a gas is chosen, the value of K is denoted by R. If m is the molecular weight, then from equation (3)

$$R = mr \tag{4}$$

and equation (1) becomes

$$pV = RT. \tag{5}$$

Since the value of R is the same for all gases, R is called the *Universal Gas Constant*.

The molecular weight of a compound in grams is called the *gram-molecular* weight, or *mole*. If any number of moles, n, are used, the more general form of the equation is

$$pV = nRT. \tag{6}$$

Since $n = \frac{g}{m}$, where g is the weight in grams, we may substitute in equation (6) and obtain

$$pV = \frac{g}{m} RT. \tag{7}$$

Solving equation (5) $pV = RT$ for R, we have $R = \frac{pV}{T}$. But we saw that for the same mass of gas under different conditions of pressure and temperature we have $\frac{pV}{T} = \frac{p_0 V_0}{T_0}$, therefore,

$$\frac{p_0 V_0}{T_0} = R.$$

And by definition we have p_0 = the pressure of one atmosphere, which is equivalent to 760 mm. of mercury, *i.e.* to the pressure of a column of mercury of one sq. cm. cross-section and 76 cm. high, or to the weight of 76 cubic centimeters of mercury. Now, since one cubic centimeter of mercury weighs 13.6 grams, 76 cc. will weigh 76×13.6, or 1033.6 grams. The pressure of one atmosphere is therefore equivalent to 1033.6 grams per unit area of one square centimeter. The temperature $T_0 = 273°$ absolute on the centigrade scale, while V_0 is defined as the volume of one gram-molecule of oxygen, O_2, *i.e.* 32 grams of oxygen. Since the weight of one liter of oxygen is 1.429 grams, this volume of oxygen will be $\frac{32}{1.429}$, or 22.4 liters. Therefore, $V_0 = 22.4$ liters, which is designated the *gram-molecular volume.*

Substituting these values in our equation $R = \frac{p_0 V_0}{T_0}$, we have

$$R = \frac{1 \times 22.4}{273} = 0.08204 \text{ liter-atmosphere per degree,}$$

or

$$R = \frac{1033.6 \times 22400}{273} = 84{,}780 \text{ gram-centimeters per degree.}$$

It is customary in Thermodynamics to express the terms in the Gas Law Equation in the English system and the Fahrenheit temperature scale.

If we have a mass of gas at the temperature of melting ice, 32° F., and at atmospheric pressure, then

p_0 = 1 atmosphere = 14.6967 lb. per square inch = 2116.32 lb. per square foot.

T_0 = 491.6° absolute on the Fahrenheit scale.

v = volume of unit weight of the gas (1 pound).

B = characteristic gas constant and is the symbol used in place of r when the English system of units is employed.

Then equation (2) becomes

$$pv = BT. \tag{B}$$

From equation (4) we obtain $R = mB$. If ρ is the mass of unit volume of the gas, we have $v = \frac{1}{\rho}$.

Substituting for v and B their values in equation (B), we obtain

$$\frac{p}{\rho} = \frac{R}{m}T.$$

Solving for R, we get

$$R = \frac{pm}{\rho T}. \tag{C}$$

If m and ρ are known for any gas, R can be calculated.

For oxygen ρ = 0.089222 lb. per cubic foot at atmospheric pressure and 32° F. and $m = 32$.

Substituting in above equation, we have

$$R = \frac{2116.3 \times 32}{0.089222 \times 491.6} = 1544 \text{ ft.-lb. per degree.}$$

The universal gas constant R is then equal to 1544 ft.-lb. per degree.

From this value of R, the characteristic or specific constant B of any gas may be determined if its molecular weight is known.

For carbon dioxide we have $B = \frac{1544}{44} = 35.09$.

It is often convenient to express the density and the volume of unit weight of a gas in terms of the molecular weight m when referred to standard conditions of temperature and pressure.

From $R = \frac{pm}{\rho T}$, we have $\rho = \frac{pm}{RT}$, hence substituting the numerical values

$p = 2116.3$ lb. per sq. ft., $R = 1544$ ft.-lb. per degree, and $T = 491.6°$ F., we have

$$\rho = \frac{2116.3 \times m}{1544 \times 491.6} = 0.002788\ m \text{ lb. per cubic foot per degree.}$$

And for the normal specific volume we have

$$V = \frac{1}{\rho} = \frac{RT}{pm} = \frac{1544 \times 491.6}{2116.3\ m} = \frac{358.65}{m} \text{ cubic feet per pound.}$$

CHAPTER IV

DETERMINATION OF MOLECULAR AND SYMBOL WEIGHTS

THE method employed for the determination of symbol weights at present is virtually that of Cannizzaro, wherein the weight of the gram-molecular volume is obtained for a large number of gaseous compounds containing that element, and the greatest common divisor of these quantities of the element occurring in the gram-molecular volume is selected as the symbol weight of the element and is also termed the atomic weight.

We selected arbitrarily as the unit volume of combination the volume occupied by one gram-molecule of oxygen, *i.e.* 32 grams of oxygen under the standard conditions of temperature and pressure. For the standard conditions we have defined the standard pressure as the pressure of one atmosphere at sea-level and latitude 45°, or 760 mm. of mercury, and the temperature as the zero on the Centigrade scale or 273° absolute. The unit for volume measurements is the cubic centimeter, one thousand of which are designated a liter. The weight of one cubic centimeter of oxygen under standard conditions of temperature and pressure has been determined very accurately and is found to be 0.001429 gram. One liter weighs 1.429 grams. The volume occupied by one gram molecule of oxygen, *i.e.* 32 grams, is $32 \div 1.429 = 22.4$ liters under the standard conditions of temperature and pressure. Hence, we *designate* 22.4 *liters as the gram-molecular volume*, as it is the volume of one gram molecule, *i.e.* the volume which the molecular weight of a gas expressed in grams would occupy under standard conditions.

Density Relations. — We have seen that $pV = nRT$ holds generally for gases. Let us assume that it does for those with which we are dealing, and let g_s = grams of a gaseous body we select as our standard, g = grams of some other gas measured at the same pressure and temperature, and occupying the same volume as the standard, m_s the weight of a gram-molecular volume, 22.4 liters of the standard, m the weight of a gram-molecular volume, 22.4 liters of the other gas. From the definition of the number of formula weights of any gas we have $n_s = \frac{g_s}{m_s}$ for the standard, and $n = \frac{g}{m}$ for the other gas. Substituting, the Gas Law Equation becomes

$$pV = \frac{g_s}{m_s} RT, \qquad (1)$$

and

$$pV = \frac{g}{m} RT. \qquad (2)$$

Solving, $$\frac{pV}{RT} = \frac{g_s}{m_s} \text{ and } \frac{pV}{RT} = \frac{g}{m}; \therefore \frac{g_s}{m_s} = \frac{g}{m}.$$

Solving this for m, we have $m = \frac{g}{g_s} m_s$. But since $s = \frac{g}{g_s}$, we have $m = sm_s$.

Since air obeys the Generalized Gas Law very closely, it is considered for this reason a very good standard. The weight of air has been determined very accurately, and it has been found that one liter of air at 0° C. and 760 mm. pressure at sea-level in the latitude of 45° weighs 1.293 grams. If one liter under standard conditions weighs 1.293 grams, then 22.4 liters, the gram-molecular volume, weighs 28.96 grams. If we now substitute this value for m_s in the equation above, we have $m = s \times 28.96$. That is, the molecular weight of a gas is equal to its specific gravity expressed in terms of air multiplied by 28.96, which is the weight of 22.4 liters of our standard (air). So, to determine the molecular weight of a gaseous substance we need only determine its specific gravity with respect to air, and multiply this by 28.96. This is nothing more than finding the weight of the gas that would occupy one gram-molecular volume under standard conditions.

It is not even necessary to determine the specific gravity with respect to air, but any other gas may be used as a standard. In that case, however, we have to multiply the specific gravity with reference to that particular gas as a standard, by an entirely different factor. For instance, if we use hydrogen as our standard, the weight of the gram-molecular volume, 22.4 liters of hydrogen, is 2.016 grams, and the equation would then become $m = s_H \times 2.016$. If we use oxygen as the standard, we have $m = s_O \times 32$, *i.e.* the specific gravity of the gas with reference to oxygen multiplied by 32 is equal to the molecular weight of the gas.

From what has preceded, in order to determine the molecular weight of a gaseous body, all we need to do is to determine the specific gravity, and from this to calculate the amount by weight that will occupy the gram-molecular volume, 22.4 liters, under the standard conditions of temperature and pressure. This number we call the formula weight, or *molecular weight.*

The two chief methods for the determination of vapor densities are the Dumas method and the Victor Meyer method. Only a brief description of the principles of these methods will be given. The technique of the operations may be found in the laboratory manuals on physico-chemical methods.

Dumas' Method. — A weighed glass bulb of about 200 cc. capacity, into which some of the substance has been introduced, is immersed in a water-bath, the temperature of which is kept about 30° above the boiling-point of the substance. When the substance is all in the form of vapor, the end of the bulb is sealed, at which time the temperature of the bath is recorded, and also the barometric pressure. The bulb is then removed, cooled, and weighed, and the weight of substance found. By filling with water at known temperature and weighing, the weight of the water is found by difference. The volume which this weight occupies is found from tables of densities of water at different temperatures. Then, knowing the volume, temperature, and weight of the substance, and the barometric reading, the density and specific gravity can readily be calculated. This method is but little used at present.

The Victor Meyer Method. — The Victor Meyer method consists in measuring the increase in volume of a quantity of air, caused by introducing into it a weighed quantity of the substance whose density is to be determined, and vaporizing it. The vaporized substance displaces an equal volume of air, and this displaced volume of air is collected and measured, and at the same time its temperature and the barometric pressure are observed and recorded. This then gives the weight of the substance taken, and the volume, temperature, and pressure, from which the density, specific gravity, and the molecular weight can readily be calculated.

Molecular Formulæ and Formula Weight. — Having just seen how the molecular weight of a gaseous substance can be obtained, we can ascertain the formula which expresses not only the relative quantities of the component elements, but also the weight of the substance which occupies a gram-molecular volume. Such formulæ we designate as *molecular formulæ*, and they are now employed to represent the quantity of the substance designated by the molecular weight, whether it exists in the gaseous, liquid, or solid condition. Suppose benzene is found by analysis to contain 92.25 per cent of carbon and 7.75 per cent of hydrogen.

Then in every 100 g. of the substance we should have as many symbol weights of carbon as $\frac{92.25}{12.00}$, or 7.69, and of hydrogen as $\frac{7.75}{1.008}$, or 7.69. That is, for every symbol weight of carbon there is one of hydrogen; there are the same number of symbol weights of the two elements. Assuming the simplest number present, the *empirical formula* is CH. The specific gravity of benzene with respect to oxygen is 2.47 at 100° C. The molecular weight is, therefore, $2.47 \times 32 = 79.04$, which is nearly six times the sum of the symbol weights of carbon and hydrogen as represented by the empirical formula. The *molecular formula* is therefore C_6H_6, and the molecular weight is 78.06.

Symbol Weight. — The symbol (or atomic) weight of an element may be deduced from the molecular weights of its gaseous elements in the following manner: In order to ascertain the symbol weight of hydrogen a large number of gaseous compounds are selected which contain hydrogen, and the molecular weight of these substances is ascertained from density and specific gravity determinations. In Table I are given the names of the substances, in the second column the molecular weights, *i.e.* the grams of the substance that occupy 22.4 liters under standard conditions of temperature and pressure, while in the third column is given the number of grams of hydrogen found by analysis in the amount of the substance represented by the molecular weight given in the second column. In the last column is the greatest common divisor of the weights of hydrogen in column three, times the factor by which it is multiplied to give the amount of hydrogen in these various gram-molecules of the gases. Now in the case of hydrogen, the greatest common divisor of the quantities of this element appearing in the gram-molecules of these various substances is 1 g.; hence we take the symbol weight of hydrogen to be 1. Proceeding in a similar manner, we can compile tables for other elements such as given for nitrogen.

TABLE I

Hydrogen				Nitrogen			
Compound	1	2	3	Compound	1	2	3
Hydrochloric acid	36.5	1	1	Ammonia	17	14	1 × 14
Hydrobromic acid	81	1	1	Nitric oxide	30	14	1 × 14
Hydriodic acid	128	1	1	Nitrogen peroxide	46	14	1 × 14
Water	18	2	2 × 1	Methyl nitrate	77	14	1 × 14
Hydrogen sulphide	34	2	2 × 1	Cyanogen chloride	61.5	14	1 × 14
Hydrogen	2	2	2 × 1	Nitrogen	28	28	2 × 14
Ammonia	17	3	3 × 1	Nitrous oxide	44	28	2 × 14
Hydrogen phosphide	34	3	3 × 1	Cyanogen	52	28	2 × 14
Methane	16	4	4 × 1			G. C. D. = 14	
Ethane	30	6	6 × 1				
		G. C. D. = 1					

In general, if an element has a large number of volatile compounds whose molecular weights can be obtained from their vapor densities, the symbol weight may be obtained in the manner just illustrated. As the weights of the element that are contained in the molecular weights of its compounds must be equal to its symbol weight (atomic weight) [1] or must be multiples of it, if we take the greatest common divisor of these weights, it must be a simple multiple of the symbol weight, or the symbol weight itself. It is hardly probable, however, that where there are a large number of volatile compounds of the element, the common divisor is a multiple of the symbol weight, but it is possible that another substance may be discovered, the molecular weight of which contains a weight of the given element which is not a multiple of our greatest common divisor. Thus the symbol weight as determined in the manner indicated above would

[1] The term *symbol weight* has been used in this book for what is usually termed *atomic weight*. Atomic weight is discussed in the following chapter.

not be the true one; however, those so obtained have a high degree of probability.

If, however, there are but very few volatile compounds containing the element, which are available for vapor density determinations, the method may fail. There are a number of other methods, however, for obtaining the molecular weight of substances, and these values may be used in our tabulations just as well as those obtained through the vapor density relations.

Some of the more recently discovered elements, the gases argon, helium, xenon, etc., are supposed to be elementary, and to contain only one symbol weight in their gram-molecular weight. As they form no compounds, we cannot use the method just suggested for determining the symbol weights. If, however, we remember that the molecular weight is the weight of the substance that occupies 22.4 l. under standard conditions of temperature and pressure, we can find the molecular weight by ascertaining the number of grams of the gas that are contained in a gram-molecular volume.

We have just seen that by our volumetric method we may determine which of several quantities is the correct one for the symbol weight of an element; but in order to determine these values with a high degree of accuracy, it is necessary to employ quantitative gravimetric methods. By the above methods it is possible to determine which of a number of values is the correct one for both the symbol weight of elements and also the molecular weight of the compounds.

The International Committee on Atomic Weights publishes periodically a table of values, which it designates the Atomic Weights, based upon the unit of oxygen taken as 16 and representing *relative* weights.

CHAPTER V

ATOMIC AND MOLECULAR THEORIES

From observed experimental scientific facts, conjectures are made as to how other substances react and these are employed as the starting point for additional experimentation and investigation. This is regarded as a *working hypothesis*. While a hypothesis is a tentative speculative conjecture of the causes for the observed facts, it is an assumption which goes *beyond* these observed facts and is to be used as a basis for their arrangement and classification as well as that of all other facts of the same class.

When a hypothesis explains all of the known facts, then it ranks as a *theory*. A theory is defined as " a systematic generalization seriously entertained as exclusively or eminently accounting for a series or group of phenomena." As soon as a number of facts are collected which the theory does not accord with or explain, the theory becomes untenable, and a new one has to be formulated which will harmonize with the known facts. We have hypotheses and some theories undergoing frequent changes, as they always contain *unproved assumptions*.

How our path of progress is blazed out and marked is indicated by the following quotations from two noted pioneer investigators.

Tyndall states: " We are gifted with the power of imagination, and by this power we can enlighten the darkness which surrounds the world of the senses. Bounded and conditioned by coöperant reason, imagination becomes the mightiest instrument of the physical discoverer. . . . By his observations and reflections in the domain of fact the scientific philosopher is led irresistibly into the domain of *theory*, his final repose depending on the establishment of absolute harmony between both domains."

Faraday wrote: "The world little knows how many of the thoughts and theories which have passed through the mind of an investigator have been crushed in silence and secrecy by his own severe criticism and adverse examination; that is, in the most successful instances not a tenth of the suggestions, the hopes, the wishes, and the preliminary conclusions are realized."

The Atomic Theory

That matter is not continuous, but composed of minute, indivisible particles or atoms is a very ancient idea. This idea was purely speculative and not founded on observation or experiment. Democritus (460 B.C.) attributed the difference in substances to the atoms of which they are constituted, and these atoms he considered to be different in size, shape, position, and motion. Lucretius (50 A.D.) formulated the ideas of the atomic constitution of matter in practically the form in which it is familiarly expressed to-day. The following are his conclusions:

1. In a solid the atoms are squeezed closely together; in a liquid the atoms are similar and less closely packed; while in a gas there are but few atoms and they have considerable freedom of motion.

2. Atoms are imperishable, of a finite number of different shapes, each shape being infinite in number.

3. The atoms are always in motion and move through space at a greater speed than sunlight.

4. The properties of substances depend upon the manner in which the atoms combine.

During the seventeenth century the atomic conception of the composition of matter was very popular and was employed by Bacon, Boyle, Hooke, and others. Newton showed that Boyle's law of gases must necessarily follow from this assumption.

The two Irish chemists, Bryan Higgins (1737–1820) and his nephew and pupil, William Higgins (1765–1825), were among the first to seek quantitative relation between the atoms and to attempt to determine the number of atoms which combined to produce a new compound. They concluded that combinations took place most readily between the single ultimate particles of two substances, and William Higgins emphasized the law of multiple proportions, and also the greater stability of the products formed by the union of these single particles (atoms).

These views are substantially the same as those formulated later by Dalton, as early as 1803. The Daltonian Atomic Theory was based on facts obtained by experiment and was Dalton's method of explaining these weight relations that he had obtained.

Dalton's Atomic Theory is stated as follows:

1. Atoms are the smallest ultimate particles attainable and therefore cannot be subdivided by any known chemical means.

2. An elementary substance is composed of an enormous number of these particles, called atoms, which are of the same kind and equal in weight.

3. Atoms of different elements have different properties, such as weight, affinity, etc.

4. Chemical compounds are formed by the union of the atoms of different elements in the simplest numerical proportions.

In 1808, Dalton in his statement of the atomic theory emphasized how important it is to be able to arrive at a knowledge of the relative weights of these ultimate particles which combine to form compounds, and that these relative weights serve as a guide in obtaining the composition of other substances. These relative weights he collected in 1803 in what was termed a Table of Atomic Weights.

Dalton considered atoms, the ultimate particles of compounds, as the ultimate particles of elementary substances. He assumed for example that one atom of hydrogen unites with one atom of oxygen to produce one atom of water. In the development of these atomic weight relations many discrepancies arose which were difficult to reconcile. Gay Lussac presented his Law of Combining Proportions by Volume (about 1801–08), which is, that the weights of equal volumes of gaseous substances are proportional to their combining weights or, as Dalton called them, atomic weights.

It has been shown that definite quantities by weight of certain substances called elements unite to form new substances termed compounds; it has further been demonstrated that when one element combines with another in two or more different ratios forming different substances, the quantities of the first element combining with a unit quantity of the second are in simple, integral ratios. It has further been shown by Gay Lussac, and has subsequently been confirmed, that when reacting gaseous elements combine, the volumes of the different gases under the same conditions of pressure and temperature are in simple ratios to one another and to the resulting gaseous product. The following facts will serve as examples:

I. 1. The combination of one volume of chlorine, bromine, or iodine with one volume of hydrogen to form two volumes of the resulting compound.

2. The combination of one volume of chlorine with one volume of iodine to form two volumes of the resulting compound.

3. The substitution of chlorine, bromine, iodine, fluorine, and cyanogen in many organic compounds are reactions of equal volumes.

II. 1. The combination of one volume of oxygen, or one volume of the vapor of sulphur or selenium, with two volumes of hydrogen to produce two volumes of the resulting product.
2. The combination of one volume of oxygen with two volumes of chlorine.
3. The combination of one volume of oxygen with two volumes of nitrogen.

III. 1. The combination of one volume of nitrogen with three volumes of hydrogen to form two volumes of the resulting product.
2. The combination of one volume of nitrogen with three volumes of chlorine.

As illustrated above, if a definite volume of hydrogen combines with chlorine, it has been shown experimentally that this volume of chlorine is the same, under the same conditions of temperature and pressure, as that occupied by the hydrogen with which it combined. We have seen that the law of combination by weight holds true and that it is absolutely exact. There must, therefore, be some weight relation existing between these volume relations, since they combine with one another in such simple integral ratios. If we take the quantity of oxygen that is equivalent to the arbitrarily selected amount of our arbitrarily selected Unit of Reference, and the same volume of hydrogen under the same conditions of temperature and pressure, we shall find that the oxygen weighs 15.88 times as much as the hydrogen. If we take 16 g. of oxygen, the same volume of hydrogen will weigh 1.008 g. This same volume of chlorine weighs 35.45 g. and the same volume of nitrogen weighs 14.0 g., it being understood that the volumes are under the standard conditions of temperature and pressure. It will be recalled that these numbers are the same as those representing the symbol weights of the elements hydrogen, chlorine, and nitrogen.

If we take the quantities of gaseous elements equivalent to these weights, called by Dalton atomic weights, the volumes which these occupy under the same conditions of temperature and pressure will be the same. Dalton concluded that in equal volumes of different gases at the same temperature and pressure there *were not* the same number of ultimate particles. Gay Lussac showed that the combining weights (or some multiple) of different substances were proportional to their densities. In 1811 Avogadro accepted this law of Gay Lussac and concluded that *the number of "integral molecules" in equal volumes of all gases is the same for the same temperature and pressure.* Avogadro insisted that if we were to assume the molecules of elementary gases identical with the atoms, the volumetric relations could not be explained, as it would necessitate the subdivision of some of the atoms. It was this particular feature which met with such marked opposition from Dalton and his contemporaries and at that time prevented the acceptance of Avogadro's hypothesis. Hence the existence of small particles of two different orders, the *molecules* and the *atoms*, as advocated by Avogadro, received little notice and the revival of the idea by Ampère in 1814 did not succeed in having it accepted.

For the next forty or fifty years a rather chaotic condition prevailed, and very little progress was made in the development of a system of atomic weights. In 1860 a conference of chemists met at Karlsruhe for the purpose of discussing the subject and eliminating the confusion arising from the use of the four systems of atomic weights then in use. These methods were that of: (1) Dalton, based on weight relations and chemical analysis; (2) Berzelius, based partly on chemical analysis, partly on physical principle (the Law of Isomorphism) and partly on the Law of Combining Proportions by Volume, all of which did not differentiate between atom and molecule; (3) Gmelin's weight method; and (4) Gerhardt and Laurent's method, in which a realization of Avogadro's hypothesis was manifest, and had a far-reaching effect. The work of Cannizzaro, in 1858, revolutionized the atomic weight methods by making Avogadro's hypothesis the basis of his system and thus established our modern system of atomic weights. This work was brought to the attention of those chemists while in session at Karlsruhe.

It was by affirming the universal applicability of Avogadro's supposition that Cannizzaro stated that results are obtained which are in keeping with certain formulated laws of chemistry and physics. Avogadro's method of determination of molecular weights, which had been practically abandoned, was revived by Cannizzaro, who changed the unit to which vapor densities were referred and restated it as follows: "Instead of taking for your unit the weight of an entire molecule of hydrogen, take rather the half of this weight, that is to say, the quantity of hydrogen contained in a molecule of hydrochloric acid."

By using the hypothesis of Avogadro, Cannizzaro examined the relative weights of compounds, the composition of which he determined, and described his method in the following exact terms: "If the body is a compound, it is analyzed and the constant weight-relations of its constituents are determined; the molecular weight is then divided into parts proportional to the relative weights of the compounds, and the result is the quantities of the elements contained in the molecule of the compound, referred to the same unit (namely, the semi-molecule of hydrogen) as is used for the expression of all molecular weights."

Cannizzaro's law of atoms has made it possible to express the composition of molecules in terms of their constituent atoms, for all gaseous and gasifiable compounds, and was stated by him as follows:

By comparing the different quantities of one and the same element which are contained, either in the molecules of the free elements, or in the molecules of its compounds, the following law stands out in relief: "*The different weights of one and the same element contained in the various molecules are* *always whole multiples of one quantity, which is justly called the atom, because it invariably enters the compounds without division.*"

The atom of an element, Cannizzaro said, "is expressed by that quantity of it which invariably enters as a whole into equal volumes of the simpler substance and its compounds; this quantity may be either the whole quantity contained in a volume of the free element or a fraction thereof." However, "In order to determine the atomic weights of any element it is essential to know the molecular weights, and the compositions, of all or most of its compounds."

We then have described by Cannizzaro a clear picture of the interrelations of all the fundamental conceptions of Dalton and Avogadro, which were at their time practically discarded; in this way there was developed a complete theory which "placed the atomic weights of the metallic elements on their present consistent bases." Cannizzaro thus advanced the theory of atomic equivalency, which emphasized "the unchangeability of the proportions between the atomic weights of the bodies which usually replace one another, whatever be the nature and number of the other constituents of the compounds." This is a law which limits the number of possible compounds and more especially applies to all cases of double exchange.

The Molecular Theory

This is the method for the determination of the combining or atomic weights which is employed at the present time, and which is illustrated in the following consideration:

For chemical reasons, chemists have accepted Avogadro's hypothesis, which leads to the molecular structure of matter. This hypothesis, known as the Molecular Theory of Matter, conceives matter as discontinuous and made up of minute particles called molecules. The molecules of the same substance are assumed to be alike in all respects. The molecules are considered to be practically independent, with space between them, and may be defined as "that minute portion of a substance which moves about as a whole so that its parts, if it has any, do not part company during the excursions the molecule makes; and the *molecular* weight is the weight of this ultimate particle referred to the weight of the molecule of a standard substance."

As a working hypothesis this assumption of Avogadro has been very fruitful, as the following illustration indicates.

1. Hydrogen and chlorine unite to produce hydrochloric acid.

Facts. We have determined experimentally:

1. Equal volumes of hydrogen and chlorine react to produce two volumes of hydrochloric acid.

Hydrogen + Chlorine = Hydrochloric acid

1 vol. + 1 vol. = 2 vols.

2. By analysis it has been shown that hydrochloric acid consists of hydrogen and chlorine in the ratio of one symbol weight of hydrogen to one symbol weight of chlorine.

Assumptions.

1. In unit volume let us assume that there are n molecules.

2. According to Avogadro's assumption equal volumes contain an equal number of molecules.

Since there are two volumes of hydrochloric acid, according to Avogadro's hypothesis this volume must contain twice as many molecules of hydrochloric acid as there are molecules of hydrogen in the one volume of hydrogen. That is, one volume of hydrogen contains n molecules of hydrogen, and two volumes of hydrochloric acid contain $2n$ molecules of hydrochloric acid.

It follows that the number of atomic weights of hydrogen in 2 *n* molecules of hydrochloric acid must be the same as in the *n* molecules of hydrogen.

If we assume, for simplicity, that each molecule of hydrochloric acid contains *one* atom of hydrogen, then 2 *n* molecules of hydrochloric acid will contain 2 *n* atoms of hydrogen; but these 2 *n* atoms of hydrogen must have been furnished by the *n* molecules of hydrogen. Therefore, one molecule of hydrogen must contain at least two atoms of hydrogen, and the formula is written H_2, which represents the molecule of hydrogen. Similarly the molecule of chlorine may be shown to contain two atoms, and its formula is Cl_2.

By pursuing a course of reasoning analogous to the above, it may be shown that the molecules of some other gaseous elements consist of at least two atoms. By grouping the symbols of the elements we obtain the formula of the element which represents the molecular weight and indicates the number of atoms of each element present in the molecule.

CHAPTER VI

DEVIATIONS FROM THE GAS LAW AND DISSOCIATION OF GASES

It has already been stated that only for ideally perfect gases does the Gas Law Equation hold, but in the case of O_2, N_2, H_2, and air the deviations are so small for moderate ranges of pressure and temperature that they conform to the laws very closely and therefore may be considered for all practical purposes as perfect gases. Although these deviations are small, they are real, and there must be certain causes which produce these deviations from the theoretical laws.

Deviation from Boyle's Law. — If gases are subjected to very high pressures, the change in volume does not conform

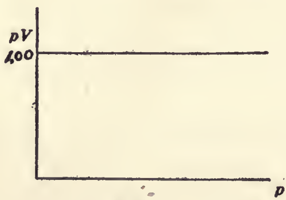


FIG. 2.

to Boyle's Law: $Vo : V :: p : po$, or $Vo \times po = Vp$, or Vp = constant. Or, expressed graphically, we would have the curve as represented in Fig. 2.

But the experimental results of Amagat on the effects of high pressure show that the value of pV is not a constant for different pressures, and this is illustrated by the data given in Table II.

TABLE II — Value of pV at 0° C.

p in Atm.	Hydrogen	Oxygen	Nitrogen	Air	Carbon Dioxide	Ethylene
100	1.069	0.9265	0.9910	0.973	0.2020	0.310
200	1.138	0.9140	1.039	1.010	0.385	0.565
300	1.209	0.9624	1.136	1.097	0.559	0.806
500	1.3565	1.1560	1.390	1.340	0.891	1.256
700	1.504	1.385	1.662	1.602	1.206	1.684
1000	1.7200	1.7350	2.068	1.992	1.656	2.289
	15.4° C.	15.6° C.	16° C.	15.7° C.		
1000	1.893	1.800	2.134	2.062		
1500	2.240	2.357	2.8995	2.661		
2000	2.562	2.888	3.398	3.286		
2500	2.870	3.375	3.990	3.855		
3000	3.162	3.888	4.569	4.398		

These data are represented graphically in Fig. 3.

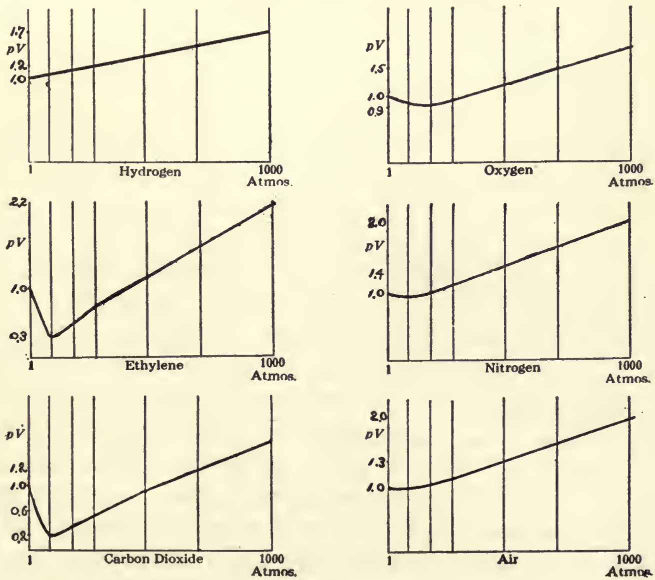


FIG. 3.

From Fig. 3 it is apparent that with increase of pressure the value of pV first decreases, reaches a minimum, and then increases, except in the case of hydrogen, where we have only the portion of the curve representing an increase in the value of pV, which led Regnault to call hydrogen a "more than perfect gas," because the volume was not decreased as much as it should be according to Boyle's Law. That portion of the curve of all gases which represents the high pressure shows that the gases are not compressed as much as they should be according to Boyle's Law.

Confirmation of these results is found in the work of Witkowski, Kamerlingh Onnes and Brook, Ramsay and Young, Barus, and others. The change of the value of pV with the change in p at various temperatures has been obtained by these workers, and this is illustrated in Fig. 4.

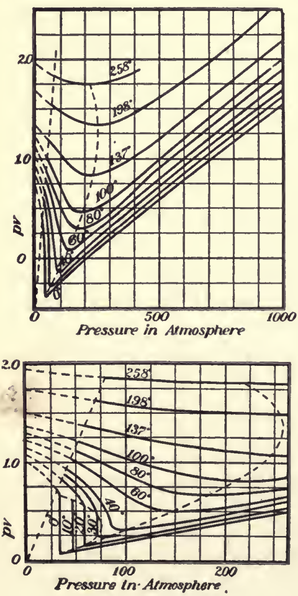


Fig. 4.

It appears, then, that there must be a particular temperature for each gas at which the depression in the isothermal just disappears, so that it is horizontal through a considerable range of pressures. At this temperature a gas follows Boyle's Law exactly, up to a fairly high pressure, and behaves to this extent like an ideal or perfect gas. This is also true for a short distance at and near the minimum value for pV, while at the high pressures the isotherms approximate nearly parallel straight lines.

Low Pressures. — In the case of very low pressures, there is not so marked a variation, and the conformity to Boyle's Law is more marked. Experimentation along this line has been carried out by Mendeléeff, Amagat, Ramsay and Barly, Battelli, Rayleigh, Regnault, Leduc, and others. The conclusion from their work is that in the equation $\frac{pV}{p_1V_1} = b$, where V is the larger volume and p is the smaller pressure, the value of b approaches and finally reaches unity as the pressure falls. In the case of hydrogen the value rises, and for other gases it falls. For the range of pressures of 75 to 150 mm. the differences from unity are quite negligible in the cases of hydrogen, air, and probably nitrogen. There is a slight difference in the case of oxygen, but this difference disappears at still lower pressures. For N_2O the value of b is fairly high between 75 and 150 mm. The following are the values of b obtained by Rayleigh:

	b
Air	0.99997
H_2	0.99997
O_2	1.00024
Argon	1.00021
N_2O	1.00066

While the deviations from Boyle's Law are apparent, they are so small at low pressures that they are difficult to detect, even by very accurate experiments, yet they prove that these gases do not follow Boyle's Law absolutely.

Deviation from Charles' or Gay Lussac's Law. — The coefficient of expansion of gases varies with a change of temperature and pressure. This is emphasized in the case of ethylene in Table III, taken from Amagat's data.

The pressure remaining constant, the horizontal lines in Table III show a variation of the coefficient of expansion with the change of temperature. There is no regularity in the change, but, in general, at higher temperatures the variation is less than at lower temperatures. The vertical columns show a marked decrease in the coefficient of expansion with increased pressure. The minimum value of the coefficient of expansion corresponds closely with the minimum values for pV.

TABLE III — COEFFICIENTS OF EXPANSION OF ETHYLENE

Pressure Meters of Mercury	30°–40°	40°–50°	60°–80°	80°–100°
30	.0084	.0064	.0646	.0040
60	.0166	.0178	.0097	.0067
80	.0121	.0195	.0132	.0088
100	.0079	.0108	.0121	.0100
120	.0062	.0075	.0095	.0082
140	.0048	.0062	.0076	0068
160	.0041	.0057	.0061	.0058
200	.0034	.0043	.0044	.0044
240	.0030	.0035	.0036	.0034
280	.0027	.0031	.0030	.0029
320	.0025	.0027	.0024	.0024

This is in confirmation of the results of Regnault, who showed that *no gas is really perfect*, but he concluded that the coefficients for different gases become more and more nearly equal as the pressure falls, and that the statement that the coefficients are equal may be taken as correct only for very low pressures.

The relations of the coefficient of expansion and the coefficient of increase of pressure are given in Table IV, compiled by Young. At constant pressure, $V_t = V_0(1 + \alpha t)$, where α is the coefficient of expansion; at constant volume, $p_t = p_0(1 + \beta t)$, where β is the coefficient of increase of pressure and p is the constant pressure at which α was determined, and p_0 the initial pressure in the determinations of β.

Gay Lussac believed that all gases had the same coefficient of expansion at constant pressure and that this was 1/273 or 0.0036675 of the original volume at 0° C. and under a pressure of one atmosphere, and since they obeyed Boyle's

Law they therefore all had the same coefficient of increase of pressure (β) at constant volume, *i.e.* $\alpha = \beta$.

TABLE IV

GAS	OBSERVER	α (0°–100°)	p	β (0°–100°)
Hydrogen . .	Regnault	0.003661	1 atmos.	0.003668
Hydrogen . .	Chappuis	0.00366004	1 meter	0.00366254
Hydrogen . .	K. Onnes and Bondin		1 meter	0.0036627
Hydrogen . .	Richards and Marks	0.0036609		
Hydrogen . .	Travers and Jaquerod		700 mm.	0.00366255
Hydrogen . .	Travers and Jaquerod		500 mm.	0.0036628
Helium . . .	Travers and Jaquerod		700 mm.	0.00366255
Helium . . .	Travers and Jaquerod		500 mm.	0.0036628
Nitrogen . . .	Regnault		1 atmos.	0.003668
Nitrogen . . .	Chappuis	0.00367313	1 meter	0.0036744
Nitrogen . . .	Chappuis		530.8 mm.	0.0036638
Air	Regnault	0.003671	1 atmos.	0.003665
Oxygen . . .	Makower and Noble	mean values	663.38 mm.	0.0036738
Oxygen . . .	Makower and Noble		353.99 mm.	0.0036698
Carbon monoxide	Regnault	0.003669	1 atmos.	0.003667
Carbon dioxide	Regnault	0.003710	1 atmos.	0.003688
Carbon dioxide	Richards and Marks	0.0037282		
Sulphur dioxide	Regnault	0.003903	1 atmos.	0.003845
Nitrous oxide .	Regnault	0.003719	1 atmos.	0.003676
				β (0°–1067°)
Nitrogen . . .	Jaquerod and Perrot		240	0.0036643
Air	Jaquerod and Perrot		230	0.0036643
Oxygen . . .	Jaquerod and Perrot		180–230	0.0036652
Carbon monoxide	Jaquerod and Perrot		230	0.0036648
Carbon dioxide	Jaquerod and Perrot		240	0.0036756
Carbon dioxide	Jaquerod and Perrot		170	0.0036713

Chappuis found as the average of the values for the coefficient of expansion of nitrogen 0.00366182, and Berthelot found for the values of hydrogen: 0.00366248, 0.00366206, and 0.00366169. The mean of the values of nitrogen and hydrogen gives 0.00366193, or $\frac{1}{273.080}$, *i.e.* $\alpha = \frac{1}{273.1^\circ}$, or 0° C. = 273.1° absolute.

These variations from the laws of Boyle and of Gay Lussac are but slight in the case of those gases which are difficult to liquefy, such as hydrogen, nitrogen, air, oxygen, etc., but the variations are very pronounced in the case of those which are readily liquefiable, such as sulphur dioxide, carbon dioxide, ethylene, etc. Various efforts have been made to explain these variations from The Gas Law, which we have seen show that at low pressures some gases are too compressible, while under high pressure they are not compressible enough. Among the most fruitful of the explanations offered is the one of van der Waals. There is another type of variation from The Gas Law in the case of certain other gases which give abnormal values for the density with increased temperature. This variation is explained upon the supposition that the gas molecules are dissociated with the formation of new chemical individuals.

Variations from The Gas Law as Explained upon the Basis of Dissociation of the Gas

Attention has been called to the fact that a number of substances do not conform to the Gas Law Equation and that the vapor density determinations give abnormal values for the molecular weights. It was recognized by the earlier workers that the results must be due to abnormal molecular conditions and that Avogadro's hypothesis did not hold for these cases, such as ammonium chloride, phosphorus pentachloride, nitrogen dioxide, etc. Almost simultaneously Cannizzaro (1857), Kopp (1858), and Kékulé (1858) advanced the idea that these abnormal values were due to the decomposition of the substance. This decomposition was termed *dissociation* by St. Claire Deville (1857). This assumption of the dissociation of the gaseous molecules to account for the low density was not readily accepted, and it devolved upon the champions of the idea to prove that dissociation did take place.

The following four typical examples were employed to prove the dissociation of these substances:

1. Deville found on raising the temperature of PCl_5 that at high temperatures the colorless gas became decidedly green. This may be explained by the following equation: $PCl_5 = PCl_3 + Cl_2$; the green color being due to the chlorine gas present.

2. On heating N_2O_4, which is colorless, it becomes dark brown, and on cooling it decolorizes again. Salet showed (1868) that the color varied with the vapor density. Under high pressures approximately normal densities for N_2O_4 are obtained, while at high temperatures and low pressures, values approximating that of NO_2 are obtained, and hence we conclude that the brown color is due to NO_2.

3. Pebael heated ammonium chloride which had been incorporated in an asbestos plug. During the heating a current of air was passed through the tube. By means of litmus paper he proved that an excess of hydrochloric acid was present in one end of the tube, while at the other end ammonia was in excess. Thau used nitrogen instead of air, and by a slight modification of the method confirmed the dissociation of ammonium chloride.

4. In the case of chloral hydrate, Toost proved that the low density was due to dissociation by distilling chloral hydrate (melting point 57° C.), and collecting its vapor in chloroform. Chloral dissolves but the water does not; hence he concluded that the chloral hydrate was dissociated according to the equation

$$CCl_3 \cdot CH(OH)_2 = CCl_3 \cdot CHO + H_2O.$$

The presentation of these data soon resulted in the general acceptance that dissociation was the cause of the abnormal values of the densities.

One of the common applications of dissociation is made use of in cleaning the soldering iron by rubbing it against solid ammonium chloride, the liberated hydrochloric acid acting as the cleaning agent. Commercial hydrochloric acid is now used extensively for that purpose.

Degree of Dissociation. —

Let α = degree of dissociation or per cent dissociation
n = number of molecules
f = number of parts into which each molecule is dissociated
then αn = number of molecules dissociated
$n - \alpha n$ = number of molecules undissociated
αnf = number of parts resulting from dissociated molecules
$n - \alpha n + \alpha nf$ = total number of parts or molecules after dissociation.

Let i denote the ratio of the number of molecules after dissociation to the number of molecules before dissociation,

$$\text{Then} \quad i = \frac{n - \alpha n + \alpha nf}{n} \text{ or } 1 - \alpha + \alpha f \tag{1}$$

$$\text{That is} \quad i = 1 + (f - 1)\alpha \text{ or } \alpha = \frac{i - 1}{f - 1} \tag{2}$$

Let ρ = density before dissociation
ρ_1 = density after dissociation
V = volume before dissociation
V_1 = volume after dissociation
n = number of molecules before dissociation
$n - \alpha n + \alpha nf$ = number of molecules after dissociation.

$$\text{Since} \quad \rho = \frac{\text{mass}}{V}$$

$$\text{and } \rho_1 = \frac{\text{mass}}{V_1}$$

From Avogadro's Hypothesis $\frac{V_1}{V} = \frac{n - \alpha n + \alpha nf}{n}$.

Substituting we have $\frac{\rho}{\rho_1} = \frac{n - \alpha n + \alpha nf}{n} = 1 - \alpha + \alpha f$

and solving for α we have

$$\alpha = \frac{\rho - \rho_1}{\rho_1(f - 1)}. \tag{3}$$

If s is the specific gravity before dissociation and s_1 the specific gravity after dissociation, then from page 5, $\rho = s\rho_s$ and $\rho_1 = s_1\rho_s$. Substituting in formula (3) we have

$$\alpha = \frac{s\rho_s - s_1\rho_s}{s_1\rho_s(f - 1)} \text{ or } \alpha = \frac{s - s_1}{s_1(f - 1)}.$$

$$\text{If } \rho_1 = \frac{\rho}{f}, \text{we have } \alpha = \frac{\rho - \frac{\rho}{f}}{\frac{\rho}{f}(f-1)} = \frac{\frac{\rho(f-1)}{f}}{\frac{\rho(f-1)}{f}} = 1.$$

That is, the degree of dissociation is complete, or 100 per cent.

If a substance dissociates into 2 parts, its vapor density $\rho_1 = \frac{\rho}{2}$, that is, $\frac{1}{2}$ of original density. If into 3 parts, $\rho_1 = \frac{\rho}{3}$, that is, $\frac{1}{3}$ of its original density. But if $\rho_1 = \rho$, then $\alpha = 0$ and no dissociation takes place.

EXAMPLE. — At 90° C. the specific gravity of nitrogen peroxide (N_2O_4) is 24.8 (H = 1). Calculate degree of dissociation.

$$N_2O_4 \rightleftarrows 2\,NO_2 \qquad f = 2 \qquad s = \frac{N_2O_4}{2} = \frac{92}{2} = 46$$

$$\therefore\ \alpha = \frac{s - s_1}{s_1(f-1)} = \frac{46 - 24.8}{24.8\,(f-1)} = 0.8547;\ \therefore 85.47 \text{ per cent dissociated.}$$

EXAMPLE. — When 5 g. of ammonium carbamate $NH_4CO_2NH_2$ are completely vaporized at 200° C., it occupies a volume of 7.66 liters under a pressure of 740 mm. mercury. Calculate the degree of dissociation.

$$NH_4CO_2NH_2 \rightleftarrows 2\,NH_3 + CO_2$$

$m = 78$, molecular weight of ammonium carbamate

$$\frac{g}{m} = \text{gram-molecules} = \frac{5}{78}$$

$$1 + (f-1)\,\alpha = i. \quad 1 + (3-1)\,\alpha = 1 + 2\,\alpha = i$$

$$(1 + 2\,\alpha)\frac{g}{m} = \text{total number of molecules}$$

$$pV = nRT: \qquad pV = \frac{g}{m}(1 + 2\,\alpha)RT;\ p = \frac{740}{760} \text{ atmosphere}$$

$$\frac{740}{760} \times 7.66 = \frac{5}{78}\,(1 + 2\,\alpha) \times 0.082 \times 473.$$

Solving, find $\alpha = 0.999$ or 99.9 per cent dissociation.

On complete dissociation, we have in the case of nitrogen peroxide a simple gas, while in the case of ammonium carbamate we have a gaseous mixture consisting of ammonia and carbon dioxide. Depending upon the temperature and pressure we have, in all intermediate states, partial dissociation. We see that certain gaseous substances which give abnormal values for their densities, upon the basis that they are dissociated, confirm Avogadro's hypothesis, and that the state of an ideal gas is realized when there is complete dissociation, as in the case of the undissociated gases we have previously considered.

The Law of Mass Action. — In the type of reactions we have been discussing, at ordinary temperatures and pressures the substances nitrogen dioxide and ammonium carbamate are distinct chemical individuals, the one a gas and the other a solid. If they are heated, they dissociate, with the formation of new chemical individuals as illustrated in the equations above. As the temperature is increased more and more, the original substance is dissociated, while at any specified temperature the products of dissociation are in equilibrium with the undissociated substance. The state of equilibrium we represent by equations, such as $N_2O_4 \rightleftarrows 2\ NO_2$, which means that the reaction may proceed in either direction and is designated a reversible reaction; but for any specified conditions it does proceed in both directions at the same rate, and consequently an equilibrium is thus maintained. The law governing the state of equilibrium or this statical condition of the reaction is known as the *Law of Mass Action* and can be developed thermodynamically; but this particular theoretical consideration of the subject will have to be deferred, and we will illustrate the meaning of the law by applying it to a few specific cases.

Suppose we have two substances, A and B, reacting to form their resulting product, AB. Then $A + B = AB$, or we may have the reverse, $AB = A + B$, or writing as one equation we have $AB \rightleftarrows A + B$. A more general statement would be where more substances react, forming a homogeneous system. The reaction is represented thus,

$$A_1 + A_2 + A_3 \cdots \rightleftarrows A_1' + A_2' + A_3' \cdots$$

which indicates that only *one molecule* of each substance takes part in the reaction. That this reaction takes place depends, according to the kinetic theory of gases, upon the collision of the molecules, and it is obvious that the nearer they are together the more numerous such collisions and the greater the relative number of molecules per unit space. Hence the reaction (*i.e.* collisions) is proportional to the concentration. Then the velocity of the reaction is proportional to the products of the concentrations.

Let V = velocity from left to right, and c_1, $c_2 \cdots$ represent the concentrations of the substances A_1, $A_2 \cdots$, *i.e.* the number of gram-molecules per liter. Then the reaction equation is $V = Kc_1c_2 \cdots$, where K is a constant for the given temperature.

If the reaction proceeds in the direction from right to left, we shall have $V' = K'c_1'c_2' \cdots$, in which the terms have analogous meaning to those in the first cases.

As the values of V and V' cannot be measured alone, the course of the reaction can only be given by the difference of the two values. The total reaction velocity is made up of the difference between the two partial reacting velocities; for the change actually observed for any amount of time is equal to the reaction in one direction minus the change in the opposite direction during this same time. When the condition of equilibrium has been reached, we are not to conclude that no further change takes place; but should assume that the change, in the sense of the reaction equation from left to right, is compensated by a change from right to left, and therefore that the total change to be observed = zero, *i.e.* the system stands in equilibrium. Then we have for equilibrium

$$V - V' = 0, \text{ or } V = V'$$
$$\therefore K c_1 c_2 \cdots = K' c_1' c_2' \cdots.$$

A more general statement would be to remove the restriction that only one molecule takes place in the reaction and that there is only one molecule of each molecular species produced. In that case the formula takes the following form for the Generalized Mass Law Equation:

$$K c_1^{n_1} \cdot c_2^{n_3} \cdot c_3^{n_3} \cdots = K' c_1'^{n_1'} \cdot c_2'^{n_2'} \cdot c_3'^{n_3'}$$

or

$$\frac{c_1^{n_1} \cdot c_2^{n_2} \cdot c_3^{n_2} \cdots}{c_1'^{n_2'} \cdot c_2'^{n_3'} \cdot c_3'^{n_3'} \cdots} = \frac{K'}{K} = k \text{ a constant,}$$

which is termed the *equilibrium constant;* but where applied to dissociation phenomena it is termed the *dissociation constant.*

Now applying this Mass Law Equation to the simplest case of dissociation, when a compound AB dissociated into the two parts A and B, we have $AB \rightleftarrows A + B$,

(1) $K c_1 = c_2 \cdot c_3$. If the reacting substance is made up of like parts, then we have

$$A_1 \rightleftarrows 2\ A_2, \text{ which becomes}$$

(2) $K c_1 = c_2^2$, which is obtained from the above when $c_2 = c_3$. That is, where the substance dissociates into two like constituents.

Let c, the concentration $= \frac{n}{V}\left(\frac{\text{no. of moles}}{\text{vol.}}\right)$. Substituting this value for the concentration in equations (1) and (2) we have

$$K\left(\frac{n_1}{V}\right) = \frac{n_2}{V} \cdot \frac{n_3}{V}. \qquad (1)$$

Now since $n_2 = n_3$, we have

$$K\frac{n_1}{V} = \left(\frac{n_2}{V}\right)^2 \tag{2}$$

which becomes

$$KV = \frac{n_2^2}{n_1}.$$

That is, *increasing the volume produces a relative increase of dissociation.*

Many times it is difficult to determine the concentration of the components. We can avoid the necessity of doing so by introducing the pressure factor and measuring that instead of determining the concentration. The final form of the Gas Law Equation was

$$pV = nRT \tag{3}$$

which becomes

$$\frac{V}{n} = \frac{RT}{p}, \text{ or } \frac{n}{V} = \frac{p}{RT}.$$

But since $\frac{n}{V} = c$, we have $c = \frac{p}{RT}$.

The concentrations are directly proportional to the pressures. The equation then becomes

$$c = K_1 p. \tag{4}$$

Now, since concentration is proportional to the pressure, for c_1 we may substitute K_1p in the equations above, and we have for equation (2) $Kc_1 = (c_2^2)$ the following

$$K(K_1p_1) = (K_2p_2)^2$$

or

$$K \cdot \frac{K_1}{K_2^2} = \frac{p_2^2}{p_1}.$$

Now since $K\frac{K_1}{K_2^2}$ represents a new constant, we may express this by some single letter, as k, hence we have $k = \frac{p_2^2}{p_1}$.

This gives us the pressures due to the individual constituents of the gas mixture, and these are designated the *partial* pressures. *The total pressure P is the sum of the partial pressures, i.e.* $P = p_1 + p_2$. This is *Dalton's Law.* From a consideration of The Gas Law we have, for several molecular species occupying the same volume at the same temperature, the relation $\frac{p_1}{p_2} = \frac{n_1}{n_2}$.

Mixtures of Gases. — We should expect that the most simple relations would be found to exist in the case of mixtures of different gases. Such is the case where there is no chemical action between the gaseous particles. Each gas remains unchanged and conducts itself as though the other one was not present. The pressure exerted upon the walls of the containing vessel, the capacity of absorbing and reflecting light, the specific heat, etc., in fact all of the properties of the gases experience no change when the gases are mixed. These particular relations should hold only in the case of ideal gases; and as all the gases only approximately follow The Gas Law, we should expect to find some slight deviations when the gases are mixed.

Dissociation of Gases. — Let us consider the following cases:

(1) $PCl_5 \rightleftarrows PCl_3 + Cl_2$ *and* (2) $2\,HI \rightleftarrows H_2 + I_2$.

Applying the mass law, we have

$$Kc_1 = c_2 \cdot c_3. \qquad\qquad Kc_1^2 = c_2 \cdot c_3.$$

Expressing concentrations in terms of number of molecules in unit volume, we have

$$K\frac{n_1}{V} = \frac{n_2}{V} \cdot \frac{n_3}{V}. \qquad\qquad K\frac{n_1^2}{V^2} = \frac{n_2}{V} \cdot \frac{n_3}{V}.$$

Multiplying through by V, and by V^2,

$$Kn_1 = \frac{n_2 \cdot n_3}{V}. \qquad\qquad Kn_1^2 = n_2 \cdot n_3.$$

In the case of PCl_5 the dissociation is proportional to the volume, while in HI as there is no value of V in the equation, the dissociation is independent of the volume.

Introducing the pressures instead of the concentrations we have

$$K_1 p_1 = p_2 \cdot p_3. \qquad K_1 p_1^2 = p_2 \cdot p_3.$$

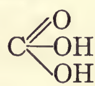
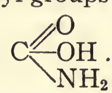
We can decrease the volume by increasing the pressure m-fold, when we shall have

$$K_1 m p_1 = m p_2 \cdot m p_3 \qquad K_1 (m p_1)^2 = m p_2 \cdot m p_3$$

which become

$$K_1 p_1 = p_2 \cdot m p_3. \qquad K_1 p_1^2 = p_2 \cdot p_3.$$

In the first case we have the dissociation forced back, while in the other case it is not affected by the increase of pressure, as the factor m disappears. *Hence, in all cases where the number of reacting substances,* i.e. *the number of molecules on both sides of the equation, are equal, the change in the volume has no effect on the degree of dissociation.*

Dissociation of Ammonium Carbamate. — Carbamic acid may be considered as carbonic acid,  in which one of the hydroxyl groups (OH) has been replaced by the amido group (NH_2),  The ammonium salt is formed by the direct addition of NH_3, as in the reaction $NH_3 + HCl = NH_4Cl$, when we have $(NH_3)_2CO_2$.

On heating ammonium carbamate, we have

$$(NH_3)_2CO_2 \rightleftarrows 2\ NH_3 + CO_2.$$

Now applying the mass law, we have

$$K \frac{n_1}{V} = \left(\frac{n_2}{V}\right)^2 \cdot \frac{n_3}{V}.$$

Since the carbamate is a solid, its concentration will remain practically constant, and the vapor pressure is so small in comparison to the pressures of the dissociated products that it can be neglected, when we will have

$$K_1 = c_2^2 \cdot c_3.$$

Substituting pressures for the concentrations, we have

$$K_2 = p_2^2 \cdot p_3.$$

But the total pressure is the sum of the partial pressures, *i.e.* $P = p_2 + p_3$, and since there are twice as many molecules of NH_3 as of CO_2, $p_2 = 2\ p_3$. Substituting this value for p_2 we have

$$P = 2\ p_3 + p_3 \text{ or } P = 3\ p_3 \text{ or } p_3 = \tfrac{1}{3} P.$$

Now substituting these values of p_2 and p_3 we have

$$K_2 = (\tfrac{2}{3} P)^2 \cdot \tfrac{1}{3} P \text{ or } K_2 = \tfrac{4}{27} P^3.$$

It is evident that the addition of ammonia should force back the dissociation more than the addition of carbon dioxide.

In the case of ammonium chloride, $NH_4Cl \rightleftarrows NH_3 + HCl$, Neuberg found the density of NH_4Cl in the vapor form to be 1.13, while the calculated value is 1.85. In an excess of 34.6 cc. of HCl the density was 1.5, while in an excess of 60 cc. of NH_3 it was 1.68. The dissociation was forced back by the addition of either of the components of dissociation.

Ammonium hydrogen sulphide dissociates according to the following equation:

$$\underset{\text{(solid)}}{NH_4HS} \rightleftarrows NH_3 + H_2S.$$

Applying the mass law and using pressures, we have

$$Kp_1 = p_2 \cdot p_3.$$

But since NH_4HS is solid, the concentration of NH_4HS is practically constant, and its vapor pressure is so small that it can be left out of consideration without introducing any appreciable error. We then have $K_2 = p_2 \cdot p_3$, and since $P = p_2 + p_3$ and the number of dissociated products, NH_3 and H_2S, are equal, $p_2 = p_3$. Substituting p_2 for p_3, we have $P = 2\ p_2$ or $p_2 = \frac{1}{2} P$. Introducing these values in the original equation we have $K_2 = (\frac{1}{2} P)^2$.

$$\therefore\ K_2 = \frac{P^2}{4} \quad \text{or} \quad K_2 = \tfrac{1}{4} P^2.$$

Isambert presents the following experimental data in confirmation of the dissociation constant:

TEMPERATURE	VALUE OF $\frac{1}{4 P^2}$	
	Observed	Calculated
4.10° C.	37,900	37,000
7.00	60,000	58,000
25.1	62,500	62,750

At 25.1°, $P = 501$ mm., hence $\frac{1}{4} P^2 = \frac{501^2}{4} = 62{,}750$, when the products of dissociation are in equal molecular quantities.

By experiment he found the following results, when the different quantities of the gases were present:

$p_2(NH_3)$	$p_3(H_2S)$	$p_2 \cdot p_3$
208	294	61,152
138	450	63,204
417	146	60,882
452	146	64,779
	Mean	62,504

This is a close agreement with the theoretical value of approximately 62,750.

CHAPTER VII

THE PERIODIC SYSTEM

Dalton presented a number of tables illustrating the "relative weight of the ultimate particles of gaseous and other bodies," but it was not until 1803 that he published his first table of atomic weights, and this was not printed until 1805. This table was on the basis of hydrogen equal to one. The other table of atomic weights that was used during the early part of the last century was that of Berzelius, which was on the basis of oxygen equal to 100. With these relative weights of the elements available, numerous efforts were made to find relations existing between the elements themselves as well as between their atomic weights and the various properties of the elements.

Prout's Hypothesis. — Among the first attempts to express some relationship was that of W. Prout, in 1815, who aimed to show that the atomic weights of the elements were exact multiples of that of hydrogen, that is, that the elements were aggregates of the fundamental element hydrogen. So, if the atomic weight of hydrogen be taken as unity, which was done in the atomic weight table of Dalton, the atomic weights of the other elements should be expressed by whole numbers. This hypothesis of Prout had many supporters, among whom was Thomas Thomson, who accepted the idea, but among those who opposed it was Berzelius, who renounced it. In the efforts to substantiate their respective positions a vigorous campaign was inaugurated, which resulted in the early establishment of accurate values for the atomic weights.

It was found that the value given by Berzelius for carbon was wrong, and Dumas and his pupil Stas redetermined it and found the value for carbon to be exactly 12. This fact aided in making Dumas a strong advocate of Prout's hypothesis and also led to the extensive accurate atomic weight determinations of Stas. It was found that about 24 out of the 70 elements had atomic weights that did not vary from a whole number by more than one unit in the first decimal place. (Of the elements listed in the Periodic Table, page 72, about half have values within one tenth of an integer.)

In Table V are given the comparative values of the atomic weights that Prout used, and the values for 1915, one hundred years later.

TABLE V — (After Harkins)

Elements	Atomic Weights	
	Prout 1815	International 1915 (H = 1)
Hydrogen	1	1.00
Carbon	6	11.91
Nitrogen	14	13.90
Phosphorus	14	30.78
Oxygen	16	15.88
Sulphur	16	31.82
Calcium	20	39.76
Sodium	24	22.82
Iron	28	55.41
Zinc	32	64.86
Chlorine	36	35.46
Potassium	40	38.80
Barium	70	136.31
Iodine	124	125.94

The values used by Prout were the best available at that time, but the result of the accurate work of Stas and others gave values, such as that of chlorine (35.5), which were hard to reconcile, and Marignac, who favored Prout's hypothesis, suggested that a unit one half that of hydrogen be selected. Then others suggested further subdivisions to account for the other irregularities, with the result that this brought Prout's hypothesis into disfavor for a time at least. In 1901 Strutt concluded from the theory of probabilities that the instances of the atomic weight approximating to or being a whole number were more numerous than chance would allow and hence were not accidental, but indicated some fundamental fact of nature. Prout's assumption, that all elements are simply condensations of hydrogen, contains the fundamental idea of the primal element or "mother substance" of which all the elements are composed and has been variously termed "earth," "fire," "protyle," hydrogen, and now the modern scientists embody this idea in the electron theory. That this idea is one of the live questions, as it was one hundred years ago, is evidenced by the extensive investigations at present along this line.[1]

Doebereiner's Triads. — Doebereiner (1817) arranged chemically similar elements in groups of three in the order of their symbol weights and showed that the symbol weight of the middle one was the mean of the other two. There is a constant difference in the symbol weights of succeeding members of the triads similar to the difference between homologous series in organic chemistry. It was not until 1851, when Dumas again took up this idea of triads, that any interest was manifested; but subsequent to this time many chemists began to investigate these relations between the

[1] A large number of articles have recently been added to the already extensive literature. Among these recent contributions reference will be given to a few, such as that of Sir William Ramsay, *Proc. Roy. Soc.*, A *92*, 451 (1916); Parson, *Smithsonian Publication*, 2371 (1915); R. A. Millikan's recent book, *The Electron* (1917); G. N. Lewis, *Jour. Am. Chem. Soc.*, *35*, 1448 (1914), *38*, 762 (1916); and Harkins, *Ibid.*, *39*, 856 (1917).

properties of the elements and the relation of their symbol weights.

Table VI, in which are given some of the more important triads, emphasizes the constant differences between the symbol weights.

TABLE VI

Elements	Symbol Weights	Differences	Mean of Extreme Symbol Weights
Lithium	6.94	16.06	
Sodium	23.00		23.02
Potassium	39.10	16.10	
Chlorine	35.46	44.46	
Bromine	79.92		81.19
Iodine	126.92	47.00	
Sulphur	32.07	47.13	
Selenium	79.2		79.8
Tellurium	127.5	48.3	
Calcium	40.0	47.7	
Strontium	87.7		88.7
Barium	137.4	49.7	
Phosphorus	31.04	43.92	
Arsenic	74.96		75.62
Antimony	120.2	45.24	

In the following series of triads the symbol weights are practically the same:

Iron	55.85	Ruthenium	101.7	Osmium	190.9
Cobalt	58.97	Rhodium	102.9	Iridium	193.3
Nickel	58.68	Palladium	106.7	Platinum	195.2

J. P. Cooke (1854) pointed out that these triads did not include all of the members of the natural groups of the elements, for example, fluorine was left out of the group of the closely related halogens. This idea of Cooke's emphasized the fallacy of trying to continue this method of grouping the elements into triads.

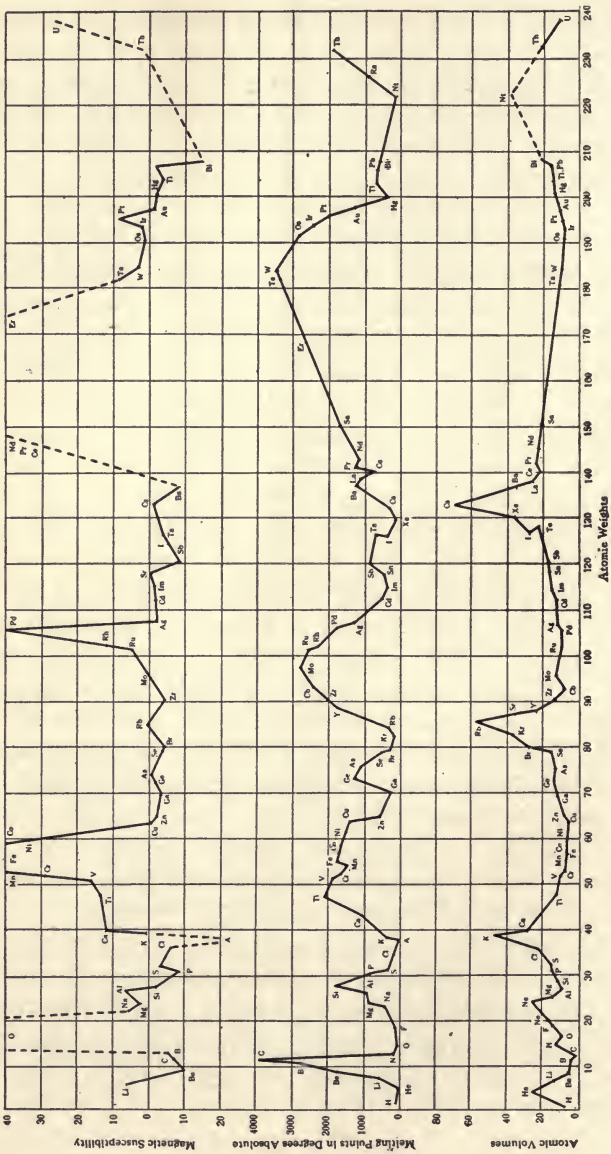

Magnetic Susceptibility
Melting Points in Degrees Absolute
Atomic Volumes
Atomic Weights

FIG. 5.

Gladstone (1853) arranged the elements in the order of increasing symbol weights, but the values were so inaccurate that no relations were really apparent. Cannizzaro's more accurate values enabled Chancourtois a few years later (1862) to point out important and remarkable relations between the physical and chemical properties and the symbol weights. He arranged the elements in a spiral around a cylinder, which he divided into 16 vertical sections. The elements in any vertical section were found to have analogous chemical and physical properties. This arrangement is known as the *Telluric Screw.*

Newlands' Law of Octaves. — Newlands (1864–66) arranged the elements in the increasing order of their symbol weights and announced his Law of Octaves as follows: "If the elements are arranged in the order of their equivalents with a few slight transpositions, it will be observed that elements belonging to the same group usually appear on the same horizontal line; members of the analogous elements generally differ either by seven or some multiple of seven. In other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music."

The Periodic Law. — Mendeléeff (1869) and Lother Meyer (1869) independently and practically simultaneously formulated periodic systems which were very similar to that put forth by Newlands, but they were not familiar with it. Their generalization, commonly known as the *Periodic Law*, is expressed by the statement that the properties of the elements are periodic functions of their symbol weights.

The Atomic Volume Curve. — Meyer paid special attention to the physical properties and expressed the symbol weights as periodic functions of the specific gravities of the elements. He pointed out that the periodicity is more closely manifest in the so-called atomic volumes, which he defined as equal to the symbol weight divided by the specific gravity, *i.e.* $\frac{\text{symbol weight}}{\text{specific gravity}}$ = atomic volume. He plotted these values of the atomic volumes against the symbol weights and obtained an atomic volume curve such as is represented in Fig. 5.

The whole curve is made up of a series of periods or waves. The summits (*i.e.* the crests) of the waves are occupied by the alkali metals:

Cs = 135, Rb = 85, K = 39, Na = 23, and Li = 7
Differences 47.5 46.5 16 16

We have *two short periods*, one between Li and Na and the other between Na and K. Then follow *two long periods*, one between K and Rb and the other between Rb and Cs. The remainder of the curve is partly of a different form and is evidently incomplete, and there is no reason to suspect another alkali of higher symbol weight than Cs.

By a consideration of the troughs of the curve, differences between the long and short periods may be indicated. The elements of minimum atomic volume are:

Pt = 191, Rh = 102, Co = 59, Al = 27, B = 11
Differences 89 43 32 16

These differences between the symbol weights of the elements at the trough of the curves are about 16 and some multiple of 16, and the same is true for the metals that occupy the crests or peaks of the curve. The elements with the smallest atomic volume do not form a group, as do those with the highest atomic volumes, but belong to two widely different groups, which do not show any chemical analogy. Other elements fall into (1) two short periods, beginning with Li and with Na; (2) two complete long series, beginning with K and with Rb; (3) a third long series, beginning with Cs followed regularly by Ba, La, and Cr and interrupted by the intrusion of closely related rare elements, followed again regularly by metals from Ta to Bi, and lastly by a small portion of a fourth long series. We thus have five maximum and six minimum sections of the curve.

The *descending* portion of the curve, representing the increase in symbol weight and decrease in atomic volume, is composed of the so-called *base*-forming elements. The *ascending* portions are occupied by the *acid*-forming elements, while the minima portions represent the elements Al, Mn, Ru, Pd, etc., which are not decidedly acid-forming or base-forming.

The position of elements on the curve is closely connected with the physical as well as the chemical properties. Elements chemically similar occupy corresponding positions on similar portions of the curve. At the maximum positions we find the light elements; at the minimum positions the heavy elements.

The Periodic Table. — The Periodic Table presented by Mendeléeff illustrates the periodicity of chemical properties much better than the curve that we have just been considering. The following modern Periodic Table given in Table VII is practically the same as the one presented by Mendeléeff, except that the symbol weights are more accurately known and the new group of the rare elements in Group III and Group 0 is added.

Discussion of the Periodic Table

Arrangement. — All the elements are arranged in succession in the order of their increasing symbol weights. Starting with Li next above H, we find that the one above fluorine, Na, has properties very similar to Li. If Na be placed in the same vertical column with Li and we then arrange the other elements in the increasing order of their atomic weights, the elements which fall in the same vertical column resemble each other very closely chemically. The set of seven elements starting with Li agree very closely with the second set in properties. The first of the next set, K,

TABLE VII — THE PERIODIC TABLE

PERIODS		GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII
Formulæ of oxides . . Formulæ of hydrides . .			R_2O RH	RO RH	R_2O_3 RH_3	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	RO_4 ...
First short period . .		He 4.00	H 1.008 Li 6.94	Be 9.1	B 11.0	C 12.005	N 14.01	O 16.00	F 19.0	
Second short period . .		Ne 20.2	Na 23.00	Mg 24.32	Al 27.1	Si 28.3	P 31.04	S 32.06	Cl 35.46	
First long period	Even series	A 39.88	K 39.10	Ca 40.07	Sc 44.1	Ti 48.1	V 51.0	Cr 52.0	Mn 54.93	Fe 55.84 Co 58.97 Ni 58.68
	Odd series	...	Cu 63.57	Zn 65.37	Ga 69.9	Ge 72.5	As 74.96	Se 79.2	Br 79.92	
Second long period	Even series	Kr 82.9	Rb 85.45	Sr 87.63	Y 88.7	Zr 90.6	Cb 93.1	Mo 96.0	...	Ru 101.7 Rh 102.9 Pd 106.7
	Odd series	...	Ag 107.88	Cd 112.4	In 114.8	Sn 118.7	Sb 120.2	Te 127.5	I 126.92	
Third long period	Even series	Xe 130.2	Cs 132.81	Ba 137.37	The Rare Earth Metals	...	...	...	...	... ...
	Odd series	...	...	...		...	...	...	...	
Fourth long period	Even series	...	...	...		...	Ta 181.5	W 184.0	...	Os 190.9 Ir 193.1 Pt 195.2
	Odd series	...	Au 197.2	Hg 200.6	Tl 204.0	Pb 207.20	Bi 208.0	...	...	
Fifth long period . . .		Nt 222.4	...	Ra 226.0	...	Th 232.4	...	U 238.2	... ...	... ...

falls into the group with Li and Na, and the remainder have a striking analogy to the corresponding element of the other sets. After manganese we have one of the weakest points in the Periodic Law, but here also certain regularities are again manifest by the subsequent elements.

Chemical Properties. — The elements on the left are elements present in the strongest alkalies, while those on the extreme right are the elements present in the acids and are the so-called acid-forming elements. Between, we have the gradation between acid properties and basic properties.

Valency. — Valency with respect to oxygen increases from unity for elements in the first column until it reaches seven, when the valency of one recurs and the other valencies are repeated. Valency with respect to H decreases from left to right.

Periods. — The first 14 elements (not counting Group 0 or H) arranged in the horizontal rows constitute what is designated two short periods, for the eighth of these, Na, has chemical properties analogous to the first Li; the ninth, Mg, analogous to the second, Be, the tenth, Al, analogous to the third, B, and so on to the seventh, F, which has chemical properties analogous to the 14th element, Cl. In the next elements we have to pass over 14 before we find one with properties similar to the 14th, K, which is the 28th element, Rb. That is, we have passed over a *long* period, and find the elements arranged in a long period, which is followed again by another long period of 14 elements. There are two short periods and five long periods. The last long periods are not completely filled out, and there are a number of vacant places. When the Periodic Tables were first prepared many of the elements known at present were unknown, and there were a larger number of vacant places in the table than at present. Notable among these were the spaces now occupied by gallium, scandium, and germanium. Mendeléeff predicted the chemical and physical properties that the elements occupying these places should have. A short time afterward the above-named elements were discovered, and they were found to have the properties Mendeléeff predicted they should have. This fulfillment of prophecy brought the attention of the scientific world to Mendeléeff's classification and resulted in the rapid adoption of it. It was soon demonstrated that in such a system as this we had not only a means of prediction but also the only way by which the elements could be grouped together as a whole for the purpose of representing conveniently and concisely their interrelations. This was of great advantage. The elements in the atmosphere, the Argon Group, fall into a vertical column to the left of the strongly basic elements, Group I, and constitute the Zero Group, because they are inert and are said to have a valency of zero.

Physical Properties. — There are many other physical properties of the elements and of their compounds which manifest a periodic function of the symbol weights, and among these may be listed a few of the principal ones.

1. Malleability.

(*a*) *Light malleable* metals occupy the points of maximum and contiguous portions of *descending* curves; Li, Be, Na, Mg, Al; K, Ca; Rb, Sr; Cs, Ba.

(*b*) The *heavy malleable* metals are found in the lowest points of the atomic volume curve and adjacent sections of the *ascending* curves; Fe, Co, Ni, Cu, Zn; Rb, Pd, Ag, Cd, In, Sn, Pt, Au, Hg, Tl, Pb.

(*c*) Less malleable metals are found just before the lowest points on the descending curves; Ti, V, Cr, Mn; Zr, Nb, Mo, Ru; Ta, W, Os, Ir.

(*d*) *Non-metallic and semi-metallic* elements are found in each section on the ascending branches of the curves preceding the maximum.

2. Hardness of elements is inversely proportional to their atomic volume.

3. Melting point data are shown diagrammatically in Fig. 5 and illustrate the periodic function of this property with increasing atomic weight.

(*a*) *All gaseous elements*, and all elements that fuse below a red heat are found on the *ascending* portions and at the maximum points of the atomic volume curve.

(*b*) All infusible and difficultly fusible elements occur at the points of the minima and descending portions of the curve. The periodicity corresponds to that shown by atomic volume and malleability. For those elements that are easily fusible the atomic volume is larger than that of the element with next smaller symbol weight. There are, however, some considerable variations: the melting point decreases with increase in symbol weight only in the following: (1) Alkalies, Li, Na, K, Rb, and Cs, (2) Alkaline earths, Mg, Ca, Sr, Ba, and in Cu, Cd, and Hg. The compounds of the elements also exhibit relations in their melting points. This has been worked out by Carnelley.

4. Volatility is intimately associated with fusibility. Easily fusible volatile metals are found on the ascending portions of the atomic volume curve. Elements on ascending portions of the curve are gaseous and easily volatile, but many elements of high atomic weight which occupy a similar position, however, require a strong red heat or even a white heat for volatilization.

5. Fizeau has shown that the volatile elements occurring on the ascending curve possess almost without exception a larger coefficient of expansion by heat between 0° and 100° than the difficultly fusible elements occupying the minimum. Carnelley states that the coefficient of expansion of an element increases as the melting point decreases.

6. The refraction of light by the elements and their compounds is also essentially related to the symbol weight.

7. Conductivity for heat and for electricity of the elements are dependent upon their ductility and malleability,

and hence are periodic functions of the atomic weights, the periodicity of which coincides with that of the atomic volume.

8. Magnetic and dimagnetic properties of the elements appear to be closely connected with their symbol weights and atomic volumes. Those elements the atomic volumes of which approach the minima are usually magnetic. Observations differ so that it is difficult to tell whether there is a periodic relation between the magnetic and dimagnetic properties and atomic weights. However, from maxima to minima, the elements are entirely magnetic, and at minimum the magnetism exhibits its greatest intensity. This is true of the iron group. From the minimum to maximum, follow dimagnetic elements only. The magnetic susceptibility is a periodic function of the atomic weight, as is illustrated in Fig. 5.

9. Electropotential series is the arrangement of elements according to electropositive and electronegative character. These properties exhibit variations similar to those exhibited in malleability and brittleness.

The electrochemical character of the elements becomes more positive as the symbol weight increases. Cu is replaced by silver. A strongly electronegative element Cl will displace a weaker one I. The electropositive character becomes less marked with increase of symbol weight in the groups Cu, Ag, Au; Zn, Cd, Hg. In the two short periods the elements become regularly less electropositive and more electronegative as the symbol weight increases, but in the long periods the change is less regular. The elements in the groups on the left-hand side of the table are electropositive and those on the right-hand side are electronegative.

Some of the other periodic properties are the following: The crystalline forms of various compounds of the elements, heats of chemical combination, ionic mobilities, distribution of the element in the earth, spectra of the elements, refractive indices, ultra-violet vibration frequencies, solubility, electrode potentials, etc.

Advantages of the Periodic Law and Classification. — 1. It affords the only known satisfactory method of classifying the elements so as to exhibit the relationship of the physical and chemical properties of the elements and of their compounds.

2. The symbol weights of the elements may be determined by means of the periodic system when their equivalent weights are known. Many of the symbol weights used when Mendeléeff presented his periodic table did not allow placing the elements in the position which corresponds to their properties, so he assumed that there had been an error made in the determination of the equivalent weight or that the incorrect multiple had been selected. For example, the symbol weight for uranium was thought to be 60; this was changed to 120, and finally to 240 (238.5).

3. The prediction of unknown elements, a statement of their properties and general chemical characteristics. As an illustration, in the following table, properties of the prophesied elements are compared with those of the elements subsequently discovered.

Prophesied Elements	Elements Discovered
Ek-aluminium Symbol weight, 68 Specific gravity, 6.0	Gallium Discovered by Lecoq de Boisbaudran in 1875 Symbol weight, 69.5 Specific gravity, 5.96
Eka-boron Symbol weight, 44 Oxide, Eb_2O_3, sp. gr. 3.5 Sulphate, $Eb_2(SO_4)_3$ Double sulphate not isomorphous with alum	Scandium Discovered by Nilson in 1879 Symbol weight, 43.8 Sc_2O_3, sp. gr. 3.86 $Sc_2(SO_4)_3$ $Sc_2(SO_4)_3 \cdot 3\ K_2SO_4$ — slender prisms

Prophesied Elements	Elements Discovered
Eka-silicon	Germanium
	Discovered by Winkler in 1887
Symbol weight, 72	Symbol weight, 72
Specific gravity, 5.5	Specific gravity, 5.47
Oxide, EsO_2, sp. gr. 4.7	Oxide, GeO_2, sp. gr. 4.7
Chloride, $EsCl_4$, liquid, boiling point slightly under 100°, sp. gr. 1.9	Chloride, $GeCl_4$, liquid, boiling point 86°, sp. gr. 1.887
Ethide, $Es(C_2H_5)_4$, liquid, boiling point 160°, sp. gr. 0.96	Ethide, $Ge(C_2H_5)_4$, liquid, boiling point 160°, sp. gr. slightly less than that of water.
Fluoride, EsF_4, not gaseous	Fluoride, $GeF_4 \cdot 3\,H_2O$, white solid mass

Imperfections of the Periodic Law and Classification. — We have seen that by this system not only all of the known elements can be classified, but also the unknown ones as well. It is not surprising then that from such a universal proposition there should be some variations and irregularities, and so we do find in this classification a few weak points.

When the Periodic Table was first presented there was a marked discrepancy in the arrangement in the case of the following elements, but according to the present accepted values for their symbol weights that has disappeared, as is shown in Table VIII.

Table VIII

Element	Symbol Weight, 1870	Symbol Weight, 1916
Osmium	198.6	190.9
Iridium	196.7	193.1
Platinum	196.7	195.2

There has been an effort, due to imperfect knowledge of the law, to make too extensive an application, or to limit its sphere of activity, and hence because of insufficient and inaccurate data concerning certain elements erroneous conclusions have been drawn. However, there still remain a few remarkable exceptions to the Periodic Law. The following are some of the most pronounced ones:

1. In Group I and in Group VII, the elements have a valency of one, and since the valency of hydrogen is unity, it could be placed in either. Owing to the fact that it has a low boiling-point and that its formula weight is represented (as many other gaseous elements) as diatomic, H_2, it is included in Group VII by many chemists. Solid hydrogen does not resemble the alkali metals in physical properties, and it is typically non-metallic. Chemically, however, hydrogen acts very similarly to the alkalies, forming stable compounds with non-metallic elements, such as the halogens. Owing to this it is placed in Group I.

2. The symbol weight of argon, 39.88, is larger than that of potassium, 39.15, and so these two elements should change places. With argon between potassium and calcium we should have a decided discontinuity in the properties, and furthermore, this would bring potassium into Group 0, and the properties of potassium are decidedly unlike those of the other members of this group.

3. The same holds for tellurium and iodine; they should be interchanged according to their symbol weights, but according to their chemical properties iodine must be placed in Group VII.

4. In Group VIII we have iron, cobalt, and nickel, but from the symbol weights nickel and cobalt should exchange places. Since cobalt and iron form two series of salts, and nickel forms only the nickelous salts, the gradual variation in the properties is represented by placing cobalt between iron and nickel.

5. The three groups of triads in Group VIII are peculiar in that the triads are arranged in horizontal lines and con-

nect the members of the three long series. They destroy somewhat the symmetry of the whole system.

6. Between lanthanum, 139, and tantalum, 181, there are a large number of blank spaces, but it is not possible to fit the fifteen rare earth elements into these places, as the symmetry of the system is destroyed. Since these elements are trivalent, they are grouped together in Group III.

Graphic Representations of the Periodic Table. — Many graphic representations of the periodic arrangement of the

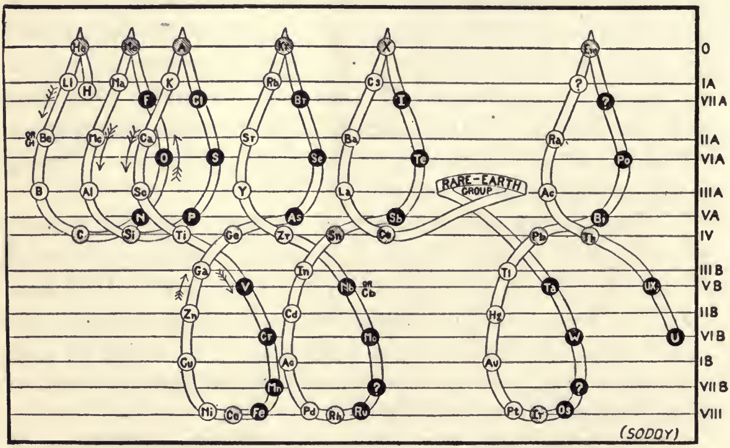


FIG. 6. — Electro-Positive Elements, above plane of paper, black letters on white ground. Electro-Negative Elements, below plane of paper, white letters on black ground. Intermediate Elements, in plane of paper, black letters on sectioned ground.

elements have been devised, and these may be classified as plane diagrams and as space forms. They are designed to bring out more distinctly the relation of the properties of the elements and the atomic weights, but while some of them well express the relations to certain properties, others do not, but represent another group of properties better. Many of the later designs of the space forms are valuable aids in the study of the periodic functions of the atomic weights.

Only one of the best of these will be presented here in Fig. 6, which is the space form according to Soddy, wherein the figure 8 design is employed.[1]

[1] For other graphic designs the following references may be consulted, where full description of them may be found: (1) Crooks, *Chem. News*, *78*, 25 (1898), employs a figure 8 form; (2) Emerson, *Am. Chem. Jour.*, *45*, 160 (1911), places the elements on a helix; (3) Harkins and Hall, *Jour. Am. Chem. Soc.*, *38*, 169 (1916), give illustrations of a number of models, many of which are their own designs.

CHAPTER VIII

THE KINETIC THEORY OF GASES

In our preceding considerations we found it desirable to adopt Avogadro's Theory of the structure of a gas, wherein it is assumed that a gas is made up of molecules in motion, which in turn are aggregates of one or more atoms which may be alike or of different kinds. Bernoulli published in 1738 the fundamental notions of the Kinetic Theory of Gases, in which he pointed out that the pressure of a gas is due to the impact of the molecules on the walls of the containing vessel. The mathematical theory, however, was developed much later by Clausius, and it is due largely to his efforts and those of Maxwell that the theory as now accepted has been promulgated and developed.

The fundamental assumptions upon which the Kinetic Theory is based may be stated as follows:

1. Gases are made up of molecules of very small dimensions.

2. The space that the molecules occupy is small when compared to the volume of the gas itself.

3. The distance of the molecules apart is very large as compared to their size, *i.e.* they are so far apart that they have no marked influence on one another.

4. The molecules are in rapid motion in all directions, and are assumed to be *perfectly elastic*.

Deduction of The Gas Law from the Kinetic Theory of Gases. — The total pressure exerted by a gas on the walls of the containing vessel is due to the impacts of the gas molecules, which are moving in all directions, against the walls.

Let M be the mass of a given gas inclosed in a box, Fig. 7, whose parallel sides are all rectangles, the inside dimensions of which are b, c, and d. If m represents the mass of one molecule, $\frac{M}{m} = n$, the number of molecules. We assume that these n molecules of the gas are moving about in all directions. Let us assume that there is but a single molecule of the gas in the box, and that it is moving with any velocity. The force that this molecule exerts on the different sides is found as follows: The velocity of the molecule, u, may be resolved into three components perpendicular to the faces of the box. Let x represent the component perpendicular to the face bc; y represent the component perpendicular to the face cd; and z represent the component perpendicular to the face bd. Then the force exerted by the face, bc, upon the molecule may be found by the formula $F = ma$, where F represents the force, m the mass of the molecule, and a represents the acceleration of the molecule in the direction of the force. But acceleration $a = \frac{v_2 - v_1}{t}$, where v_2 represents the velocity after impact with the face, and v_1, the velocity before impact. Substituting, we have $F = \frac{m(v_2 - v_1)}{t}$. The molecule strikes the face bc with the velocity x normal to the face, then rebounds from the face with a velocity $-x$. That is, $v_1 = x$ and $v_2 = -x$. The effect of the force of impact upon one face is distributed over the period of time that it takes the molecule to travel the distance $2d$, when another similar impact occurs. This time, t, is equal to $\frac{2d}{x}$.

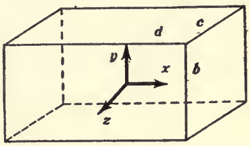


FIG. 7.

Substituting these values, for v_1, v_2, and t, in the above equation, gives $F = \frac{\frac{m[-x-x]}{2d}}{x}$ or $-\frac{mx^2}{d}$. Now, since the force exerted upon the face by the molecule is equal to that exerted by the molecule upon the face, but in opposite direction, we may write the force exerted by one molecule upon the face bc, as $F = \frac{mx^2}{d}$. The force exerted by the molecule upon the two parallel faces, bc, then, is $\frac{2\,mx^2}{d}$. In the same way the force exerted by the molecule upon the two parallel faces cd, is $\frac{2\,my^2}{b}$, and similarly upon the two faces bd is $\frac{2\,mz^2}{c}$.

Let us assume that this force exerted by the one molecule is the mean force of all of the molecules; then if there are n molecules the total force or pressure upon the two parallel faces bc will be $\frac{2\,nmx^2}{d}$. Similarly on the two parallel faces cd the pressure will be $\frac{2\,nmy^2}{b}$, and on the two parallel faces bd, it will be $\frac{2\,nmz^2}{c}$.

If we designate the force on unit area by p, which is the intensity of pressure, then the pressure p on each face will be the same. The area of the two faces bc is $2\,bc$, and the total force is $\frac{2\,nmx^2}{d}$; hence the pressure p will be $\frac{2\,nmx^2}{2\,bc\,d}$. Similarly, for the pressures on the other faces we have $\frac{2\,nmy^2}{2\,cd\,b}$ and $\frac{2\,nmz^2}{2\,bd\,c}$. That is,

$$\frac{2\,nmx^2}{2\,bc\,d} = p$$

$$\frac{2\,nmy^2}{2\,cd\,b} = p$$

$$\frac{2\,nmz^2}{2\,bd\,c} = p.$$

Adding these three equations, we have

$$3\,p = \frac{2\,nm}{2\,bcd}(x^2 + y^2 + z^2).$$

Simplifying and writing the mean square velocity for the sum of the squares of the three components, $u^2 = x^2 + y^2 + z^2$, we have $3p = \frac{nmu^2}{bcd}$; but the product, *bcd*, of the three dimensions of the box is the volume, hence, substituting V for *bcd*, the equation becomes

$$p = \frac{nmu^2}{3\,V} \text{ or } pV = \tfrac{1}{3}\,nmu^2.$$

Deduction of Boyle's Law. — We may define *heat* as the energy due to the position or velocity of the molecules of a substance. Heat, due to the velocity of the molecules, we term *Thermal Kinetic Energy.* A measure of this Thermal Kinetic Energy is *Temperature*, then $T = f(mu^2)$.

For any constant temperature, u is a constant, and the mass, nm, of the gas, is also constant; therefore, the right-hand member of the equation, $\frac{1}{3}\,nmu^2$, is a constant. The equation may then be written $pV = a$ *constant.* This is Boyle's Law, which we have deduced from the Kinetic Theory of Gases.

Deduction of Charles' or Gay Lussac's Law. — If we assume that T is a linear function of mu^2, *i.e.* $T = k(mu^2)$, then substituting in $pV = \frac{1}{3}\,mnu^2$ we get $pV = \frac{1}{3}\,n\frac{T}{k}$, but $\frac{1}{3}\frac{n}{k}$ is a constant, hence $pV = T \times a$ *constant* or $\frac{pV}{T} = a$ *constant.* Thus, from the Kinetic Theory of Gases we have derived The Gas Law. From this equation we also have the conclusion that at constant pressure the volume of a constant mass of gas is directly proportional to the absolute temperature; or, if the volume is constant, the pressure is directly proportional to the absolute temperature, *i.e.* the coefficient of expansion of a gas is a constant, which is Charles' Law.

Deduction of Avogadro's Hypothesis. — Let us now apply the equation just obtained in the deduction of Boyle's Law to two different gases which are under the same conditions of temperature and pressure and which occupy the same volume. This equation for the two gases becomes respectively

$$pV = \tfrac{1}{3}\, m_1 n_1 u_1^2 \text{ and } pV = \tfrac{1}{3}\, m_2 n_2 u_2^2$$

Hence $\tfrac{1}{3}\, m_1 n_1 u_1^2 = \tfrac{1}{3}\, m_2 n_2 u_2^2$. (1)

It has been shown experimentally that when two gases are under the same conditions of temperature and pressure they are in physical equilibrium and may be mixed without change in temperature. We conclude from this that the kinetic energy of the two molecular species remains unchanged, and further, that at the same temperature the kinetic energy of a molecule of one gas must be equal to the kinetic energy of a molecule of any other gas. Since the kinetic energy of a molecule is $\tfrac{1}{2} mu^2$, then

$$\frac{m_1 u_1^2}{2} = \frac{m_2 u_2^2}{2}. \qquad (2)$$

Dividing equation (1) by equation (2) we have $\tfrac{2}{3}\, n_1 = \tfrac{2}{3}\, n_2$ or

$$n_1 = n_2.$$

That is, the equal volumes of all gases at the same temperature and pressure contain the same number of molecules. This is Avogadro's Hypothesis.

Molecular Velocity. — Solving equation $pV = \tfrac{1}{3}\, nmu^2$ for u, we have $u^2 = \frac{3\,pV}{nm}$ or $u = \sqrt{\frac{3\,pV}{nm}}$ or $u = \sqrt{\frac{3\,p}{\rho}}$. (3)

This equation then gives us the velocity of the molecules of any gas, providing we know its volume and pressure and the quantity of gas present.

Let us calculate the velocity of the hydrogen molecule at 0° Centigrade when under one atmosphere pressure.

$$m \times n = \textit{mass of gas}.$$

One gram-molecular weight of a gas at 0° and 1 atmosphere pressure occupies 22.4 liters. It will require 2.016 grams of hydrogen to occupy this volume under the conditions specified. Hence, substituting these values in the above equation, we have

$$u = \sqrt{\frac{3 \times 1033 \times 980.6 \times 22400}{2.016}}.$$

Solving for u we obtain u = 183,700 cm. per second, or 1.837 kilometers per second, as the velocity of the hydrogen molecule under the conditions of our problem.

Diffusion of Gases. — The molecules of a gas moving in an inclosed space bombard the walls. Now, if there is an opening in one side, the molecule will meet with no resistance and will continue in its path on through the opening and thus pass out. It will pass through with the original speed it possessed inside the vessel, and this speed of *diffusion* originated directly from the speed of the molecular motion, and we conclude that the mean speed of the issuing molecules must therefore be proportional to the mean speed of the molecules within the vessel. Since this speed is proportional to the pressure on the gas, the rate of outflow will be dependent somewhat on the resistance the gas meets in flowing out. If the gas flows through a very small aperture in a thin membrane into a vacuum, then the resistance is reduced practically to the minimum.

If we have two gases under the same conditions of pressure and temperature, from the equation $u = \sqrt{\frac{3p}{\rho}}$ we have $u_1 : u_2 : : \sqrt{\rho_2} : \sqrt{\rho_1}$. That is, *the molecular velocities are inversely proportional to the square roots of the densities of the gases.*

This relationship may be deduced not only from the Kinetic Theory of Gases, but it has also been developed from flow of liquids through orifices, which fact is presented as an argument in favor of the kinetic theory. Bernoulli presented a theory of the process of effusion by an extension to gases of Torricelli's Law, which states that the velocity with which a liquid issues through an orifice is proportional to the square root of the pressure, or the head of the liquid. This law is expressed as follows: $v = \sqrt{\frac{2p}{\rho}}$, which gives us the same relation as $u = \sqrt{\frac{3p}{\rho}}$ deduced from the Kinetic Theory, which states that the pressure varies as the square of the molecular velocity.

The diffusion of gases through membranes and porous media as well as through cracks has been the subject of investigation since the time of Priestley. Graham (1833) recognized the similarity of diffusion and the passage of a gas as a whole through fine openings, which process he termed *effusion* in distinction from the passage of a gas through capillary tubes, which he designated *transpiration.* The latter process did not conform to the law of diffusion, while the process of effusion did conform to the diffusion law. *Graham's Effusion Law* is stated as follows: The times required for equal volumes of different gases to flow through an aperture is proportional to the square roots of their densities. This law is true for the flow of all liquids through a small orifice and was employed by Bunsen as a method for the determination of the specific gravity of gases. It has also been extended to the determination of molecular weights.

If $u_1 : u_2 : : \sqrt{\rho_2} : \sqrt{\rho_1}$, and we assume the same volume of the two gases under the same conditions of temperature and pressure, then $m_1 : m_2 : : \rho_1 : \rho_2$, since the molecular weights are in the same ratios as the densities of the gases. If we refer the densities to that of some standard, such as air, we have the specific gravities s_1 and s_2. Substituting, we have $u_1 : u_2 : : \sqrt{s_2} : \sqrt{s_1}$. Since the times of efflux of equal volumes are inversely proportional to the velocity of effusion, then we have $t_1 : t_2 : : \sqrt{s_1} : \sqrt{s_2}$. That is, *the times required for the effusion of equal volumes of different gases under the same conditions of temperature and pressure are directly proportional to the square roots of the specific gravities of the gases.* The molecular weights are proportional to the specific gravities; substituting, we have

$$t_1 : t_2 : : \sqrt{m_1} : \sqrt{m_2}.$$

Table IX contains some of Graham's data arranged and recalculated by O. E. Meyer.

TABLE IX

Gas	Square Root of the Specific Gravity	Time of Effusion Through a		
		Drawn Out Glass Tube	Perforated Brass Plate	
			I	II
Hydrogen	0.263	0.277	0.276	——
Marsh gas	0.745	0.756	——	0.753
Carbon monoxide	0.984	0.987	——	——
Ethylene	0.985	——	——	0.987
Nitrogen	0.986	0.984	0.984	0.988
Air	1.000	1.000	1.000	——
Oxygen	1.051	1.053	1.050	1.056
Nitrous oxide	1.237	1.199	——	——
Carbonic acid	1.237	1.218	1.197	1.209

CHAPTER IX

SPECIFIC HEAT OF GASES

THE amount of heat required to raise the temperature of a substance one degree is known as the *heat capacity* of the body and will be designated by q. If the amount of heat absorbed by a body when its temperature is raised from $t_1°$ to $t_2°$ is H units of heat, then the *mean heat capacity* (q_M) would be $q_M = \frac{H}{t_2° - t_1°}$.

The specific heat capacity, C, usually called the specific heat, of a substance is the amount of heat required to raise one gram of the substance one degree. The unit of heat, the calorie, is defined as the amount of heat required to raise one gram of water one degree Centigrade. The amount of heat required to raise the temperature of one gram of water one degree is different at different temperatures. Therefore it is necessary to define very accurately the temperature used.

Table X illustrates the variation of the specific heat of water with the temperature as given by Callendar at 20° C. as the unit.

The unit employed is the calorie at 20° C., while the calorie at 0° would be 1.0094 calories at 20°, and the mean calorie between 0°–100° is equal to 1.0016 calories at 20° and the value at 15° is equal to 1.0011 calories at 20°.

The *atomic heat* of an element is the specific heat multiplied by the atomic weight, that is, C times atomic weight = the atomic heat. Similarly, the *molecular heat* is the specific heat of the substance multiplied by the molecular weight.

TABLE X — SPECIFIC HEAT OF WATER

Temperature	Specific Heat	Temperature	Specific Heat
0	1.0094	20	1.0000
1	1.0085	25	0.9992
2	1.0076	30	0.9987
5	1.0054	40	0.9982
10	1.0025	50	0.9987
15	1.0011	60	1.0000
16	1.0009	80	1.0033
17	1.0007	100	1.0074

If a gas be subjected to compression, its temperature is raised thereby. On heating a gas the amount of heat required to raise its temperature depends upon whether this is done under constant pressure or constant volume. To keep the volume of a gas constant when it is heated, an increase in pressure is required, because the kinetic energy of rectilinear motion of the molecules is increased. That is, the added energy is changed into energy of motion of the molecules, which produce additional pressure. If, however, the gas is allowed to expand when it is heated and the pressure kept constant, work must be done to move this external pressure as the gas expands. In the latter case we have what is designated the specific heat at constant pressure C_p, and in the first, the specific heat at constant volume C_v.

The difference between these two specific heats is the work done against the external pressure. The relation between the two specific heats may be easily determined.

Let us assume that we have one gram-molecule of gas under standard conditions of temperature and pressure, and it will occupy 22.4 liters. If it is heated from 0° to 1° C, it expands $\frac{1}{273}$ of its original volume, or $\frac{1}{273}$ of 22.4 liters = 0.08204 liter. During this expansion, work is done in increasing the volume against the pressure. This work is equal to 0.08204 liter atmosphere. But 0.08204 liter atmosphere per degree is the constant R of the Gas Law Equation. Therefore the difference between the molecular heat at constant pressure, mC_p, and at constant volume, mC_v, is R, that is, $mC_p = mC_v + R$.

R may be calculated in calories as follows: 1 calorie = 42,690 gram-centimeters; R expressed in gram-centimeters is

$$\frac{1033.6 \times 22400}{273} = 84780 \text{ and } \frac{84780}{42690} = 1.986 \text{ calories or } R$$

= approximately 2 calories.

The molecular heats, mC_v and mC_p, of some of the more common gases are given in Table XI.

TABLE XI

The values for mC_p were determined experimentally and mC_v by difference.

GAS	SPECIFIC HEAT C_p	mC_p	mC_v	$\frac{C_p}{C_v}$
Argon	——	——	——	1.66
Helium	——	——	——	1.66
Mercury	——	——	2.965	1.66
Hydrogen	3.409	6.880	4.880	1.412
Oxygen	0.2175	6.960	4.960	1.40
Chlorine	0.1241	8.810	6.810	1.29
Hydrochloric acid	0.1876	6.85	4.85	1.409
Nitrous oxide	0.2262	9.99	7.99	1.247
Methane	0.893	9.51	7.51	1.266

The heat added to a substance may be utilized in (1) increasing the kinetic energy of rectilinear motion of the molecules, manifesting itself only in a rise of the temperature; (2) in performing work against the external pressure in order to expand the gas, or (3) utilized within the molecule itself when it is an associated or polyatomic molecule; and (4) in overcoming the mutual attraction of the molecules. In the case of ideally perfect gases the molecules are out of the sphere of action of one another, and consequently the effect of this last consideration is very small and therefore practically negligible.

If the law $pV = RT$ holds for the gas, the specific heat of the gas must be independent of the pressure and also of the volume. The whole work done during a change of volume will be external. If the volume changes from v_1 to v_2 under constant pressure p, the external work will be $p(v_2 - v_1)$. Now, as we have seen, the specific heat at constant pressure exceeds that at constant volume by the thermal equivalent of the work required to overcome the resistance offered to the expansion of the gas.

In equation $mC_p - mC_v = R$, substituting for R its value, $\frac{pV}{273}$, we have

$$mC_p - mC_v = \frac{pV}{273}.$$

From the consideration of the Kinetic Theory of Gases we found that $pV = \frac{1}{3}\, mnu^2$, and for the kinetic energy $K = \frac{1}{2}\,(mn)u^2$.

Equating these, we have

$$3\,pV = 2\,K,$$

or

$$pV = \tfrac{2}{3}\,K,$$

which enables us to express the molecular energy in a form which can be readily determined. The pressure and kinetic energy of a gas are in an invariable ratio which is independent of the temperature. Substituting this value for pV in the equation above, we have

$$mC_p - mC_v = \frac{2\,K}{273 \times 3}.$$

All of the energy, E, possessed by the substance is the heat required to warm it from absolute zero to the given temperature at constant volume. This is increased by the heat required to warm the gas from 0° to 1°, that is, by $\frac{1}{273}$ of E. But this heat at constant volume is the specific heat at constant volume, that is, $mC_v = \frac{1}{273} E$. Then dividing the above equation by this, we have

$$\frac{mC_p - mC_v}{mC_v} = \frac{\frac{1}{273} \cdot \frac{2}{3} K}{\frac{1}{273} \cdot E} = \frac{2}{3} \frac{K}{E}.$$

In case the total energy is the kinetic energy, then $K = E$ and the equation becomes

$$\frac{mC_p - mC_v}{mC_v} = \frac{2}{3} \text{ or } \frac{C}{C_v} = \frac{5}{3} = 1.666$$

which is the maximum value of the ratio of the specific heat at constant pressure to the specific heat at constant volume. This value has been obtained experimentally in the case of monatomic gases, mercury vapor, argon, and helium.

In the case of diatomic or polyatomic gases, an appreciable portion of the heat applied to raise the temperature is utilized in overcoming the mutual attraction of the molecules or in intermolecular work. It is possible to raise the temperature of some substances to such an extent that this portion of the energy increases the speed of the atoms within the molecule whereby they are separated from their combination with the others, and the freed atoms thus become like independent molecules, the atomic energy going to increase the total molecular energy. This would lead us to the conclusion that the kinetic energy of the atoms would be decreased and the molecular energy increased, hence $K < E$. It is apparent that in the case where the amplitude of vibration of the atoms of the molecules has not been increased sufficiently to cause them to pass beyond the influence of the other atoms within the molecule, just before dissociation takes place, that we will have the maximum of heat energy being utilized in the atomic energy. The more atoms there are in the molecule, the greater will be the amount used in this way and consequently the greater the decrease in the kinetic energy and the less the value of the ratio:

$$\frac{\text{molecular heat at constant pressure } mC_p}{\text{molecular heat at constant volume } mC_v} = y.$$

Hence it follows that by determining y for a given gas or vapor, it would be possible to determine the complexity of the molecules.

There are a number of methods by which the value of y may be obtained, and it is not always necessary actually to determine both of the specific heats.

Laplace showed that the velocity of sound in a gas is expressed as follows: $v = \sqrt{\frac{yp}{\rho}}$, where v is the velocity, y is the ratio of the two specific heats, p the pressure, and ρ the density. The method of Kundt and Warburg, which is usually employed, is a means of finding experimentally the value of v. The apparatus consists of a "Kundt's dust tube," and as employed by Ramsay in the determination of the specific heat of helium consisted of a long tube of narrow bore, closed at one end, through which is sealed a glass rod extending for an equal distance inside and outside of the tube. Some lycopodium powder is distributed along the tube and dry air is introduced. The glass rod is set in vibration by rubbing it with a cloth wet with alcohol. By moving the clamp on the rubber tubing which closes the other end of the tube, the length can be adjusted till it resounds to the proper note. The interference of the waves deposits the lycopodium in piles at the nodes. The distance between these nodes represents one half the wave length and can be readily measured. Air is then removed by evacuation, and the tube is refilled with the gas under investigation and the wave length determined.

Let λ represent the wave length of a sound of frequency n in any specified gas; let p = the pressure and ρ its density, then from Laplace's formula we have for any two gases under the same pressure and temperature:

$$v_1 = \sqrt{\frac{y_1 p}{\rho_1}} \text{ and } v_2 = \sqrt{\frac{y_2 p}{\rho_2}}, \text{ or } \frac{v_1}{v_2} = \sqrt{\frac{y_1}{\rho_1}\frac{\rho_2}{y_2}}.$$

Since the densities are proportional to the molecular weights, we may write the equation

$$\frac{v_1}{v_2} = \sqrt{\frac{y_1}{y_2}\frac{m_2}{m_1}}$$

which becomes

$$\frac{v_1^2}{v_2^2} = \frac{y_1}{y_2}\frac{m_2}{m_1}.$$

Taking air as the standard gas, $y_1 = 1.408$; the value of y for any other gas is then obtained by comparing the wave lengths of the same sound in the gas and in air, providing the molecular weight or density of the gas is known. The velocity is equal to the wave length times the number of vibrations (pitch) in a unit of time. If x is the distance between the nodes or ridges of dust, then $\lambda = 2x$ and the velocity is $2nx$. Then we would have $v_1 = 2nx_1$, and $v_2 = 2nx_2$, which, substituted in the above equation, gives

$$\frac{2nx_1}{2nx_2} = \sqrt{\frac{y_1}{y_2}\frac{m_2}{m_1}} \text{ or } \frac{x_1^2}{x_2^2} = \frac{y_1}{y_2}\frac{m_2}{m_1} \text{ or } y_2 = y_1 \frac{x_2^2}{x_1^2}\frac{m_2}{m_1}.$$

Substituting the value for air, $y_1 = 1.408$ and $m_1 = 28.9$, the value for y_2 can be obtained if the other values are known; x_2 and x_1 being obtained experimentally and m_2 being known.

CHAPTER X

VAN DER WAALS' EQUATION

WE saw that the Laws of Boyle, Gay Lussac, and Avogadro are only strictly applicable to *perfect* gases. Under low pressure the deviation is small, but it is greater when gases are highly compressed. We considered that the kinetic energy of rectilinear motion of the molecules is directly proportional to the absolute temperature under all conditions, and so certain modifications in the Kinetic Theory were suggested by van der Waals to explain the observed variations.

In the Kinetic Theory the pressure due to the bombardment of the walls of the vessel by the molecules of the gas is calculated on the assumption (1) that the actual volume occupied by the molecules is inappreciable compared with the total volume of the gas, and (2) that the molecules exert no appreciable attraction for each other. It is found that when the gas is greatly rarefied, this assumption is admissible, but when the molecules are brought close together by compression of the gas, it is not; hence the Gas Law Equation must be modified to take these facts into consideration. Many attempts have been made to correct the Gas Law Equation for this purpose, the most successful being that of van der Waals (1879).

According to the Kinetic Theory the total volume occupied by the molecules is small in comparison to the total volume of the gas. Van der Waals corrected for the volume actually occupied by the molecules thus:

Let b = volume occupied by molecules of gas

v = volume of the gas

then $(v - b)$ = the actual or free space in which the molecules are free to move, and when the gas is subjected to pressure this is the part which decreases in volume.

In 1854 Joule and Thomson showed experimentally that strongly compressed gases are cooled by expansion. Then, on expansion, work is done against the molecular force, and we conclude that the molecules have attracted one another. Hence a certain cohesion is ascribed to the gases, which is more noticeable the greater their density. Under high pressure gases contract more than they should according to Boyle's Law, and this is explained on the supposition that in compression the molecules are drawn more closely together by their attractive force, and this tends to aid the external pressure in making the volume smaller. Therefore this factor should be *added* to the external pressure. This force must be proportional to the number of molecules attracting each other, that is, to the density of the gas, since the density of a given gas is proportional to the number of molecules per unit volume. Van der Waals concluded that the attraction is proportional to the square of the density or inversely to the square of the volume, and gave $\frac{a}{V^2}$ as the expression for this correction.

Substituting these two values in the Gas Law Equation we have

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

which is known as van der Waals' *Equation of Condition.* This equation gives the behavior of the so-called permanent gases, of the easily condensed gases, and it is also claimed that it can be applied to the liquid state as well, although Tait has pointed out that it does not hold for any real liquid.

It is apparent that when the volume is large, the correcting factors, $\frac{a}{V^2}$ and b, have no appreciable influence and the equation is really $pV = RT$. When the pressure is very great, the factor b ceases to be negligible, and its influence increases more rapidly than $\frac{a}{V^2}$. The product pV reaches a minimum, and afterwards increases, and eventually becomes much greater than at low pressures.

For ethylene, which is readily liquefiable, Baynes calculated the values of pV from the following formula:

$$\left(p + \frac{0.00786}{V^2}\right)(V - 0.0024) = 0.0037\,(272.5 + t)$$

where $pV = 1000$ for $p = 1$ atmosphere at 20° C. The observed values in Table XII are from Amagat's results.

TABLE XII

p	pV	
	Observed	Calculated
1	1000	1000
31.6	914	895
72.9	416	387
110.5	454	456
176.0	643	642
282.2	941	940
398.7	1248	1254

Van der Waals assumed that the molecules of an ordinary substance undergo no alteration during the process of liquefaction, and his equation is intended to apply only to such substances. When association takes place, the relation between pressure, volume, and temperature becomes complex.

If V remains constant, then

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

takes the form

$$(p + C)C' = RT$$

$$p + C = \frac{R}{C'}T \text{ or } p = \frac{RT}{C'} - C \text{ or } p = kT - C$$

where C and C' are constants and $k = \frac{R}{C'}$.

That is, the p is a linear function of the absolute temperature when the volume of the mass remains constant.

The constants a and b in van der Waals' equation may be calculated from experimental data; or from a number of isotherms the pressure and temperature at a series of constant volumes may be read off and the values of the constants k and C in the formula $p = kT - C$ calculated for each volume.

Clausius (1880) claimed that van der Waals' equation did not represent the facts with sufficient exactness and developed an equation himself which allowed for the variation of molecular attraction with change in temperature.

The Clausius equation, $p = \frac{R\theta}{V - a} - \frac{c}{\theta(V + B)^2}$, contains four constants, R, c, a, B, which necessitate four experiments on p and V at different temperatures to establish, and it is claimed to give greater range and better agreement than van der Waals' equation which contains only three constants.

Application of van der Waals' Equation

The following quotation is Andrews' description (1863) of his experiments on the behavior of carbon dioxide when subjected to changes of pressure and of temperature: "On partially liquefying carbonic acid by pressure alone and gradually raising at the same time the temperature to 88° F.

the surface of demarcation between the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout its entire mass. At temperatures above 88° F. no apparent liquefaction of carbonic acid, or separation into two distinct forms of matter, could be effected even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results."

Andrews plotted the results of his experiments, and the curves in Fig. 8 represent them.

The p–V curve of constant temperature, *isothermal curve*, for gases that obey Boyle's Law, should be a rectangular hyperbola, and the curve for CO_2 at 48.1° approximates this closely. At 35.5° the curve has a decided flexure, while at 32.5° this is more marked, and at 31.1° still more marked, when we have a double flexure. This curve runs for a short distance parallel to the V-axis and represents the critical temperature of CO_2. The volume diminishes regularly with increase in pressure at this temperature until a pressure of 73 atmospheres is reached, when the volume decreases very rapidly, about one half of it disappearing. A steady increase in pressure is required to produce this change, and by the time 77 atmospheres are reached we have a homogeneous mass which responds to a regular change in volume with increased pressure. At 21.5° we have the volume gradually decreasing with increased pressure until about 60 atmospheres are reached, when there is a sudden break in the curve which

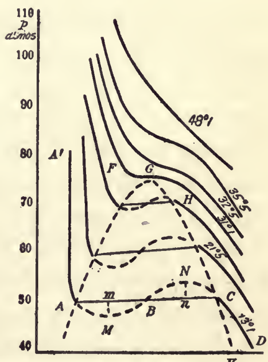


FIG. 8.

runs parallel to the V axis, showing a marked decrease in volume without change in temperature. This is similar to the curve at 13.1°, which becomes horizontal at 49 atmospheres pressure, showing a change of about $\frac{3}{5}$ the volume a perfect gas should occupy at this temperature.

Andrews from his experimental work insisted on the idea of the continuous passage of vapor into the liquid form on increasing the pressure, and Thomson, in an effort to explain the shape of the isotherms just above the critical temperature, prescribed an hypothesis in confirmation of this idea as illustrated by Fig. 8.

FGH represents the isotherm above the critical temperature and pressure, where van der Waals' equation assumes a continuous passage from the liquid to the vapor state or *vice versa.* The line *ABC*, which is a broken line, represents the ordinary isotherm of a substance passing from the liquid to the gaseous state. The part *AB* refers to the liquid state, at *B* the vapor pressure is equal to the external pressure, and the substance begins to separate into saturated vapor and liquid. The horizontal portion *BC* shows that while this change is taking place the pressure remains constant and represents the isotherm of the mixture. The portion *CD* represents non-saturated vapor, and the isotherm approximates more nearly that of a perfect gas.

James Thomson suggested that AA' and *CD* are portions of the same continuous curve and are connected by some ideal branch, such as *AMBNC*, along which the substance might pass continuously from liquid to gaseous condition below the critical temperature, as it does above that temperature, without separation into two distinct states simultaneously existing in contact with each other. Along *AM* we have the condition of superheated liquids, and along *CN*, supersaturated vapors. So the abnormal conditions of both liquid and vapor are represented by Thomson's curve *AMBNC*, as conditions of unstable equilibrium. The vapor at N is supersaturated, it condenses when equilibrium is destroyed, and if the temperature be kept constant, a decrease of pressure to the point n will take place. Similarly at M we have a superheated liquid which on disturbing the equilibrium assumes a condition of stable equilibrium with explosive violence and assumes the condition represented by m when the substance is partly liquid and partly vapor. Between N and M we have the volume and pressure increasing simultaneously, a condition difficult to realize in a homogeneous mass. It is apparent that the pressure curve cuts the Thomson hypothetical curve at three points, A, B, and C, which would correspond to three different values for the volume for the one value of the pressure. As the pressure increases it is apparent that the Thomson curve decreases in length, the difference between the three values of the volumes becomes less; and as we approach the critical point these values likewise approach this value of the critical volume as their simultaneous and limiting value.

Realization of Parts of Curve Experimentally. — 1. Methyl formate (31.9° B. Pt.) was heated to 80° and the whole of the vapor condensed. Pressure was lowered below 800 mm. without boiling taking place; at 80° the vapor pressure is 3500 mm., so that the pressure was reduced to less than one fourth of the vapor pressure; in other words, it was more than 45° above its boiling point under 800 mm. and 80° C. Boiling finally took place with explosive violence.

2. Worthington showed that when a sealed tube, nearly full of pure liquid free from air, is gently warmed until the liquid fills the tube completely, a bubble of vapor will not form on cooling until a very large negative pressure is reached. The tubes collapsed in some cases.

3. Aitken showed that temperature of dust-free vapors could be lowered many degrees below the condensing point before liquefaction takes place.

It is therefore proved that part of the continuous isothermal (Fig. 8) from A to M and from C towards N may be realized experimentally. From M to N increase in volume is attended with rise of pressure, and if it could be brought about, would take place with explosive rapidity.

Calculation of Critical Constants from van der Waals'. Equation

The Gas Law Equation $pV = RT$, when corrected for the volume b, actually occupied by the molecules and the mutual attraction of the molecules, $\frac{a}{V^2}$, gives us van der Waals' equation:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad (1)$$

which, when rearranged in the order of the decreasing powers of V, gives

$$V^3 - \left(b + \frac{RT}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0 \qquad (2)$$

Under normal conditions of temperature, when $V = 1$, $p = 1$, and $T = 273$, equation (1) becomes

$$(1 + a)(1 - b) = 273\ R \qquad (3)$$

Solving for R, we have

$$R = \frac{(1 + a)(1 - b)}{273}$$

Substituting this value of R in equation (2), we have

$$V_3 - \left(b + \frac{(1 + a)(1 - b)\ T}{273\ p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0 \qquad (4)$$

This is a cubic equation with respect to V, if p is constant, with three roots, one or all of which may be real. We saw that there is one temperature at which the three values of V for one value of p become equal and that is at the Critical Temperature. But at this temperature the pressure is designated the *critical pressure* and the volume the *critical volume*. Let us designate these critical values for V, p, and T respectively as follows: V_c, p_c, and T_c. If the three roots are equal, they become the critical volume V_c, and the cubic equation becomes $(V - V_c)^3 = 0$, which, on expanding, becomes

$$V^3 - 3\,V_cV^2 + 3\,V_c^2V - V_c^3 = 0 \qquad (5)$$

which is equivalent to our equation (4).

Equating[1] the coefficients of equations (4) and (5), where V_c is the critical volume, and remembering that the corresponding values for T and p are their critical values, we then have

$$3\,V_c = b + \frac{(1 + a)\,(1 - b)}{273\,p_c}\,T_c \qquad (6)$$

$$3\,V_c^2 = \frac{a}{p_c} \qquad (7)$$

$$V_c^3 = \frac{ab}{p_c} \qquad (8)$$

From these three equations we can calculate the critical values in terms of a and b, the constants of van der Waals' equation.

Dividing (8) by (7), we have

$$\frac{V_c^3}{3\,V_c^2} = \frac{ab}{p_c} \times \frac{p_c}{a}$$

$$\frac{V_c}{3} = b$$

[1] Wells states the Theorem of Undeterminate Coefficients as follows: If the series $A + Bx + Cx^2 + Dx^3 + \ldots$ is always equal to the series $A' + B'x + C'x^2 + D'x^3 + \ldots$ where x has any value which makes both series convergent, the coefficients of like powers of x in the two series will be equal; that is, $A = A'$, $B = B'$, $C = C'$, $D = D'$, etc. From this we have the following rule: If two equations represent the same locus and one term of one equation is exactly the same as one term of the other, then the coefficients of like powers of the variable are equal.

Then $V_c = 3\,b$ (critical volume). (9)

Substituting this value in (7), we have

$$3\,(3\,b)^2 = \frac{a}{p_c}$$

Solving for p_c,

$$3 \cdot 9\,b^2 = \frac{a}{p_c}$$

$$p_c = \frac{a}{27\,b^2} \text{ (critical pressure).} \quad (10)$$

Substituting these values of V_c and p_c in equation (6) we have

$$3 \cdot 3\,b = b + \frac{(1 + a)\,(1 - b)\,T_c}{\frac{a}{27\,b^2}273}$$

$$T_c = \frac{8}{27}\frac{a \cdot 273}{b(1 + a)\,(1 - b)} \text{ (critical temperature).} \quad (11)$$

If we desire to retain the value of the gas constant R in the equation, instead of expressing the initial standard conditions as $\frac{p_0 V_0}{T_0}$ and defining them as $p_0 = 1$, $V_0 = 1$, and $T_0 = 273$, we could have kept this as R, and equation (4) would take the form

$$V^3 - \left(b + \frac{RT}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0 \quad (12)$$

and equation (6) would become

$$3\,V_c = \left(b + \frac{RT_c}{p_c}\right) \quad (13)$$

From which T_c can be calculated by substituting values of V_c and p_c from equations (9) and (10) respectively, and we have

$$3 \cdot 3\,b - b = \frac{RT_c}{\frac{a}{27\,b^2}}$$

$$8\,b = \frac{27\,b^2 R T_c}{a}$$

$$T_c = \frac{8\,a}{27\,bR}. \qquad (14)$$

Conversely, we may express the values of the constants a, b, and R in terms of the critical values.

From equation (9),

$$V_c = 3\,b$$

Solving for b, we have

$$b = \frac{V_c}{3} \qquad (15)$$

From equation (10),

$$p_c = \frac{a}{27\,b^2}$$

Solving for a, we have

$$a = 27\,b^2 p_c \qquad (16)$$

Substituting the value of b from (15), we have

$$a = \frac{27\,V_c^2}{9}\,p_c = 3\,V_c^2 p_c \qquad (17)$$

Solving equation (14) for R, we have

$$R = \frac{8\,a}{27\,bT_c} \qquad (18)$$

and substituting the value of a from (17) and b from (15), we have

$$R = \frac{8 \cdot 3\,V_c^2 p_c}{27 \frac{V_c}{3} T_c}$$

which simplifies to

$$R = \frac{8}{3}\frac{V_c p_c}{T_c} \tag{19}$$

$$\therefore \frac{p_c V_c}{T_c} = \frac{3}{8} R. \tag{20}$$

The Reduced Equation of State

If we substitute in van der Waals' equation the values of critical values of the pressure, volume, and temperature, we have

$$\left(p + \frac{3\,V_c^2 p_c}{V^2}\right)\left(V - \frac{V_c}{3}\right) = \frac{8}{3}\frac{V_c p_c}{T_c} T. \tag{21}$$

This may be simplified if we divide each side of the equation by $\frac{V_c p_c}{3}$; dividing the first factor of the left member by p_c and the second by $\frac{V_c}{3}$, we have

$$\left(\frac{p}{p_c} + \frac{3\,V_c^2}{V^2}\right)\left(\frac{3\,V}{V_c} - 1\right) = 8\frac{T}{T_c}. \tag{22}$$

It is apparent that the values of the pressure, volume, and temperature are expressed as factors of the critical values, hence if we substitute for these fractions

$$\pi = \frac{p}{p_c},\quad \phi = \frac{V}{V_c},\quad \theta = \frac{T}{T_c},$$

we have

$$\left(\pi + \frac{3}{\phi^2}\right)(3\,\phi - 1) = 8\,\theta.$$

Therefore, expressing V, p, and T respectively in fractions of the critical volume, pressure, and temperature, the equation of condition assumes the same form for all substances, or if two liquids be taken under the conditions of temperature and pressure which are the same fractions of their respective critical values, such conditions are known as *corresponding* conditions; the law is called the *Law of Corresponding States*, and the equation is the *Reduced Equation of State.*

This equation is independent of the substance and of the physical state of the substance, as there are no arbitrary constants, provided that molecular association or dissociation does not take place. Young investigated this relationship and showed that the value for the reduced pressures is the same for all substances and is 0.08846. The substances at their boiling point are under *corresponding states*, and the value of the ratio of the boiling temperature to the critical temperature is about 0.75. If the substance is under corresponding pressure and temperature, the volume is also a *corresponding volume.* This is emphasized by the data given in Table XIII.

TABLE XIII — REDUCED VALUES IN CORRESPONDING STATES

(COMPILED FROM YOUNG'S STOICHIOMETRY)

Ratio of Pressure to Critical Pressure = 0.08846

SUBSTANCE	$\frac{T}{T_c} = \theta$	$\frac{V\ \text{liquid}}{V_c} = \phi$	$\frac{V\ \text{gas}}{V_c} = \phi$
Acetic Acid	0.7624	0.4100	25.4
Benzene	0.7282	0.4065	28.3
Carbon Tetrachloride	0.7251	0.4078	27.45
Ether	0.7380	0.4030	28.3
Ethyl Acetate	0.7504	0.4001	30.25
Ethyl Alcohol	0.7794	0.4061	32.15
Ethyl Formate	0.7385	0.4003	29.6
Methyl Acetate	0.7445	0.3989	30.15
Methyl Alcohol	0.7734	0.3973	34.35
Methyl Formate	0.7348	0.4001	29.3
Stannic Chloride	0.7357	0.4031	28.15

The data confirm van der Waals' generalization that: "When the absolute temperatures of two substances are proportional to their absolute critical temperatures, their vapor pressures will be proportional to their critical pressures, and their orthobaric (the volume of a liquid at a given temperature and under a pressure equal to the vapor pressure) volumes, both as a liquid and vapor, to their critical volumes."

CHAPTER XI

THE PHYSICAL PROPERTIES OF LIQUIDS

Molecular Volume

Kopp (1858) showed that it is possible to calculate the volume of one gram-molecule of a liquid organic substance at its boiling point from its composition.

Molecular volume equals the specific volume times the molecular weight; that is,

$$Molecular\ volume = \frac{Molecular\ weight}{density}$$

or

$$mol.\ vol. = \frac{m}{\rho}$$

Kopp selected their boiling points as his condition for comparing substances. The question arises, was he justified in selecting this particular condition, and if so, then the boiling temperatures must represent *corresponding states* and consequently *corresponding temperatures.* If the boiling points are *reduced* temperatures, his selection of the boiling temperatures has been justified.

Guldberg (1890) and Guye (1890) both showed that the boiling temperature at atmospheric pressure is about two thirds of the critical temperature expressed on the absolute scale. We have just seen that the work of Young presented in Table XIII confirms this and that the boiling temperature of liquids is a reduced temperature and that the substances at their boiling points are at corresponding states.

Kopp determined the molecular volume of a number of liquids at their boiling points and drew the following conclusions:

1. Among homologous compounds, the same difference of molecular volume corresponds to the same difference of composition.

2. Isomeric liquids have the same molecular volume.

3. By replacing two atoms of hydrogen by one atom of oxygen the molecular volume is unchanged.

4. An atom of carbon can replace two atoms of hydrogen without change of volume.

The first conclusion stated above is illustrated in Table XIV, where m = molecular weight, v the specific volume, $v = \frac{1}{\rho}$, where ρ = the density. The molecular volume $V_m = \frac{m}{\rho}$.

TABLE XIV

	m	Vm	DIFFERENCE
Methyl alcohol CH_3OH . .	32	39.4	
			17.7
Ethyl alcohol C_2H_5OH . .	46	57.1	
			16.3
Propyl alcohol C_3H_7OH . .	60	73.4	
			16.5
Butyl alcohol C_4H_9OH . .	74	89.9	
			16.2
Amyl alcohol $C_5H_{11}OH$.	88	106.1	
			16.4
Hexyl alcohol $C_6H_{13}OH$.	102	122.5	
			16.2
Heptyl alcohol $C_7H_{15}OH$.	116	138.7	
			16.2
Octyl alcohol $C_8H_{17}OH$.	130	154.9	
			16.2
Nonyl alcohol $C_9H_{19}OH$.	144	171.1	

The difference in composition of these compounds is CH_2, which makes a difference in the molecular volume of 16.2 units, under the given conditions, while under other conditions the value for a constant difference in composition may be different.

In his later more accurate investigations Kopp found the value for CH_2 in two homologous series as given in Table XV.

TABLE XV

		Molecular Volume	Difference
Formic acid	$H\,COOH$	41.8	
Acetic acid	$CH_3\,COOH$	63.5	21.7
Propionic acid	$C_2H_5\,COOH$	85.4	21.9
Butyric acid	$C_3H_7\,COOH$	106.6	21.2
Valeric acid	$C_4H_9\,COOH$	130.3	23.7
Ethyl formate	$H\,COOC_2H_5$	85.4	
Ethyl acetate	$CH_3\,COOC_2H_5$	107.6	22.2
Ethyl propionate	$C_2H_5COOC_2H_5$	125.8	18.2
Ethyl butyrate	$C_3H_7COOC_2H_5$	149.1	23.3

From this he concluded that the value of CH_2 is equal to 22. He also found that by replacing 2 C by 4 H, or C by 2 H, the molecular volume did not change. That is, CH_2 would be equivalent then to 2 C = 22, therefore C = 11 and 2 H would = 11 and H = 5.5. In this manner the *atomic* volumes of other elements were obtained and the following values have been assigned: C = 11; H = 5.5; O = 11. It would follow from this that the molecular volume would be the sum of the atomic volumes just as the molecular weight is the sum of the atomic weights. Hence, it follows that isomeric bodies would have the same molecular volume. Methyl acetate, CH_3COOCH_3, Boil. Pt. 57.1°, has a molecular volume of 84.8, while for ethyl formate, $HCOOC_2H_5$, Boil. Pt. 54.3°, the molecular volume was found to be the same, 85.4. Hence the molecular volume is an *additive property*. However, in attempting to calculate the molecular volume from the atomic volumes it was found that for compounds of different types there was a marked consistent discrepancy between the observed and the calculated volumes. This fact led Kopp to assign different values to the same element, depending upon the influence of the nature of the atom and its linking or architectural relation to the other atoms. Hence there was a constitutive relation which had to be taken into consideration which demonstrated that this property is *not strictly* additive.

Kopp found that for oxygen singly linked, as in the hydroxyl group (OH), the value of the atomic volume is 7.8, while for doubly linked oxygen, in the carbonyl group (CO) it is 12.2. On this basis, the calculated values for forty-five different compounds did not vary more than four per cent. Kopp gives the following values for the elements:

C	11.0	Cl	22.8
O (OH)	7.8	Br	27.8
O (CO)	12.2	I	37.5
H	5.5	S	22.6

Sulphur and nitrogen show variations similar to oxygen; they have different values in some different types of compounds; in ammonia, N = 2.3, in the cyanogen group, CN, it = 28, and in the nitro group, NO_2, it = 33, which shows great variations in the value of the nitrogen.

Schroeder, as well as Kopp, suggested that the atomic volume of different elements is the same or some multiple of the same number, which unit is called a *stere*, the value of which was between 6.7 and 7.4. Later Buff (1865) showed that unsaturated elements gave higher values than saturated ones; that is, a correction had to be made for the double bond, which was estimated at about four units. But in the case of the paraffins and their corresponding olefines this value of the double bond is practically *nil*.

The formation of ring compounds results in the decrease in the molecular volume. By comparing the values in Table XVI for the homologous series of paraffins with the cycloparaffins, which differ by 2 H, Willtstätter (1907) showed the effect of the ring structure.

TABLE XVI

PARAFFIN	V_m AT 0°	CYCLOPARAFFIN	V_m AT 0°	DIFFERENCE
Butane . . .	96.5	Cyclobutane . . .	79	17.5
Pentane . . .	112.4	Cyclopentane . .	91.1	21.3
Hexane . . .	127.2	Cyclohexane . . .	105.2	22.0
Heptane . . .	142.5	Cycloheptane . .	118.0	24.5
Octane . . .	158.3	Cyclooctane . . .	130.9	27.4
Nonane . . .	174.3	Cyclononane . . .	159.5	14.8

If the value for 2 H be deducted from the differences, it is apparent that the ring formation is accompanied by a marked contraction.

More recently Ramsay, Thorpe, and Lossen, as well as Schiff, have worked over the old data and collected new evidence which confirms in general Kopp's law and his first approximations.

SURFACE TENSION OF LIQUIDS

Within a liquid a molecule is attracted equally in all directions by those near it, and this force diminishes rapidly as the distance from the molecule increases. It is apparent that this attractive force must be uniform, since there is no accumulation of the molecules of the liquid in one portion; *i.e.* the densities of all portions of the liquid are the same.

As we approach the surface of a liquid the attraction from above diminishes and the *tension* from the sides increases. This increased tension along the surface in all directions is much greater than that between the molecules in the interior of the liquid. The resultant of these forces is normal to the surface inward and *not* outward, which results in a tendency for the molecules to be drawn into the liquid with a corresponding decrease in the surface. This force acting along the surface and tending to decrease the volume is designated the *surface tension*, and hence the unit surface tension, γ, of a liquid is the force acting at right angles to a line one centimeter in length along the surface of the liquid. The molecules on the surface must have more energy than those on the interior, and this increase in energy expressed in ergs per square centimeter of surface is numerically equal to the surface tension expressed in dynes per linear centimeter.

The surface tension may be determined from the height to which the liquid will rise in a capillary tube.

Let h = height in centimeters that the liquid rises,
r = radius of the capillary tube,
γ = surface tension, expressed in dynes per centimeter.

The length of contact of the surface of the liquid with the inner surface of the tube, multiplied by the tension per centimeter, gives the total force acting, *i.e.* $= 2\pi r\gamma$; but this is equivalent to supporting a column of liquid of height h, and density ρ, against the force of gravity. Therefore we have

$$\pi r^2 g\rho h = 2\pi r\gamma$$

Solving for γ we then have

$$\gamma = \frac{\pi r^2 g\rho h}{2\pi r} = \frac{gr\rho h}{2}$$

which is expressed in absolute units.

The surface tension decreases with the rise in temperature, and vanishes at the critical point.

Ramsay and Shields (1893) employed the surface tension of liquids for the determination of molecular weights of pure substances in the liquid state, which was an extension of the earlier work of Eötvös (1886).

In the gas equation $pV = RT$, pV may be termed the volume energy of the gas, and it was shown by Eötvös that a similar equation expresses the relation, within certain limits, between the surface energy of the liquid and the temperature, which is

$$\gamma V^{\frac{2}{3}} = k(t_0 - t)$$

in which γ = surface tension, t_0 = temperature at which $\gamma V^{\frac{2}{3}} = 0$, t = temperature of observation, and V = molecular volume which is equivalent to mv. If mv = volume of a cube, then the area of one of the faces is $(mv)^{\frac{2}{3}}$, and since the molecular volumes contain the same number of molecules, the molecular surface $(mv)^{\frac{2}{3}}$ or $V^{\frac{2}{3}}$ would have an equal number of molecules distributed on it.

Experimentally the temperature, t_0, was found to coincide practically with the critical temperature, *i.e.* $t_0 = t_c$. If we define $\tau = t_c - t$, then it is apparent that τ is the temperature measured downward from the critical temperature. We may then write our equation

$$\gamma V^{\frac{2}{3}} = k\tau$$

and as $V^{\frac{2}{3}}$ = surface (s) over which a definite number of molecules are distributed, substituting we have

$$\gamma \cdot s = k\tau.$$

Ramsay and Shields, from carefully determined surface tension measurements over the whole range of temperatures up to the critical temperature, showed that this equation holds only approximately. By plotting the values of $\gamma \cdot s$ against temperatures (t) we have the curve represented in Fig. 9. At $t_c = t$, $\tau = 0$ and $\gamma \cdot s = 0$; but at lower temperatures, τ increases and the values of $\gamma \cdot s$ are represented by *ABC*, a portion, *AB*, being curved

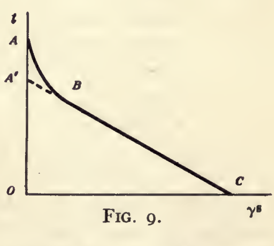


FIG. 9.

and the remainder, *BC*, being a straight line. Hence at temperatures represented by *AA'* the equation does not hold, but beyond a certain distance from the critical point it does hold.

Ramsay and Shields suggested that a correction for this be introduced and that we begin to count from a point A'. Making this correction for the distance d represented by $A - A'$, the equation becomes

$$\gamma \cdot s = k(\tau - d).$$

The value of d is usually 6.

This formula may be rewritten thus:

$$\gamma\,(mv)^{\frac{2}{3}} = k(\tau - d).$$

In order to obtain the value of the constant k, measurements of the surface tension will have to be made at two temperatures. Then for simultaneous values we have

$$\gamma_1(mv_1)^{\frac{2}{3}} = k(\tau_1 - d) \text{ and}$$
$$\gamma_2(mv_2)^{\frac{2}{3}} = k(\tau_2 - d).$$

Solving for k we have

$$k = \frac{\gamma_1(mv_1)^{\frac{2}{3}} - \gamma_2(mv_2)^{\frac{2}{3}}}{\tau_1 - \tau_2}.$$

Substituting the values obtained by Ramsay and Shields and solving for k, the following results were obtained:

	k
Ether	2.1716
Methyl formate	2.0419
Ethyl acetate	2.2256
Carbon tetrachloride	2.1052
Benzene	2.1043
Chlorbenzene	2.0770
Average	2.1209

Hence, using the molecular weight, m, of the substance in the gaseous state, they conclude that the constant k is 2.12 (C.G.S. units) for *normal* liquids whose molecular aggregate is the same in the liquid as in the gaseous state. That is, it holds for *non-associated* liquids. It follows that if a liquid gives a value of the constant 2.12, or more, it is non-associated, and if less, it is associated; hence we have a method of determining the degree of association by determining the relation of the found value of k and the value 2.12 for normal liquids.

If x = the number of molecules in the associated molecule,
mx = number of times the mass of the associated molecule is greater than that of the unassociated molecule.
Our equation would then be

$$\gamma (mxv)^{\frac{2}{3}} = 2.12(\tau - d) \qquad (1)$$

but from the data we would obtain

$$\gamma (mv)^{\frac{2}{3}} = k_1(\tau - d). \qquad (2)$$

Dividing (1) by (2) we have

$$x^{\frac{2}{3}} = \frac{2.12}{k} \text{ or } x = \left(\frac{2.12}{k}\right)^{\frac{3}{2}} \qquad (3)$$

in which x is termed the *association factor* and represents the number of gaseous molecules combined to form the liquid molecule.

Morgan has worked out the practical details by means of which the proportionality of the surface tension of a liquid to the weight of a falling drop of it can be determined. This relationship is known as *Tate's Law*. Morgan substituted the weight of the drop, falling from a fine capillary tube, for the surface tension of the drop and obtained the following equation:

$$w(mv)^{\frac{2}{3}} = k(\tau - d)$$

where k is established by using the non-associated liquid benzene.

Walden makes use of the term *specific* cohesion (a^2) which he defines as $a^2 = \frac{2\gamma}{\rho}$, where γ is the surface tension and

ρ, the density. If the surface tension is measured at the boiling point of the liquid, Walden finds a relation existing between the latent heat of vaporization and the specific cohesion, which is expressed thus: $\frac{L_v}{a^2}$ = constant, where L_v is the latent heat of vaporization at the boiling point. The average value of this constant is given as 17.9. Trouton showed that the latent heat of vaporization, L_v, multiplied by the molecular weight, m, was proportional to the boiling point of the liquid measured on the absolute scale; *i.e.* $\frac{mL_v}{T}$ = constant. This is known as *Trouton's Law*, which emphasizes that the boiling points of liquids are corresponding states, and hence we are justified in using these temperatures as comparable temperatures, and as the boiling points are approximately the same fraction of the critical values, they are *reduced* temperatures. Walden emphasized this, too, when he obtained for a large number of liquids 20.7 as the value of the constant for the equation representing Trouton's Law.

As
$$\frac{L_v}{a^2} = \text{constant} = 17.9 \qquad (1)$$
and
$$\frac{mL_v}{T} = 20.6 \qquad (2)$$
solving for m we have
$$m = \frac{20.6\ T}{17.9\ a^2} = \frac{1.16\ T}{a^2}$$
from which the molecular weight can be calculated.

Using this formula Walden has calculated the molecular weight of a large number of substances and found the usual formula to represent the substance in the liquid state, such as $SnCl_4$, $SiCl_4$, CCl_4, PCl_3, CS_2, etc.

He extended his formula and showed that it is applicable to the melting point of substances and that this temperature is also a *reduced* temperature and consequently a comparable temperature. The formula takes the form

$$m = \frac{3.65\ T}{a^2}.$$

From this fused salts appear to be highly associated, for he obtained for sodium chloride $(NaCl)_{10}$, for sodium bromide $(NaBr)_8$, and for sodium iodide $(NaI)_{6.2}$, as the respective formulæ representing the molecules in the solid state.

NOTE. — See Appendix for further discussion of the relative surface tension and association factors.

CHAPTER XII

REFRACTION OF LIGHT

THE refraction of light furnishes, for transparent liquids, a set of physical constants which may be conveniently and accurately measured. When a ray of light passes from one medium into another, the direction of the entering ray (the incident ray) changes at the surface separating the two media, and will pass into the other medium as the *refracted* ray. The angle this refracted ray makes with the normal to the surface of separation is called the *angle of refraction*, and the angle the incident ray makes with the normal to the surface is termed the *angle of incidence*. The refracted ray lies in the plane of incidence and on the opposite side of the normal to the incident ray.

Let the surface of separation of the two media be represented by AB in Fig. 10, the incident ray by bo, the refracted ray by oc and the normal to the surface by aod, while i is the angle of incidence, and r is the angle of refraction. Then $\sin i = \frac{ba}{bo}$ and $\sin r = \frac{cd}{co}$, or $\frac{\sin i}{\sin r} = \frac{ab}{cd}$, since bo and co are radii of the circle. This ratio, which is termed the relative index of refraction, is designated by n, and we have

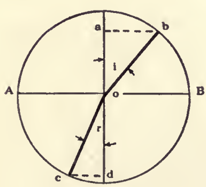


FIG. 10.

$$n = \frac{\sin i}{\sin r}.$$

That is, the sine of the angle of refraction bears a constant ratio to the sine of the angle of incidence. This is *Snell's Law*. The numerical value of this ratio depends on the nature of the two media and on the character of the incident ray.

According to the wave theory of light, this ratio of the sines of the angles of incidence and of refraction is the same as the ratio of the velocities with which the light wave traverses the two media. The *absolute* index of refraction is the value for light passing from a vacuum and would be slightly higher than the value for air; but this correction is rarely made.

In the determination of the index of refraction of liquids, we have the passage of a ray of light through the liquid into the glass prism and then into the air, that is, we have the passage of the ray through the glass prism. In the Pulfrich refractometer, which is one of the principal ones in use, the entering ray of light is adjusted so as to pass horizontally between the liquid and the prism, and the angle of incidence then becomes 90°. If a ray of light be allowed to enter the prism as is indicated in Fig. 11, it will be refracted as it passes into the glass from the liquid and again as it passes from the glass into the air, where it is observed by means of the telescope of the instrument. We desire an expression for *the index of refraction* between the air and the liquid as it is customary to define the ratio when the ray passes from air into the denser medium. For these three media we would have the following relations:

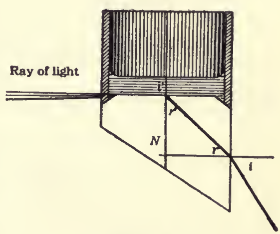


FIG. 11.

$$n_1 = \frac{liquid}{glass};\ N = \frac{air}{glass},\ \text{then}\ \frac{N}{n_1} = \frac{air}{liquid}$$

which we shall designate by n.

Now we have

$$N = \frac{air}{glass} = \frac{\sin i}{\sin r} \quad (1) \quad \text{and} \quad n_1 = \frac{liquid}{glass} = \frac{\sin i'}{\sin r'}$$

and remembering the angle of incidence is 90°, then we have

$$n_1 = \frac{\sin 90^\circ}{\sin r'} \qquad (2)$$

Since $\sin 90^\circ = 1$, this becomes

$$n_1 = \frac{1}{\sin r'} \qquad (3)$$

But $\sin r' = \cos r = \sqrt{1 - \sin^2 r}$. (4)

Transposing (1) we have $\sin r = \frac{\sin i}{N}$ (5)

Substituting in (4)

$$\sin r' = \sqrt{1 - \frac{\sin^2 i}{N^2}} \quad \text{or} \quad \sin r' = \frac{\sqrt{N^2 - \sin^2 i}}{N}$$

Substituting this value in (3), we have

$$n_1 = \frac{1}{\frac{\sqrt{N^2 - \sin^2 i}}{N}} = \frac{N}{\sqrt{N^2 - \sin^2 i}}.$$

Substituting in $n = \frac{N}{n_1}$, we have

$$n = \sqrt{N^2 - \sin^2 i}.$$

Therefore the index of refraction, $n = \sqrt{N^2 - \sin^2 i}$.

The value of N is usually furnished with the instrument, and tables are provided for obtaining the value of n for any observed value of the angle i.

It is necessary to use monochromatic light, as light of different wave lengths is differently refracted and consequently gives different indices of refraction. It is customary to use sodium light, the D line, but the light of other elements is also used, such as that of lithium, strontium, or the three rays of the hydrogen spectrum: the red line H_α, the blue line H_β, and the violet line H_γ.

Methods of Expressing Refractive Power

The index of refraction varies with the temperature and with the pressure, in general, with all conditions that influence the density, and hence efforts have been made to find an expression which will be independent of these various physical factors and which is dependent only upon the chemical nature of the substance. Gladstone and Dale developed the empirical formula $r = \frac{n - 1}{\rho}$, and named this r, the specific refractive index or *specific refractivity.*

Lorentz of Leyden proposed (1880) a formula deduced from the electromagnetic theory of light,

$$r = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{\rho}.$$

Lorenz of Copenhagen simultaneously derived the same formula deduced from the undulatory theory of light. This formula is independent of temperature, pressure, and change of state. Table XVII represents the specific refractivity of water at different temperatures as calculated from both formulæ. The n^2 formula, as it is termed, apparently gives more constant values:

Table XVII

Temperature	Gladstone and Dale $\frac{n-1}{\rho}$	Lorentz $\frac{n^2-1}{n^2+2} \cdot \frac{1}{\rho}$
0°	0.3338	0.2061
10	0.3338	0.2061
20	0.3336	0.2061
90	0.3321	0.2059
100	0.3323	0.2061

The effect of the change of state is shown in Table XVIII. The n^2 formula gives more uniform values, there not being such great differences between the value of the vapor and liquid as by the Gladstone-Dale formula.

TABLE XVIII

Substance	$\frac{n-1}{\rho}$				$\frac{n^2-1}{n^2+2}\cdot\frac{1}{\rho}$		
	Temp.	Vapor	Liquid	Difference	Vapor	Liquid	Difference
Water	10°	.3101	.3338	0.0237	0.2068	0.2061	.0007
Carbon bisulphide	10	.4347	.4977	.0630	.2898	.2805	.0093
Chloroform	10	.2694	.3000	.0306	.1796	.1790	.0006

Molecular refractivity is obtained by multiplying the specific refractivity by the molecular weight (m) of the substance. Our formulæ then become

$$mr = \frac{n-1}{\rho}\cdot m$$

$$mr = \frac{n^2-1}{n^2+2}\cdot\frac{m}{\rho}.$$

From the above data it would appear that there is no question as to which of the two formulæ is the more trustworthy, but all data do not give such conclusive evidence, hence there is still a difference of opinion, and the workers in Continental Europe use the formula of Lorentz-Lorenz, while in England the Gladstone-Dale formula is employed. Most of the data have been calculated by means of the Lorentz-Lorenz formula, and hence this is the one more generally used.

The first systematic study of the refractivity of organic compounds was made by Gladstone and Dale (1858–63). They showed that " Every liquid has a specific refractivity energy composed of the specific refractivity energies of its component elements modified by the manner of combination and which is unaffected by change of temperature." Landolt (1864), from extensive data, confirmed the refractive values for the elements carbon, hydrogen, and oxygen, and showed that the constitution had an effect on the refractivity. Brühl (1891) extended the work of the previous investigators and tabulated the following values for the refractivity constants.

The refractivities of the commoner elements are given in Table XIX for the D line, and the hydrogen lines, H_α, H_β, H_γ, and also the dispersive power for $H_\beta - H_\alpha$ and $H_\gamma - H_\alpha$. These are the recalculated values of Eisenlohr and are practically the same as the original values of Brühl and Conrady.

TABLE XIX

Element	Na D Line	H_α	H_β	H_γ	$H_\beta - H_\alpha$	$H_\gamma - H_\alpha$
Carbon C	2.42	2.41	2.44	2.46	0.025	0.056
Hydrogen H	1.10	1.09	1.11	1.12	0.023	0.029
Oxygen O′ in hydroxyl . .	1.52	1.52	1.53	1.54	0.006	0.015
Oxygen O< in ether . . .	1.64	1.64	1.65	1.66	0.012	0.019
Oxygen O″ in ketone . .	2.21	2.19	2.24	2.26	0.057	0.078
Chlorine Cl	5.96	5.93	6.04	6.10	0.107	0.168
Bromine Br	8.86	8.80	9.00	9.15	0.211	0.340
Iodine I	13.90	13.75	14.22	14.52	0.482	0.775
Double Bond = ...	1.73	1.68	1.82	1.89	0.138	0.200
Triple Bond ≡	2.40	2.33	2.50	2.53	0.139	0.171

Homologous series of paraffin compounds with a difference of CH_2 have a difference in the molecular refractivity of 4.57, therefore the value of $CH_2 = 4.57$. Landolt found 4.56. The value fluctuates between 4.58 and 4.61 for different series, while individual values show even greater variation, 4.11 to 4.86.

The data in Table XX show the value for CH_2 in a number of different types of compounds with the number of substances investigated in each series:

TABLE XX

(After Cohen)

	Number in Series	H_α	Na D Line	H_β	H_γ	Dispersion	
						$H_\beta - H_\alpha$	$H_\gamma - H_\alpha$
Hydrocarbons . .	66	4.60	4.62	4.67	4.72	0.072	0.118
Aldehydes and ketones	92	4.60	4.62	4.67	4.71	0.069	0.112
Acids	74	4.58	4.61	4.66	4.71	0.070	0.115
Alcohols	81	4.61	4.63	4.68	4.72	0.070	0.112
Esters	190	4.58	4.60	4.65	4.69	0.069	0.111
Mean	503	4.59	4.62	4.66	4.71	0.071	0.113

Since the refractivities of the individual elements are constant, it follows that the molecular refractivity (M_a) of isomeric substances should be identical. The data in Table XXI show this to be the case:

TABLE XXI

(After Cohen)

Substance	Formula	H_α	M_α	$M_\gamma - M_\alpha$
Propyl alcohol	$C_3H_7(OH)$	0.2903	17.42	0.41
Isopropyl alcohol . . .	$C_3H_7(OH)$	0.2907	17.44	0.42
Propyl aldehyde	C_3H_6O	0.2747	15.93	0.41
Acetone	C_3H_6O	0.2767	16.05	0.43
Propionic acid	$C_3H_6O_2$	0.2354	17.42	0.42
Methyl acetate	$C_3H_6O_2$	0.2437	18.03	0.44
Ethyl formate	$C_3H_6O_2$	0.2423	17.93	0.44
Butyl alcohol	$C_4H_9(OH)$	0.2974	22.01	0.52
Isobutyl alcohol	$C_4H_9(OH)$	0.2967	21.96	0.51
Trimethyl carbinol . . .	$C_4H_9(OH)$	0.2985	22.09	0.53
Ethyl ether	$(C_2H_5)_2O$	0.3015	22.31	0.55
Butyl iodide	C_4H_9I	0.1807	33.25	1.26
Isobutyl iodide	C_4H_9I	0.1807	33.25	1.26

TABLE XXI — *Cont.*

Substance	Formula	H_α	M_α	$M_\gamma - M_\alpha$
Isocaproic acid	$C_6H_{12}O_2$	0.2691	31.22	0.77
Isoamyl formate	$C_6H_{12}O_2$	0.2729	31.66	0.77
Ethyl butyrate	$C_6H_{12}O_2$	0.2690	31.20	0.75
Methyl isovalerate	$C_6H_{12}O_2$	0.2712	31.46	0.78
Ortho xylene	C_8H_{10}	0.3350	35.51	1.52
Meta xylene	C_8H_{10}	0.3370	35.73	1.54
Para xylene	C_8H_{10}	0.3368	35.70	1.56
Ethyl benzene	C_8H_{10}	0.3343	35.44	1.50
Pseudo cumene	C_9H_{12}	0.3363	40.35	1.69
Mesitylene	C_9H_{12}	0.3361	40.33	1.63

Determination of the doubly linked oxygen, O″, was obtained by subtracting from the molecular refractivity of a series of aldehydes or ketones ($C_nH_{2n}O$), the calculated value of $(CH_2)_n$. The value obtained was 2.32. The difference between the molecular refractivity of aldehydes and acids gave the value for hydroxyl oxygen (O′). The calculated value for $(CH_2)_nO''$ subtracted from the observed values for the aliphatic esters gave a mean value of 1.65 for the ether oxygen (O <). Brühl and Conrady obtained the value for the double bond by deducting the constant for a saturated carbon from the observed values and obtained 1.63 to 2.17 with a mean value of 1.83.

The following, Table XXII, according to Eykman, gives the values for a number of different types:

TABLE XXII

No radicals	$CH_2 : CH_2$	1.51
One radical	$RCH : CH_2$	1.60
Two radicals	$RCH : CHR$	1.75
Three radicals	$R_2C : CHR$	1.88
Four radicals	$R_2C : CR_2$	2.00

The effect of simple ring formation gives very small values, not much greater than the variations due to experimental error. Tschugaeff from a large amount of data found a value of about $M_D = 0.67$, while Oesterling found nearly the same value ($M_D = 0.71$). These values were used to establish the cyclic structure of various compounds.

Upon the basis that benzene has three double bonds, the value for the molecular refractivity may be calculated as follows, from the atomic refractivities given in Table XIX, for the red H line, H_α.

6 C atoms	$6 \times 2.41 =$	14.46
6 H atoms	$6 \times 1.09 =$	6.54
3 double bonds	$3 \times 1.68 =$	5.04
Sum of atomic refractivities		26.04

Experimentally at 20°, $n = 1.4967$, $\rho = 0.8799$, and the molecular weight is 78.

Substituting in the n^2 formula we have

$$\frac{1.4967^2 - 1}{1.4967^2 + 2} \times \frac{78}{0.8799} = 25.93$$

which is a close agreement.

Similarly, some of the other simple benzene derivatives give the following values according to Cohen.

Substance	M_α	
	Observed	Calculated
Benzene	25.93	26.04
Toluene	30.79	30.89
Ethyl benzene	35.44	35.37
Phenol	27.75	27.82
Benzyl alcohol	32.23	32.31
Chlorobenzene	30.90	31.22

The following complex compounds do not show such a close agreement:

Substance	M_α	
	Observed	Calculated
Naphthalene	43.93	41.65
Anthracene	61.15	55.15
Phenanthrene	61.59	56.99

The refractivity is employed as an aid in deciding the structural relation of compounds.

The refractive index is used as a means of identifying substances, determining the purity or presence of adulterants, and also the strength of solutions or concentration. For analytical purposes, then, the index of refraction is a property that is coming into very general use. A number of special types of instruments are being employed for this purpose, among which may be mentioned, in addition to the Pulfrich refractometer:

(1) The Abbé refractometer, which has a scale giving the index of refraction direct. This is employed extensively for the analysis and identification of oils.

(2) The butyrometer is employed for analysis of butter fat and has an arbitrary scale.

(3) The Immersion refractometer is employed in analysis of milk serum to determine whether the milk has been watered, and in the analysis of various other types of solutions. These are also provided with an arbitrary scale, which is divided into 100 arbitrary divisions comprising indices from 1.325 to 1.367.

(4) The Zeiss refractometer is particularly adapted to determination of alcohol.

The greater the wave length of light, the less the refractive index, and hence the index of refraction varies with the kind of light employed. The difference between the specific refractivities for light of greatly different wave lengths is called the *specific dispersive power* or *dispersivity*. This is obtained by using either of the formulæ and subtracting the specific refractivities.

$$r_\gamma - r_\alpha = \frac{n_\gamma^2 - 1}{n_\gamma^2 + 2} \cdot \frac{1}{\rho} - \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2} \cdot \frac{1}{\rho}.$$

The molecular dispersivity is the molecular weight (m) times the specific dispersivity.

$$mr_\gamma - mr_\alpha = \left(\frac{n_\gamma^2 - 1}{n_\gamma^2 + 2} - \frac{n_\alpha^2 - 1}{n_\alpha^2 + 2}\right)\frac{m}{\rho}.$$

The dispersivity values have been determined in a manner similar to the method for obtaining the refractivity constants for the elements and the different linkages. Brühl concludes that dispersivity is preëminently a constitutive property and is much more valuable as an aid in establishing structural relations than the refractivity. Eykman has shown that dispersivity affords a valuable indication of the position of the double bond. Auwers and Ellinger have shown that dispersivity is increased by the double bond in the side chain as compared with it in the nucleus. In Table XIX is given the atomic dispersive power of a number of elements using the hydrogen lines and in Table XXI is given the molecular dispersive power of a few isomeric compounds.

CHAPTER XIII

OPTICAL ROTATION

ORDINARY light consists of transverse vibrations which take place in all directions at right angles to the direction of the ray. If a ray of light is allowed to pass through a piece of tourmaline (an aluminium boron silicate) cut parallel to the crystallographic axis, a part of the light will pass through. If another similar piece of tourmaline is placed with its axis parallel to the first, the ray of light will pass through this second piece also. If this second piece be rotated in a plane perpendicular to the ray of light, the intensity of the light will gradually diminish with the rotation, and when the axes are at right angles the light which passes through the first tourmaline plate will not pass through the second when in this position. Transverse vibrations in only one plane pass through the first plate of tourmaline, and the light which comes through is said to be *plane polarized.*

If a ray of light be allowed to pass through a piece of Iceland spar normal to one of the faces, it will be broken up into two rays which are differently refracted. This phenomenon is termed *double refraction*, and the two rays are designated the *ordinary* ray, which follows the laws of refraction, and the *extraordinary* ray, which does not follow these laws. These two rays are polarized at right angles to each other. Hence Iceland spar can be used for the purpose of obtaining plane polarized light, but in order to do this it is necessary to intercept one of the rays, and thus permit only one to pass through. This may be done by taking a long crystal of Iceland spar, grinding the ends so as to change the angle about three degrees, thus making the angle (Fig. 12) $DAB \gtreqqless 68°$, and then cutting it in two along the line DB perpendicular to the new face AD, thus making the angle ADB a right angle. These cut surfaces are then polished and cemented in their original position by Canada balsam.

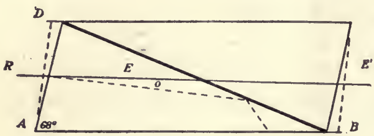


FIG. 12.

The ray of light entering at R is doubly refracted, the ordinary ray following the law of refraction is refracted and meets the surface of Canada balsam, which has an index of refraction of 1.55, which is greater than that of the Iceland spar, 1.48, for the ordinary ray. If it strikes the Canada balsam at an angle greater than the critical angle, it will be totally reflected at the surface. The extraordinary ray, RE, is refracted less than the ordinary ray. Its index of refraction in the medium is greater than that of the Canada balsam, consequently it can never be reflected at that surface and so will pass through the prism as indicated by REE'. At the point of entrance, R, and also at the surface where the two pieces are cemented together, the extraordinary ray is refracted, but the amount is so small that on a diagram of this size, it can hardly be represented in any other way than by a straight line through both sections of the prism. This prism is known as a Nicols prism, and since it produces plane polarized light it is known as a *polarizer*. The plane in which the plane of polarization is located can be ascertained by means of a second Nicols prism; when it is used in this manner it is designated *an analyzer*.

Method of Measuring Optical Rotation. — The amount of rotation can be measured by placing the substance between two Nicols prisms, one a polarizer to produce the polarized light, and one an analyzer to determine the amount the plane of polarization has been rotated. This is measured by having a scale divided into degrees and fractions thereof attached to the analyzer so as to determine the angle through which the analyzer has to turn in order to permit the light to pass through. Such an instrument is called a *polarimeter*. The light which comes through would produce either a bright field or total darkness; in either case it would be difficult to read accurately. In order to obtain a field which can be read easily a number of devices have been designed and are now employed, such as the *bi-quartz* disk, the quartz wedge compensator, and the Lippich half-shadow apparatus consisting of small Nicols.

The angle of optical rotation is proportional to the thickness of the liquid through which the light passes. The specific rotation is the angle of rotation, α, divided by the length, l, of the column of liquid times its density, ρ. Since the rotation varies with the temperature, it is customary to state the temperature of the solution at which the determination is made as well as the kind of light used. The equation for the specific rotation is

$$[\alpha]_D^{t^\circ} = \frac{\alpha}{l \cdot \rho}$$

in which t° represents the temperature and D, the spectrum line, sodium in this case.

For solutions when the concentration is expressed in grams, g, in definite volume, v, we have

$$[\alpha]_D^{t^\circ} = \frac{\alpha v}{lg}$$ or, for concentration in per cent, p,

$$[\alpha]_D^{t^\circ} = \frac{100\,\alpha}{p \cdot l \cdot \rho}\ .$$

The molecular rotation of liquids would be expressed

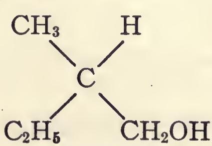
$$m[\alpha]_D^{t°} = \frac{\alpha \cdot m}{l \cdot \rho}$$

or it is sometimes written

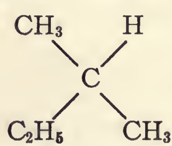
$$[\alpha m]_D^{t°} = \frac{\alpha m}{l\rho}$$

and owing to the large value of the rotation it is customary to divide the result by 100.

Asymmetry. — It was early recognized by Biot that many substances in aqueous solutions had the power of rotating the plane of polarized light, while an explanation was offered through the classic researches of Pasteur. One peculiarity of compounds and their solutions which manifest optical activity is that the compounds contain one or more *asymmetric* atoms of either carbon, nitrogen, sulphur, selenium, tin, silicon, etc. In fact, there is no authentic case in which an active compound has been found that does not contain an asymmetric atom. That is, a carbon atom is said to be asymmetric when all four of the valences are satisfied by groups which are different chemically or structurally. For example, amyl alcohol, which is optically active, may be represented by the formula designated *active*. If, however, the OH group be replaced by hydrogen, we obtain the formula

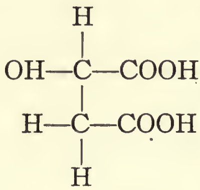


ACTIVE

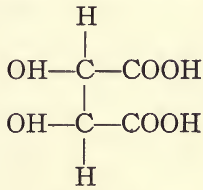


INACTIVE

designated *inactive*, and the groups attached to the carbon atom are not all different, as they are in the formula marked active. In the substitution, however, it is necessary to destroy the asymmetric character of the carbon atom before the substance will become inactive. In the case of malic acid (monohydroxysuccinic acid) and of tartaric acid, there are four different groups attached to the asymmetric carbon atoms as the following formulæ indicate:



Malic Acid



Tartaric Acid

These active compounds have isomers which have analogous properties, and while they are both optically active, and the rotation is of the same magnitude, it is in opposite directions for the two compounds, one rotating the plane of polarized light to the right, and the other rotating it to the left. Those that rotate the plane of polarized light to the right are termed *dextro-rotatory*, and those that rotate the plane of polarized light to the left are termed *lævorotatory*.

In 1867, Kekulé proposed that the carbon be conceived as located at the center of a regular tetrahedron and that the four affinities be represented by lines drawn to the four vertices. For convenience of writing, the symbol for carbon is omitted and the elements or groups in combination with the carbon are indicated at the vertices, as shown in the following figures. In order to explain isomerism, Le Bel and van't Hoff simultaneously (1874) and independently made use of the idea of the tetrahedron carbon atom and grouped the elements or groups in combination with the carbon atom around the base of the tetrahedron in one direction to represent one isomer and in the opposite direction to represent the other isomer. This is illustrated in Fig. 13, where we have in I the symbols *acd* arranged from right to left, while in II they are arranged from left to right. The rotation would be represented as – or lævorotatory in I and + or dextro-rotatory in II. These two figures, I and II, are the mirrored images of each other, and while they are alike, they cannot be superposed; that is, they are right-handed and left-handed. It is known that solutions of two isomeric compounds can be mixed in equal quantities so as to produce an inactive mixture, and such mixtures are termed *racemic* mixtures. There are, however, certain forms of isomeric active compounds which are *inactive*, and this property is explained upon the assumption that by an *internal compensation* the compound is rendered inactive. Such inactive compounds are designated the *meso form*. Here we have an illustration of a compound containing an asymmetric carbon atom without rendering the compound optically active.

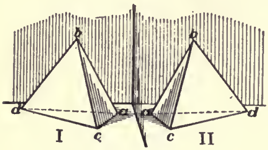
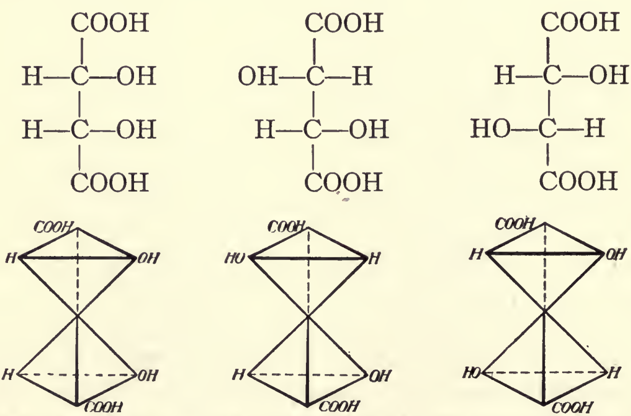


FIG. 13.

In the case of tartaric acid we have the example of a compound existing in these three forms, and in Fig. 14 is illustrated the structural arrangements by means of which they are explained.



MESOTARTARIC ACID LÆVOTARTARIC ACID DEXTROTARTARIC ACID

FIG. 14.

The meso form manifests no rotation, the lævotartaric acid rotates the plane of polarized light to the left, and the dextrotartaric acid rotates the plane of polarized light to the right. In addition, we have the racemic acid, which is a mixture of equimolecular parts of *l*- and of *d*-tartaric acids.

Many substances are optically active, and the specific rotation of these is listed in tables of physical constants. The use of this property is one of the principal methods employed in identifying, testing the purity, as well as making quantitative determinations of such substances as sugars; essential oils, including lemon, wintergreen, peppermint, etc.; the alkaloids, nicotine, brucine, strychnine, etc.; turpentine, camphor, and a long list of others. In the case of sugars, this method is generally employed, as the rotation is proportional to the concentration:

$$[\alpha]_D^{t^\circ} = \frac{\alpha}{l \cdot \rho} = \frac{\alpha}{l \cdot c}$$

in which c equals concentration in 100 cc. of solution. Then $\alpha = [\alpha] l \cdot c$, and since a tube of constant length, l, expressed in decimeters, is employed, and the specific rotation of cane sugar is constant, $[\alpha] = (66.5,\ l = \text{one decimeter})$; substituting we have $\alpha = 66.5 \cdot l \cdot c$, but $66.5\ l$ is a constant, k, then $\alpha = kc$, the rotation is proportional to the concentration. In Table XXIII are given the values of the specific rotation, $[\alpha]_D^{20^\circ}$, at 20° for sodium light, the *D*-line of the spectrum, for the carbohydrates commonly occurring in foods. These values are the ones usually employed in analytical work and are sufficiently exact for that purpose.

Effect of Temperature. — We have seen that the temperature affects the specific rotation, and the formula contains a term designating the temperature at which the determination is made. The rotation may increase or decrease with the change of temperature. Methyl tartrate is practically inactive at 0° C., while below this temperature it is lævorotatory, *i.e.* negative. Many of the esters of tartaric acid pass through a maximum value for the specific rotation with change of temperature, while some of those with large negative rotation change but little with a large change in temperature. For most sugars the specific rotation is practically constant for all temperatures. In general, however, the specific rotation decreases with the temperature, as is shown by lævulose and arabinose, particularly while xylose increases and dextrose remains practically constant for temperature changes up to 100°. It is necessary to determine the temperature accurately in all sugar analysis and to make the necessary corrections. Browne has compiled formulæ by which such corrections can be made and these are given in Table XXIII.

TABLE XXIII

SUGAR	BROWNE'S SUGAR ANALYSIS $[\alpha]^{20°}_D$	WOODMAN'S FOOD ANALYSIS $[\alpha]^{20°}_D$	CONCENTRATION
Arabinose	$+6$	$+104.5$	
Dextrose	$+52.50+0.018796p+0.00051683p^2$	$+52.5$	p = 0 to 100 per cent
Lævulose	$+[101.38-0.56t+0.108(c-10)]$	-92.5	
Invert sug.	$-[27.9-0.32t]$	-20.0	
Lactose	$+52.53-0.07(t-20)$	$+52.5$	[t = 15° to 25° C.]
Galactose	52.53 = constant	$+80.5$	c = 24 to 40
Maltose	$140.375-0.01837p-0.095t$	$+138.5$	
Sucrose	$+66.435+0.00870c-0.000235c^2$	$+66.5$	0–65 gr. per 100 cc.
Xylose		$+19.0$	

Effect of Concentration. — That the specific rotation of sugar solutions is practically constant for all concentrations is illustrated in Table XXIII. Biot (1834) found that for aqueous solutions of tartaric acid the specific rotation increases with the dilution. The specific rotation of alcoholic solutions of camphor decreases with the dilution.

Effect of Varying the Solvent. — The rotation of optically active substances is very different in solution from the rotation of the pure substance, and the nature of the solvent has a marked effect upon the magnitude of this rotation. Table XXIV shows the change in the specific rotation of ethyl tartrate and of nicotine when dissolved in different solvents, the specific rotation of the pure substances being respectively +7.8 and −161.5.

TABLE XXIV

(Thorp's Dictionary)

Solvent	$[\alpha]_D$ At Infinite Dilution	
	Ethyl Tartrate	Nicotine
Formanide	+ 30.4°	− 70°
Water	26.85	77.4
Methyl alcohol	11.5	129.4
Ethyl alcohol	9.13	140.1
Benzene	6.1	163.5
Ethylene bromide	− 19.1	183.5

The order of rotation is the same for these two active compounds in these various solvents, and Walden has found this to be true for a number of other substances and solvents.

When mixed solvents are employed, various results are obtained as is illustrated in the case of *d*-tartaric acid, which, when dissolved in a mixture of acetone and ether, rotates the plane of polarization to the left, while in aqueous solutions it is dextro-rotatory.

Muta-rotation. — In the case of freshly prepared solutions of certain substances the specific rotation undergoes a change when the solution is allowed to stand, but finally a constant value is obtained. This change may be either an increase or a decrease. This phenomenon is known as *muta-rotation*, and is also called *birotation*, *multirotation*, etc. This change in the specific rotation is very pronounced in the case of the reducing sugars, certain oxy-salts, and lactones. Dextrose gives a value of 105.2 for freshly prepared solutions, which finally gives the constant value of 52.5. This phenomenon is explained by Landolt and others on the assumption of different molecular arrangements of active forms in the freshly prepared solutions which gradually break down into molecules of lower rotation. This change to a constant rotation can be produced by allowing the solution to stand for several hours, by boiling the solution, or by the addition of a small quantity of alkali or acid.

Electromagnetic Rotatory Power. — Optical activity is due to the inner structure, and not many substances possess this property. Electromagnetic rotatory power is possessed by all substances. This property was discovered by Faraday in 1846. He placed glass between poles of a magnet and found that the plane of polarized light was turned. This phenomenon lasts only while the current is passing.

The electromagnetic rotatory power is a function of the temperature, depends upon the strength of the magnetic field, and, as in the case of optically active substances, is dependent upon the density of the solution and length of the observing tube. If polarized light which passes through a solution in the electric field is reflected back through it, the plane will be turned back to its original position; while in case of an optically active compound, if the ray be sent back through it, the amount of rotation will be doubled.

The formula for the magnetic rotation is similar to that for the specific rotation of optically active substances. The *specific magnetic rotation* is, however, the ratio of the rotation of the given substance to the rotation of water which Perkin used as the standard, *i.e.* $\frac{\omega}{l\rho} \div \frac{\omega_0}{l_0\rho_0} = \frac{\omega l_0\rho_0}{l\rho\omega_0}$, where $\frac{\omega_0}{l_0\rho_0}$ refers to water. The *molecular magnetic rotation* is the specific rotation multiplied by the molecular weight of the substance divided by the molecular weight of water, *i.e.* $\frac{\omega l_0 \rho_0 m}{l \rho \omega_0 18}$ = molecular magnetic rotation.

The molecular magnetic rotatory power is an additive as well as a constitutive property. The value for CH_2 is obtained from homologous series such as the following:

Series	CH_2	Series	CH_2
Paraffins	1.051	Alkyl chlorides	1.015
Alcohols	1.057	Alkyl bromides	1.031
Aldehydes	1.022	Alkyl iodides	1.031
Fatty acids	1.021	Phenyl esters	1.053
Esters	1.023		

The individual values vary; as in the case of alkyl iodide they range from 1.005 to 1.066. Perkin takes as the mean value, CH_2 = 1.023. If there are a number of carbon atoms in the molecules of a particular group of compounds, then by deducting n times the value of CH_2 from the total magnetic rotation, a value is obtained which is called the *series constant* (S). In the fatty acid series we have:

Acid	Molecular Magnetic Rotation	$n \times 1.023$	S
Propionic	3.462	3 × 1.023	0.393
Butyric	4.472	4 × 1.023	0.380
Valeric	5.513	5 × 1.023	0.398
Œnanthylic	7.552	7 × 1.023	0.391
Caprylic	8.565	8 × 1.023	0.381
Pelargonic	9.590	9 × 1.023	0.383
		Mean value	0.393

in which n is the number of carbon atoms belonging to the CH_2 group, and S is the *series constant* which is obtained by subtracting the value of nCH_2 from the molecular magnetic rotation. In a similar manner the series constant for a large number of series of organic compounds has been worked out, and in Table XXV a few of these are given.

TABLE XXV

SERIES	FORMULA	S
Paraffins, normal	C_nH_{2n+2}	0.508
Alcohols, primary	$C_nH_{2n+2}O$	0.631
Alcohols, iso	$C_nH_{2n+2}O$	0.699
Aldehydes	$C_nH_{2n}O$	0.261
Ketones	$C_nH_{2n}O$	0.375
Fatty acids	$C_nH_{2n}O_2$	0.393
Unsaturated acids	$C_nH_{2n-2}O_2$	1.451
Dibasic acids	$C_nH_{2n-2}O_4$	0.196
Formic esters	$C_nH_{2n}O_2$	0.495
Acetic esters	$C_nH_{2n}O_2$	0.370
Ethyl esters	$C_nH_{2n}O_2$	0.337
Alkyl chlorides	$C_nH_{2n+1}Cl$	1.988
Alkyl bromides	$C_nH_{2n+1}Br$	3.816

By means of these series constants, the value for the elements may be determined as well as the effect of the linkage and the establishment of the value of the double bond. Having these different values, and knowing the molecular magnetic rotation, these may be employed in determining the structure of organic compounds. One illustration of the method will suffice.

The molecular magnetic rotation of acetoacetic ester was observed to be 6.510, and checking by this method we have:

For acetic ester the series constant is	0.370
For ketone the series constant is	0.375
Giving as the mean of these values	0.372
Since n is 6 we have $6 \times 1.023 =$	6.138
or	6.510

as the calculated value which checks the observed value closely and indicates the ketonic form of the ester. Hence we conclude that the structure of acetoacetic ester is ketonic.

CHAPTER XIV

SOLUTIONS

It is a familiar fact that the physical form in which matter exists is dependent on temperature and pressure. Water exists in three physical forms which can be changed one into the other by slight variations in the temperature without changing the pressure. This is true of a very large number of substances; but in many cases, these changes in form can be much more easily accomplished by changing the pressure also, whereas some substances which exist ordinarily in the gaseous form cannot be changed to the other forms unless there is a change in the pressure as well as in the temperature. Theoretically matter exists in all three forms, — solid, liquid, and gaseous — and to these forms of matter we are to apply the term *phase*, a concept which was created by Willard Gibbs and which he defined as follows: "We may call such bodies as differ in composition or state different *phases* of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase." This is analogous to our conception of *form of matter*, *physical modification*, or *state*. By the term *phase* we understand a *mass* that *is chemically* and *physically* homogeneous. Any mass of matter under consideration which may exist in one or more phases is termed *a system*.

The homogeneity of a system results from the system being in a state of equilibrium which is independent of the time. For in heterogeneous (non-homogeneous) systems, such as a salt in contact with a solvent, or two gases that have just been brought into contact, the concentration is different at different places, and the mixtures are of different composition in different parts of the systems. The systems not being in equilibrium will change simultaneously into homogeneous systems, and equilibrium will result. This would also take place if different parts of the same system were at different pressures or different temperatures. Hence, our considerations are limited to the state of equilibrium of bodies or systems of bodies and consequently to homogeneous systems. The existence of water in contact with water vapor might be considered contradictory to the idea of physical homogeneity, yet when the system is of uniform temperature and pressure, equilibrium exists, although we have it consisting of more than one homogeneous body, for the water is itself homogeneous and the water vapor too. In such systems we must have the same temperature and the same pressure throughout, for otherwise there would not be equilibrium and consequently a change would occur in the volume energy of the bodies that constitute the system. Such a system is said to be a *one-component system* because it consists of only one chemical individual, species, or compound.

Now this system — water and water vapor — consists of two phases, the liquid and the vapor. It is not necessary that a phase consist of only one body, for it may be distributed among a large number; or, in other words, a very large number of bodies of one particular chemical individuality may constitute a phase, as the vast number of globules of butter fat in milk all constitute one phase. Or, a large number of different chemical individuals may constitute one phase, as the casein and milk sugar in the water solution constitute the second liquid phase in milk. This last case is an example of a multiple component system. This then would give a two-phase system for milk. If to distilled water sodium chloride is added, we obtain a solution which is physically as well as chemically homogeneous and therefore constitutes one phase. If we continue to add salt, we reach a point beyond which no more salt will go into solution and the solid added will remain undissolved and be eventually in equilibrium with the solution. We now have an additional phase — one solid phase; but if we were to decrease the temperature of the system sufficiently, there would appear solid water (ice) as a second solid phase, and we should have with the vapor above the solution a *four-phase* system. It is possible to make our selection such that the solid substance used is capable of existing in two solid modifications, and with the appropriate solvent we could then have five phases: two solid phases of the dissolved substance, the solid phase of the solvent, the liquid phase (solution), and the vapor phase of the pure solvent. If we select two non-miscible substances, we should then have two liquid phases; the vapor phase, and, if the temperature is very low, possibly a solid phase. So by the judicious selection of substances we can make any complexity of phases we desire.

Components. — As in the case of physical homogeneity, so also with chemical homogeneity, it is necessary that the system be in a state of equilibrium, otherwise there may be a gradual transformation of one of the chemical individuals into the other, or *vice versa*, and it is not with the process of change that we have to do, but with the state of equilibrium to which the subsequent considerations apply. The determination of the number of components that constitute a system is not always an easy matter, hence it is necessary that the idea of components be clearly in mind. In the water system consisting of the three phases, — solid, liquid, and vapor, — an analysis of all the phases would show that they are composed of oxygen and hydrogen and that the proportion is the same in all three phases, and further, that this proportion is that in which oxygen and hydrogen combine to form water. The system is said to consist of one chemical individual or substance and consequently is designated a *one-component system*. The same is true of sulphur; there would be four phases, but all of them would show the same composition by analysis. In the case of water, however, if the temperature was raised very high, it would be found that the water was decomposed into its constituents, hydrogen and oxygen, and that they existed as the elemental substances in equilibrium with water vapor. Here we should have a somewhat different state, as they would then be considered as components, because they take part in the equilibrium. Hence, a change in the conditions of the system may necessitate a change in the number of components. We therefore distinguish *the components of a phase or system as the constituents of independently variable concentration*, and they may be either elements or compounds. Therefore we define the components or "individuals of any reacting system as the separate chemical substances undecomposed in the reactions concerned, which are necessary to construct the system. The number of such (components or) individuals to be chosen is the smallest number necessary to construct the system." (Richards.)

This may be illustrated by the system $CaCO_3 \rightleftarrows CaO + CO_2$, wherein only two of the three constituents, CaO and CO_2, are "undecomposed in the reaction concerned." Consequently the system is a *two-component system*.

The composition of Glauber salt is $Na_2SO_4 \cdot 10H_2O$, that of its solution Na_2SO_4 and H_2O, and that of the vapor of the solution is H_2O, so that, varying the ratios of Na_2SO_4 and H_2O, the constituents of the solution, we can produce all of the three phases, therefore this is a two-component system. Similarly other hydrates can be obtained by variation of two components. This is also true for double salts, such as $K_2SO_4 \cdot MgSO_4 \cdot 3H_2O$ (Schönite), $K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$, etc., where the components are the undecomposed single salts and water, therefore a three-component system, such as they are, is sufficient to form all modifications that can exist.

Separation of Phases. — The tests employed by the organic chemist for the identification and purity of substances are by means of phase transformations with a record of the accompanying heat change. If he desires to determine the purity of a beautiful crystalline product, he determines its so-called melting point. This consists in nothing more than determining at a constant pressure at what temperature the solid and liquid phases are in equilibrium. On the other hand, if the substance is a liquid, he determines at constant pressure the temperature at which the liquid and vapor phases are in equilibrium, that is, the boiling point. If either is constant, the substance has the same composition in both phases, and he is working with a one-component system and concludes that the substance is pure. (This is true except in some special cases that will be considered in detail subsequently.) Not only in the preparation and identification of substances do we make use of the phase conceptions, but in the preparation and purification of the same.

Our gravimetric methods are based on the separation of the pure solid phase which is one of the components of our multiple component system. In fractional crystallization we have the separation of a solid phase, while in the process of fractional distillation we make use of the vapor phase for the separation of components. So in a large majority of our chemical manipulations we have to do with the separation of phases. When these phases are alike, both solid, both liquid, or both vapors, the operation becomes much more difficult and particularly is this true in the separation of vapor phases. In the separation of these latter we have not as yet made very rapid progress.

When the components are increased, the complexity of some of the systems is very much increased, for there are a great many possibilities in multiple component systems. These compounds may be so selected that they form a phase which conforms to the laws of Definite and Multiple Proportions. Then the phase is known as a *chemical compound*. If, however, the components do not conform to this law, the phase is called a *solution*. A *solution* may better be defined as a phase in which the relative quantities of the components can vary continuously within certain limits, or as a phase of continuously varying concentrations. There is, however, no stipulation as to the particular phase of which a solution may be formed, therefore it is possible that a solution may be of any of the three phases — solid, vapor, or liquid.

In the case of solutions that are in the form of liquids, one of the components is called the *solvent* and the other the dissolved substance or *solute*. We are familiar with many examples of solutions wherein the solvent is liquid and the dissolved substance is a solid, a liquid, or a vapor (or gas). Where solids act as the solvent and the so-called *solid solutions* result, we have a conception which is perhaps not quite so well known but which is very common. Examples of solid solutions include such double salts as potassium and ammonium alum, ammonium and ferric chlorides, potassium and thallium chlorates, etc.; the occlusion of gases by metals, such as hydrogen by palladium; and the absorption of oxygen and carbon dioxide by glass at a temperature of 200° under 200 atmospheres pressure. Copper diffuses into platinum and into zinc. For the same reason hot platinum crucibles should not be handled with brass tongs. Another very interesting case is the passage of sodium through sodium glass without any visible change. If electrodes of lithium amalgam are used, the sodium is replaced by lithium and the glass becomes opaque and crumbly, owing to the fact that there was a contraction. It has, however, been found impossible to electrolyze a sodium glass between electrodes of potassium amalgam. Many other examples of solid solutions will be met in the course of our work.

Gas as Solvent

When hydrogen is introduced into a vessel containing oxygen at ordinary temperature, after a short time the two gases will be mixed thoroughly. It is immaterial what relative quantities of the two are brought together, there will be produced a homogeneous mixture of the two. This is true of any other gases that do not react chemically. So it may be stated that gases are miscible in all proportions. Here we have a simple intermingling of the gases, and as a result we should expect the properties of the mixtures to be the summation of those of the individual constituents, and in fact this is the case, each individual gas conducting itself as though the other were not present. The pressure of the gas mixture is the sum of the individual pressures. The specific heat, the power of absorbing and refracting light, the solubility, in fact all of the physical properties of the gases remain the same when they are mixed.

Dewar has shown that a vessel containing air is more highly colored by iodine than when the iodine is introduced into one from which the air was removed. This is also true of a number of gases, thus showing that the gas present exerts a solvent action on the iodine and more of it is therefore present. Villard (1895) has shown that iodine is dissolved by CO_2, as the spectra of the vapor do not show the least characteristic of gaseous iodine. That iodine and bromine are soluble in CS_2 above its critical temperature, and that KI is soluble in alcohol vapor, have been fully demonstrated by Pictet, Wood, Hannay, and Hogarth, and others. While the question of a gas acting as a solvent has been quite fully demonstrated in cases where the solute is a gas, liquid, or solid, the subject does not present anything of importance in our present consideration further than the fact that a gas may be considered as a solvent, thus illustrating our second group of solvents.

LIQUID AS SOLVENT

Gas as Solute. — When a gas is brought into contact with any selected liquid, the gas is absorbed by it; but the quantity absorbed varies greatly with the liquid employed, with the gas used, as well as with the temperature and pressure. In the case of oxygen, hydrogen, nitrogen, and many other gases, the quantity of the gas dissolved is very small whatever the liquid employed. In any case when the maximum amount has been absorbed under the prevailing conditions, there results a state of affairs such that the same number of molecules of the gas pass into the liquid and pass from the liquid into the gaseous space above, in unit time. The system consisting of the gas and the liquid is said to be in a state of equilibrium.

It was shown by Henry (1803) that the mass of any gas that dissolves in a selected solvent is in direct ratio to the pressure of the gas. For example, at three atmospheres pressure three times as much can be dissolved by a liquid at a constant temperature as is dissolved at one atmosphere pressure. This law of Henry may be expressed in a number of ways.

Statement of Henry's Law. — 1. If we designate the mass of the gas in unit volume of the liquid as the concentration of the gas in the liquid, C_l, and represent the concentration of the gas in the space above the liquid by C_v, then the ratio of these two concentrations remains constant for all values of the pressure, *i.e.* $\frac{C_l}{C_v} = k$.

2. The total quantity of a gas absorbed is always proportional to the pressure on the gas. As we usually express the quantity as the mass (*i.e.* the weight) then the mass of the gas per unit volume, *i.e.* the concentration (C_l) is proportional to the pressure. We then have $C_l = k'p$.

3. If the quantity be expressed in terms of volume, then it follows from Boyle's Law that twice the mass occupies the same volume under twice the pressure, and as Henry's Law states that the quantity of gas absorbed is proportional to the pressure, it follows that the same volume of gas is dissolved in a specified quantity of a liquid at all pressures.

Confirmation of Henry's Law. — Henry's Law has been subsequently confirmed by a number of workers, particularly by Bunsen and by Khanikof and Luginin, the results of whose experiments on the solubility of CO_2 in water are given in Table XXVI.

TABLE XXVI

p	C_l	$k=\frac{C_l}{p}$	p	C_l	$k=\frac{C_l}{p}$
69.8	0.9441	0.01352	218.9	3.1764	0.01451
80.9	1.1619	0.01436	236.9	3.4857	0.01472
128.9	1.8647	0.01447	255.4	3.7152	0.01455
147.0	2.1623	0.01471	273.8	4.0031	0.01463
200.2	2.9076	0.01451	311.0	4.5006	0.01447

It is apparent that the value for k is a constant and that the ratio of $C_l : p$ is independent of the pressure. In other solvents this law has been shown to hold for nearly all of the gases that have been studied, which include N_2, H_2, O_2, CO_2, CO, N_2O, CH_4, H_2S, NO, C_4H_{10}, C_2H_4, C_2H_6.

Exceptions to Henry's Law. — In the case of a number of gases, the amount of the gas absorbed has no relation whatever to the pressure. For example, HCl, NH_3, SO_2, HI, etc., are very soluble in water, and their properties in solution are different from those in the gaseous state. There appears to be a reaction between the solvent and solute, for in the case of HCl and water at atmospheric pressure, a mixture of a definite composition distills over at 106°, and in the case of HBr and H_2O, a mixture of definite composition comes over at 126°. These gaseous substances which are so very readily soluble in water do not follow Henry's Law.

Coefficient of Absorption is defined as the number of cubic centimeters of the gas absorbed by one cubic centimeter of the liquid at 0° C. and 760 mm. pressure. This coefficient for the so-called permanent gases is very small and varies from 0.01 to 0.05, while in the case of those gases which are exceptions to Henry's Law the coefficient is much larger. The solubility of gases decreases with an increase of temperature, as is illustrated in Table XXVII.

TABLE XXVII — COEFFICIENT OF ABSORPTION

GAS	0°	10°	20°	30°	50°	100°
Oxygen	0.04890	0.03802	0.03102	0.02608	0.02090	0.01700
Hydrogen . . .	0.02148	0.01955	0.01819	0.01699	0.01608	0.0160
Nitrogen . . .	0.02348	0.01857	0.01542	0.01340	0.01087	0.00947
Carbon dioxide .	1.713	1.194	0.878	0.665	0.436	
Ammonia . . .	1305.0	915.5	715.4			
Hydrochloric acid	506.9	474.3	442.3	411.8	361.9	
Sulphur dioxide .	79.789	56.647	39.374	27.161		

When the temperature is raised, the gas can be entirely removed from the liquid, except in some cases in which the solubility does not conform to Henry's Law. The removal of the gas can also be accomplished by diminishing the pressure. A solution of sodium bicarbonate under greatly reduced pressure loses one half of its carbon dioxide. By diminishing the pressure the blood loses the carbon dioxide and oxygen dissolved in it.

Dalton's Law. — When two different gases are mixed, if there is no chemical reaction between the gaseous particles, it has been found that each gas conducts itself as though the other gas was not present. In fact, all of the physical properties, such as the pressure exerted on the walls of the containing vessel, the specific heat, etc., experience no change. Hence, if we have a mixture of gases in contact with a liquid, each individual gaseous species exerts its own individual pressure, and according to Henry's Law the amount of this particular gas absorbed should be proportional to this pressure. In fact, it has been shown by Dalton (1807) that the solubility of a gas is unaffected by the presence of other gases and that the amount of each absorbed is proportional to its own partial pressure. This is known as the *Absorption Law of Dalton.* By the partial pressure of a gas we mean the pressure exerted by that particular gas. For example, if we have a mixture of two gases, oxygen and nitrogen, the total pressure, p, which would be required to keep them at a certain volume would be the pressure of one atmosphere. Now the oxygen in this volume would exert its own pressure, p_O, and the nitrogen its own pressure, p_N, the sum of which would equal the total atmospheric pressure exerted upon the mixture, *i.e.* $p = p_O + p_N$, which is the expression for Dalton's Law that the total pressure is equal to the sum of the partial pressures of the individual species of a gaseous mixture.

Water exposed to air becomes saturated at the given temperature and pressure. Let us assume that the pressure is 760 mm. This is the total pressure, and since the oxygen constitutes 20.9 and the nitrogen 79.1 per cent by volume of the air, then the partial pressure of the oxygen will be $\frac{20.9}{100.0}$ of 760 mm., or 158.84 mm., and that of nitrogen will be $\frac{79.1}{100.0}$ of 760 mm., or 601.16 mm. At 18° the solubility of oxygen is 0.0324 and of nitrogen is 0.01605 under 760 mm.

$$\frac{158.84}{760} \times 0.03242 = 0.006776; \quad \frac{601.16}{760} \times 0.01605 = 0.01269.$$

0.006776 : 0.01269 : : 34.8 : 65.2 per cent of oxygen and of nitrogen respectively.

CHAPTER XV

SOLUTION OF LIQUIDS IN LIQUIDS — I

Solubility

When liquids mix in all proportions they are termed *consulate* liquids. Water and alcohol are miscible in all proportions. They are termed a pair of consulate liquids. Mercury and water do not mix in any proportion, neither do kerosene and water. These are *non-miscible* liquids. Intermediate between these two types of pairs of liquids we have a very large number of liquids which manifest a partial solubility of the one in the other. These pairs of liquids are termed *partially miscible liquids*.

If we add ether to water, there is formed a solution of ether in water, and this becomes more and more concentrated as ether is added. Finally a concentration is reached in which a second liquid layer appears. We have *saturated* the water with ether; we have two liquid layers that are *non-miscible*. If we were to add water to ether, the same result would be obtained, — the formation of two non-miscible layers. If we continue to add ether in the first case, the relative volumes of the two layers would change, the lighter one increasing in volume and the lower one decreasing until finally it would disappear, when we should have water dissolved in ether. If we were to add water to ether, we should have practically the same result, the water dissolving, two liquid layers formed, the volume of the layers changing until one (the lighter in this case) disappeared with the formation of a homogeneous solution of ether in water. This may be represented graphically by Fig. 15.

If A = 100 per cent of water and B = 100 per cent ether, then AB will represent all possible concentrations of water and ether.

Let the concentration of the liquid layers be represented by the vertical axis AC.

If we start out with pure water, at A, and add ether, the concentration of the solutions would be represented by the line AE. At the concentration represented by E the second liquid layer would appear. The two liquid layers would have the concentrations represented by E and E' respectively, E' being the concentration of the upper layer.

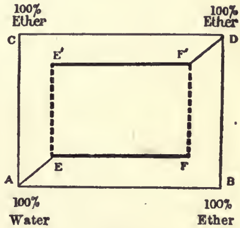


FIG. 15.

Now as more ether is added, the concentration of the two liquid layers when in equilibrium would remain constant, as represented by the lines $E'F'$ and EF. By the continued addition of ether a point, F, would finally be reached at which the lower layer would disappear, and we should have a homogeneous solution of water in ether, the concentration of which would be represented by F'. As the addition of ether is continued, solutions of water in ether would be formed, which are represented by the line $F'D$. EF and $E'F'$ represent the two non-miscible liquid layers, and since these are in equilibrium, they represent saturated solutions; EF saturated with respect to ether and the lighter layer $E'F'$ saturated with respect to water.

Hence it is apparent that the two non-miscible liquids formed from the partially miscible liquids are saturated solutions, and these saturated solutions are themselves non-miscible liquids, so we may consider the pair of saturated solutions formed from partially miscible liquids in the class of non-miscible liquids.

The determination of the mutual solubilities of this system at different temperatures would give us the different concentration in the two layers. So a study of the behavior of a pair of partially miscible liquids resolves itself into the determination of the solubility at different temperatures. Alexejeff (1886) took a definite weight of water and of aniline, put them into a tube, sealed it, and determined the temperature at which the mixture became clear. He did this for a number of concentrations and obtained the following data:

TEMPERATURE	16°	55°	77°	142°	156°	164°	157°	68°	39°	25°	8.4°
Aniline per cent . .	3.1	3.8	5.3	14	21	37	74	94	94.5	95	95.4

Let us represent on the horizontal axis the concentration of aniline and water in Fig. 16 by the line AB, and on the vertical axis the temperature, then A represents 100 per cent of water and B represents 100 per cent of aniline, and AB represents all possible concentrations of water and aniline. Plotting the above data we obtain the curve DCE. The point D represents the solubility of aniline in water and E the solubility of water in aniline at 0° C. It is apparent then as the temperature increases the solubility of aniline in water increases, and DC represents this. Similarly the part of the curve EC represents the increased solubility of water in aniline with the increase in temperature.

Above the temperature represented by C (164°) aniline and water are miscible in all proportions, *i.e.* they are consulate liquids above this temperature, which is termed the *critical solubility* temperature. The area outside and above the curve represents those concentrations and temperatures where aniline and water are mutually soluble forming one liquid layer. Within the solubility curve DCE we have the concentrations and temperatures where two liquid layers are found. If quantities of aniline and water represented by any point within this area, as m, be mixed and allowed to come to equilibrium at any temperature below C, the mixture will separate into two liquid layers, the composition of the layers will be represented by the two points x y on the curve DCE. The point x represents the upper water layer and y the lower aniline layer, and the relative quantities of the layers are represented by the distances xm and my respectively, *i.e.* the weight of the layer x is to the weight of the layer y as the length xm is to the length my.

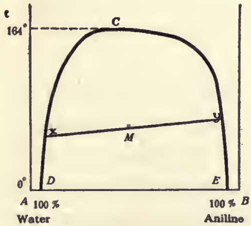


FIG. 16.

Most partially miscible liquids become consulate at high temperatures, but there are a number of interesting exceptions to this. A mixture of di- or trimethyl amine and water separates into two liquid layers when the temperature is lowered, the mutual solubility increases, and if the temperature be lowered sufficiently the liquids become consulate. This decrease in solubility with rise of temperature has been observed in many other cases, such as butyl alcohol in water, and also paraldehyde in water.

In Fig. 17 we have minimum solubility, while with decrease in temperature the solubility increases and finally reaches a temperature below which the liquids are consulate.

Many ketones and lactones show a peculiar characteristic in that they have a minimum solubility at an intermediate temperature, and the solubility increases with either an increase or a decrease of temperature. In Fig. 18 we have

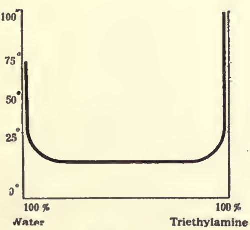


FIG. 17.

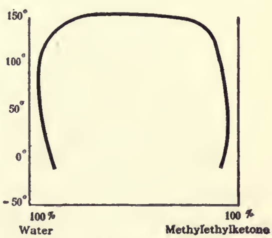


FIG. 18.

represented the temperature of minimum solubility, and either above or below this temperature the solubility increases.

It is conceivable that the solubility curve may be a closed curve as these figures represent the three different portions of a closed curve. Recently Hudson found this to be realized in the case of nicotine and water. Figure 19 represents the effect of temperature on the solubility of nicotine in water.

By heating mixtures of non-miscible liquids, we saw that above a certain temperature for all concentrations they become consulate. If, however, we keep the temperature constant, we can accomplish practically the same result by adding a liquid which is consulate with both the components. So if we have three liquid components *A*, *B*, and *C*, and if *C* is consulate with *A* and *B*, then the mutual solubility of *A* and *B* is increased, and by addition of a sufficient quantity of *C* one liquid layer can be produced. It is conceivable, however, that if *C* is consulate with *A*, but only partially miscible with *B*, the addition of *C* to a mixture of *A* and *B* would increase the solubility of *A* but might decrease the solubility of *B*. By the proper selection of the three components we could obtain combinations which would result in the formation of these three classes of reactions:

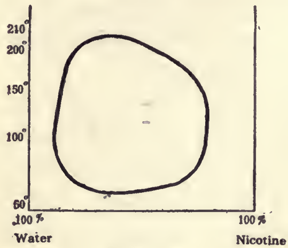


Fig. 19.

1. The three components form only one pair of partially miscible liquids.

2. The three components form two pairs of partially miscible liquids.

3. The three components form three pairs of partially miscible liquids.

Triangular Diagram. — In representing the relation of the mutual solubility to the change in temperature we used the horizontal axis to represent the concentration and the vertical axis to represent the temperature. To represent the concentration of three liquid components use is made of the triangular diagram, and since this is on a plane surface it represents the concentration at *one* temperature. There are two methods of representing the concentration by means of a triangular diagram, and we shall use the method of Roozeboom, and only refer to that of Gibbs indirectly.

Construct an equilateral triangle, ACB, Fig. 20. We saw that a line such as AB would represent all possible concentrations of A and B. Similarly let BC represent all possible concentrations of B and C, and AC represent all possible concentrations of A and C. The concentration of any mixture of A, B, and C will be represented by some point within the triangle. Assume the ends of the lines, *i.e.* the corners of the

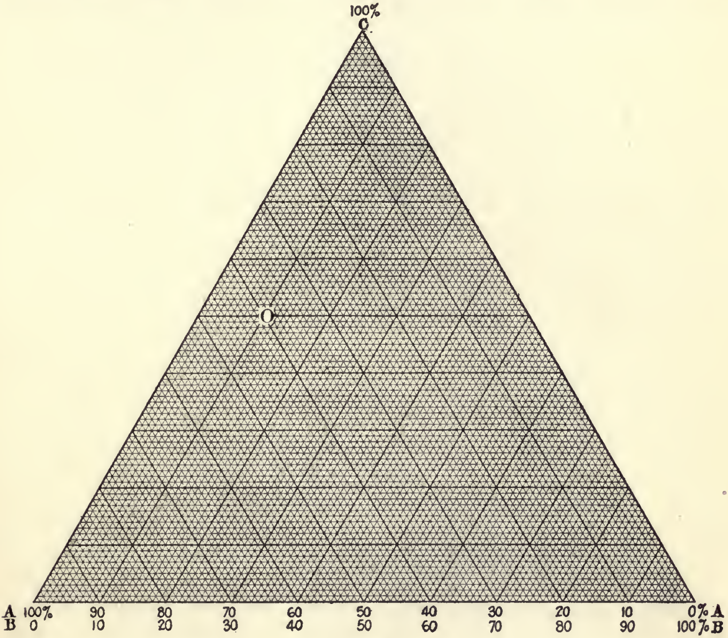


FIG. 20.

triangle, to represent 100 per cent respectively of A, B, and C; then divide the sides into 10 equal parts and draw lines parallel to the sides of the triangle. Then from the intersection of these lines the composition of a mixture represented by any point, such as O, can be readily ascertained. Counting the composition of A on the lines parallel to the side opposite A, we have 4, *i.e.* 40 per cent; counting similarly for B, we find 1.0 or 10 per cent, and since O is on 5th line from the side opposite C, then the concentration of C is 50 per cent, and that of our mixture is A = 40 per cent, B = 10 per cent, and C = 50 per cent.

Ether and alcohol are miscible in all proportions (and also water and alcohol), but water and ether are only partially miscible. So if a mixture of ether and water be taken in known proportions of about equal quantities and shaken with a little alcohol and allowed to come to equilibrium, two

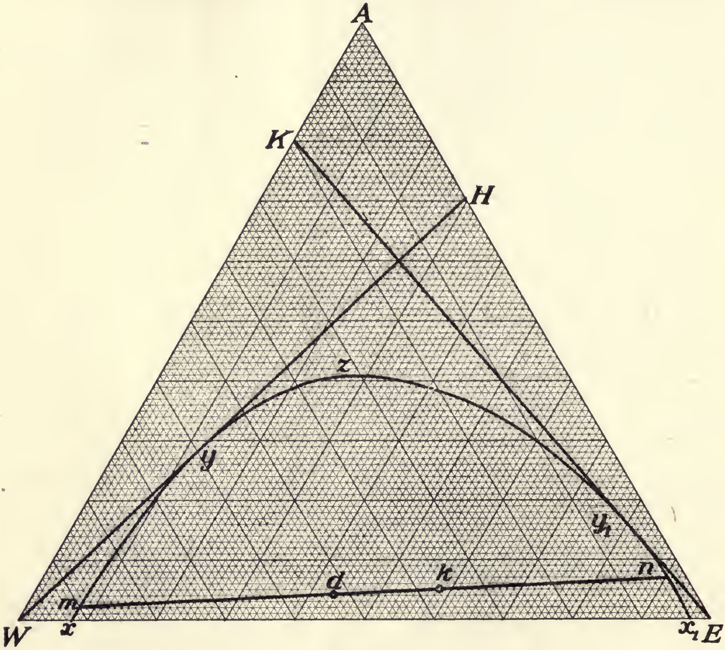


FIG. 21.

liquid layers will be formed. By repeating this with successive additions of alcohol a concentration will eventually be reached at which but one liquid layer is formed. If the point of concentration be established where just one drop of the alcohol will cause the disappearance of one of the two liquid layers, we have a point of saturation. Similarly successive points of saturation could be established synthetically for all concentrations of ether and water. Then by plotting these results on a triangular diagram, we would have a curve similar to $x\ y\ z\ y_1\ x_1$ in Fig. 21.

Let *W* represent water, *E* ether, *A* alcohol; then the sides of the triangle will represent all possible mixtures of the three pairs of liquids, taken two at a time. Since ether is partially soluble in water, x represents the saturated solution of ether in water, similarly x_1 represents a saturated solution of water in ether. The line Wx would represent solutions of ether in water and Ex_1 solutions of water in ether.

The series of saturated solutions of water, ether, and alcohol at constant temperature may be represented schematically by the isotherm $x\ y\ z\ y_1\ x_1$. If one starts with the liquid phase designated by x and varies the three components, the line xyz would represent one series of saturated solutions. From x_1 the same point z would be reached, and the curve x_1y_1z would represent the composition of the other series of saturated solutions. So by starting with the concentration designated by either x or x_1 and varying the composition, the same concentration of saturation as represented by the point z would be reached, where the two solution phases become identical. Hence the isotherm $x\ y\ z\ y_1\ x_1$ represents the series of saturated solutions of the three components which are in equilibrium at a definite constant temperature.

Above and outside of this isotherm is the field of unsaturated solutions, and the portion of the figure included by the curve represents the field of mixtures which separate into two liquid phases, the composition of which is given by some two points on the isotherm. Since the isotherm represents the composition of these saturated solutions in equilibrium, the addition of the component *W* or *E* will cause clouding. Now let us inquire whether it makes any difference which of the constituents is added. We saw that the location of x was due to the saturation of *W* by *E*, so any further addition of *W* would not cause clouding of this solution, but as we follow up the isotherm there must come a point at which the addition of *W* will cause clouding. Such a point, y, is where the line *WH* drawn through *W* is tangent to the curve. The same is true for the addition of the component *E*, the line *EK* through *E* being tangent to the curve at y_1. It has been shown experimentally that if to a mixture of *A* and *E* containing more of *E* than indicated by *H*, *W* be gradually added, clouding will eventually take place and the mixture separate into two liquid phases; but if *W* be added to a mixture of *E* and *A* containing less of *E* than indicated by *H*, no clouding will result. The same reasoning may be applied to the addition of *E* to solutions of *W* and *A* containing more or less of *W* than indicated by *K*, clouding occurring in the first case and not in the second.

It is therefore apparent that the isotherm is divided into four parts which correspond to the following four distinct sets of equilibria:

1. The solutions represented by the line xy are saturated with respect to E, and an excess of W does not produce a precipitate.

2. The solutions represented by the line yz are saturated with respect to E, and an excess of W or E produces a precipitate of E.

3. The solutions represented by the line zy_1 are saturated with respect to W, and an excess of W or E produces a precipitate of W.

4. The solutions represented by the line y_1x_1 are saturated with respect to W, and an excess of E does not produce a precipitate.

Above the solubility curve we have the area of unsaturated solutions, while within the curve all possible mixtures of water and ether and alcohol which will separate into two liquid layers may be represented. Any point, such as d, represents the proportions of water, ether, and alcohol which when shaken together and allowed to come to equilibrium would separate into liquid layers; the composition of the lower heavier liquid layer would be represented by some point, as m, on the solubility curve and the upper liquid layer by n on the other side of the solubility curve. The straight line passing through the point d and connecting these two points is designated the *tie line*. If any other mixture, represented by a point k on this line, was to be prepared and allowed to come to equilibrium, the composition of the two layers would also be represented by the same two points m and n on the solubility curve. That is, if we were to take a number of mixtures represented by points on this tie line and allow them to come to equilibrium, the upper layers on analysis would all be found to have the same composition represented by n, while the lower layers would all have the composition represented by the point m on the solubility curve.

Another case similar to the water-ether-alcohol system is that of silver, lead, and zinc. Molten lead and silver are miscible in all proportions, silver and zinc are also consulate, but lead and zinc are only partially miscible. This system has been worked out by Wright, who obtained the data given in Table XXVIII.

The values given in the horizontal rows represent composition of upper and lower layers in equilibrium at the particular temperature. These would compare to such points as n and m in Fig. 21, which are designated *conjugate* points, and the liquids are termed conjugate liquids. The composition of the upper layer is much richer in silver than is the lower layer. So by this means silver can be separated from lead and the upper layer rich in silver can be

TABLE XXVIII

Upper Layer Percentage Amount of			Lower Layer Percentage Amount of		
Silver	Lead	Zinc	Silver	Lead	Zinc
40.89	3.38	55.73	1.54	96.28	2.18
47.68	3.79	48.53	2.39	95.78	1.83
52.80	4.09	43.11	4.18	94.43	1.39
60.14	9.00	30.86	10.22	88.02	1.76
65.34	13.67	20.79	15.69	81.88	2.43
60.35	28.42	11.23	29.53	68.03	2.44

skimmed off from the lower liquid layer. This method constitutes the *Parkes' Process* for the desilverization of lead. In fact, this process is simply an example of the distribution of a substance between two liquid layers.

Saturated solutions are non-miscible and so this is a special case of two non-miscible liquids; and if we have a third component soluble in both the liquid components, this third component will be distributed between the two liquid phases. We saw according to Henry's Law that the ratio of the concentration (C_v) of a gas in the gaseous space and the concentration (C_l) in the liquid at equilibrium is always equal to a constant $\frac{C_v}{C_l} = k$. Now if we apply this law to the distribution of a substance between two liquid layers, then the coefficient of distribution is constant if the molecular species are the same in both liquids. For the equilibrium between two non-miscible liquids in which the third component is dissolved we find that the ratio of the concentrations, C_1 of the third component in the one liquid and the concentration C_2 in the other liquid, is a constant, *i.e.* $\frac{C_2}{C_1} = k$. That is, the ratio of distribution between two liquids is a constant. This is known as *Nernst's Distribution Law.*

This law has its application, as we have seen, to metallurgical processes, and it is apparent that the greater the constant the more of the dissolved substance (Ag, for example) can be removed from the liquid by adding zinc. As the solubility of silver is greater in aluminium than in zinc, the substitution of aluminium for zinc would give a larger value for the constant, and consequently a greater quantity of silver would be found in the upper layer, and therefore a greater percentage extraction. So the practice consists in adding a considerable quantity of aluminium to increase the efficiency of the desilverization of the lead.

Shaking Out Process. — The ordinary shaking out process employed in the organic laboratory is nothing more than the application of this principle. If a compound is prepared in an aqueous solution and this solution shaken with ether, in which the substance is more soluble, and the ether is then removed by means of a separatory funnel and evaporated, the separated material is obtained in the free state. The greater the distribution ratio the more efficient the extraction, and it is better to extract with successive small quantities of the solvent than to use the total quantity at one time, as the following consideration will show.

Let us assume that we have 12 grams of a substance dissolved in 100 cc. of water and that it is twice as soluble in benzene as it is in water. If we add an equal volume of benzene to the 100 cc. of water, then the substance dissolved will distribute itself between the benzene and water in the ratio of 2 : 1, and $\frac{2}{3}$ of 12, or 8 grams, or $66\frac{2}{3}$ per cent, will be contained in the benzene, and $\frac{1}{3}$ of 12, or 4 grams, or $33\frac{1}{3}$ per cent, will remain in the water. Hence, by extracting with equal quantities of the benzene, $66\frac{2}{3}$

per cent of the substance could be extracted. Now assume that we divide the benzene into two portions of 50 cc. each and extract the 100 cc. of aqueous solution with them successively. Since the substance is twice as soluble in benzene as in water, 50 cc. of benzene will dissolve as much of the substance as the 100 cc. of water, and so after shaking 100 cc. of water with 50 cc. of benzene the substance would be equally divided between the two solvents or in the ratio of 1 : 1, and one half of the substance would be extracted, *i.e.* 50 per cent. By extracting again with 50 cc. of benzene it is apparent that 50 per cent of the remainder would be extracted, or 25 per cent of the original quantity. Hence, by extraction with 100 cc. of benzene, using successively 50 cc. portions, the total amount of the dissolved substance removed is 75 per cent as against $66\frac{2}{3}$ per cent when it was all used at once. It is better, therefore, to extract several times with small quantities of the liquid than to extract once with a volume equal to the aggregate of the volumes used.

CHAPTER XVI

SOLUTION OF LIQUIDS IN LIQUIDS — II

Vapor Pressure

Water boils at a lower temperature on a high mountain than it does in a valley. This is commonly explained by saying that the pressure exerted by the atmosphere on the surface of the water is less at the higher altitude, or that the liquid water passes into the vapor phase at a lower temperature when the pressure is diminished. This fact is made use of in organic chemistry when we carry on the operation known as distillation under diminished pressure. At these respective temperatures under their corresponding pressures there exists a state of equilibrium between the vapor and the liquid, and the liquid will all pass over into the vapor phase without change in temperature, if heat be continuously supplied. If at these various temperatures of equilibrium the corresponding pressures be determined and represented diagrammatically so that the ordinates represent the pressures and the abscissæ the temperatures, and if the points are connected by a curve, we should have the values for all intermediate temperatures and pressures. Such a curve is known as the *Vaporization Curve* and represents all possible temperatures and pressures at which the liquid and vapor are in stable equilibrium. It can therefore be designated an *Equilibrium Curve*. The pressure that the vapor exerts under these conditions of equilibrium is designated the *Vapor Pressure* of the substance.

Methods of determining vapor pressures of substances are usually classified as the static method and the Ramsay and Young or dynamic method. By the *static method* the substance is placed in a Torricellian vacuum above a column of mercury, is heated, and the pressure determined by change in height of the column of mercury.

By the Ramsay and Young method the pressure is kept constant and the temperature is varied until equilibrium at that pressure is established.

We shall consider the vapor pressure determinations of two substances, benzene and water, and represent them diagrammatically. When the pressures are represented as ordinates and the temperatures as abscissæ, the diagram is known as a *p-t* diagram, that is, a pressure-temperature diagram.

The following values for benzene have been found by Ramsay and Young, and subsequently confirmed by Fischer:

TABLE XXIX — VAPOR PRESSURE OF BENZENE

t	*p* in mm. Hg.	*t*	*p* in mm. Hg.	*t*	*p* in mm. Hg.
0°	26.54	5°	34.80	40°	180.20
1	28.04	6	36.69	50	268.30
2	29.61	10	45.19	60	388.51
3	31.26	20	74.13	70	548.16
4	32.99	30	117.45	80	755.00

The curve, *AB* in Fig. 22, represents the *vapor pressure curve* of liquid benzene, and is an *equilibrium curve*, as it represents the pressures and the corresponding temperatures at which the liquid and vapor of benzene are in equilibrium. The curve *AB* divides the area into two parts, and is then the boundary between the area above the line representing the liquid phase and that below which represents the vapor phase. The area between the curve *AB* and the temperature axis represents the pressures and temperatures at which benzene exists as a vapor, while the area above and bounded by *AB* and

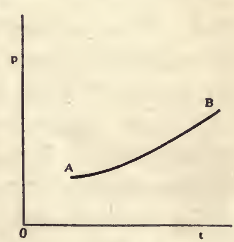


FIG. 22.

the pressure axis represents the pressures and temperatures at which benzene will exist as a liquid.

In a like manner we give values for the vapor pressure of water:

TABLE XXX — VAPOR PRESSURE OF WATER

t	p in mm. Hg.	t	p in mm. Hg.
− 10°	2.144	120°	1484
0	4.58	130	2019
+ 20	17.54	150	3568
40	55.34	200	11625
60	149.46	250	29734
80	355.47	270	41101
100	760.0	364.3	147904 (194.6, atmospheres C. P.)

In Fig. 23 *AB* represents the vapor pressure curve for water and is an equilibrium curve as well, for it represents the equilibrium between liquid water and vapor for all intermediate temperatures. It likewise represents the boundary between areas where the liquid and the vapor phases of water exist.

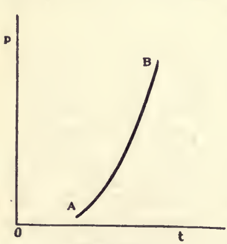


FIG. 23.

These two examples are sufficient to illustrate the method of representing the condition of equilibrium in a two-phase liquid-vapor one-component system, and this method is general in its application. With a constant mass the state of a system is defined by arbitrarily fixing one of the variable factors. For if the temperature is fixed, then the pressure at which the liquid and vapor coexist is also fixed, and is represented by a point on the curve *AB* at which a line perpendicular to the t axis at that particular value for the temperature cuts the curve *AB*. If we fix the pressure, the temperature at which the vapor and liquid coexist is also fixed.

The mass of the phase or phases does not influence the equilibrium of the system, for if we increase the pressure, the vapor phase will disappear. The pressure is independent of the relative or absolute volumes of the vapor and liquid phases. If the pressure and temperature are maintained constant, it does not matter whether we have 500 or 50 cc. of the liquid present, the equilibrium will be preserved and we could remove most of the liquid without disturbing the equilibrium.

Limits of the Vapor Pressure Curve. — It is natural to inquire to what pressure and temperature it is possible to subject a two-phase liquid-vapor one-component system, such as water or benzene, and still obtain a condition of equilibrium between the two phases. The vapor pressure curve is a boundary curve and separates the area of the diagram into the areas of pure liquid and pure vapor; hence, if we follow this curve to a sufficiently high temperature with its corresponding pressure, we reach the point at which there is no distinction between the liquid and the vapor phases, and the system ceases to be heterogeneous and is a homogeneous single phase. This would occur at the temperature at which there is no distinction between the vapor and liquid, that is, at the *critical temperature*, and the corresponding pressure, called the *critical pressure*. Hence, the vapor pressure curve must end at the critical point, and above this temperature there is no pressure great enough to produce the liquid phase. In the case of water the vapor pressure curve would terminate at a temperature of 633° absolute, and a pressure of 195.5 atmospheres, which are called respectively the critical temperature and critical pressure of water. For benzene the critical values are 561.5° absolute and 47.89 atmospheres pressure.

It is a familiar fact that if the temperature of a liquid, as water, is lowered, there occurs a time when the substance ceases to exist in the liquid phase and a new phase appears — the solid phase. Hence, it follows that there must be a lower limit to the vapor pressure curve for liquid water, that is, to the vaporization curve. It is also a familiar fact that when clothes are placed on the line in winter, they freeze, thus becoming stiff and hard. Later they are all found to be soft and dry. This is due to the fact that the water on exposure to the cold becomes ice and later disappears in the form of vapor. That is, the solid water (ice) passes directly from the solid to the vapor phase without passing through the intermediate liquid phase. This happens in the case of a large number of substances, for example, if mercuric chloride is heated at ordinary atmospheric pressure, it liquefies, and if the heat be increased, the liquid passes into the vapor phase. If, however, the pressure is diminished to 200 or 300 mm. and heat applied, it is found that the solid passes over into the vapor phase without passing through the intermediate liquid phase. This passage of a substance from the solid to the vapor phase without passing through the intermediate liquid phase is designated *sublimation*. The solid like the liquid has a certain tendency to pass into the vapor phase, and as this can be measured as a pressure, we speak of the *vapor pressure of solids*. This tendency to sublime can be measured in a manner somewhat analogous to the determination of the vapor pressure of liquids, and it may be represented on the *p-t* diagram; the curve representing the vapor pressure of a solid is an equilibrium curve and represents the equilibrium between the solid (ice) and vapor, and is called the *Sublimation Curve*.

FIG. 24.

In the case of benzene the vapor pressures are given in Table XXIX. Representing these data on the *p-t* diagram, Fig. 24, we have *CD*, which terminates at the melting point of benzene, that is, where the sublimation curve intersects the vaporization curve.

In the case of water we have the following values for the vapor pressure of ice:

TABLE XXXI — VAPOR PRESSURE OF ICE

t	p IN MM. OF MERCURY	t	p IN MM. OF MERCURY
− 50°	0.029	− 8°	2.322
− 40	0.094	− 6	2.762
− 30	0.280	− 4	3.277
− 20	0.770	− 2	3.879
− 15	1.237	− 1	4.215
− 10	1.947	− 0	4.579

Representing these values on the *p-t* diagram, Fig. 25, we have *CD*, which intersects the vaporization curve *CB* at *C*. This is the melting point of ice and is therefore the upper limit or termination of the sublimation curve, which is an equilibrium curve between the vapor and solid phases, thus dividing the area represented by the *p-t* diagram into still smaller divisions.

FIG. 25.

In systems composed of two miscible liquids, the vapor pressure of the one liquid phase is found to depend on its concentration and on the temperature. At constant temperature the variation of the vapor pressure with change of concentration may be represented on a *p-conc.* diagram, and three different types of curves are found to represent the vapor pressure of mixtures of different pairs of miscible liquids.

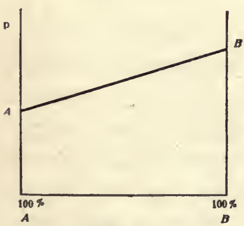


FIG. 26.

Let us represent on a pressure-concentration diagram, Fig. 26, the concentration of mixtures of two miscible liquids and by *A* and *B* the vapor pressures at a given temperature.

If the vapor pressures of all mixtures of *A* and *B* are intermediate between the vapor pressures of *A* and *B*, then the curve *AB* represents the vapor pressures of all mixtures, and the total pressure is the sum of the partial pressures of the vapor of the two components. The addition of a second component to a solvent may affect the vapor pressure in one of three ways: (1) it may lower the vapor pressure, (2) it may raise the vapor pressure, or (3) it may not affect it.

In the pressure-concentration diagram, Fig. 27, let *C* and *D* represent the vapor pressures of two miscible liquids, then as we add *D* to *C* the vapor pressure of *C* is raised. If we take *D* as the solvent and add *C*, the vapor pressure will be raised, and if we plot these results we obtain a curve represented by *COD* which indicates a *maximum* vapor pressure for some mixture of these two miscible liquids.

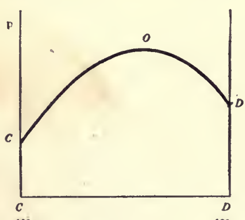


FIG. 27.

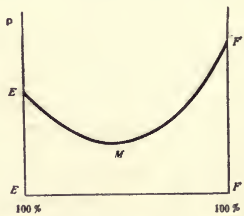


FIG. 28.

In the pressure-concentration diagram, Fig. 28, let *E* and *F* represent the vapor pressures of two miscible liquids. Let us assume that the addition of the second component diminishes the vapor pressure of the solvent; then by adding *F* to *E* the vapor pressure will be decreased, and similarly by adding *E* to *F* the vapor pressure of the mixture will be less than that of *F*. By plotting such results we obtain the curve *EMF*, which represents a *minimum* vapor pressure; while in the first case, where the vapor pressures of the mixtures were intermediate between the vapor pressures of the two components, we have neither maximum nor minimum pressures.

We have already seen that the vapor pressure is the pressure which is necessary to balance the tendency of the solvent to pass into the vapor phase, and at a given temperature this tendency is much less than it was before the solute was added. It will be necessary to raise the temperature considerably to form the amount of vapor sufficient to produce the pressure equivalent to the pressure of the vapor of the pure solvent. Therefore, the liquid with the lower vapor pressure at a given temperature is the liquid with the higher boiling point. Representing the pairs of liquids *A* and *B* on a temperature-concentration diagram, Fig. 29, we would have the boiling point of *A* higher than that of *B*, and since the vapor pressure of mixtures of the two liquids is intermediate between that of the liquids themselves, the boiling point of their solutions is intermediate between the boiling points of the pure liquids, as is shown by the line *AB*, which represents the boiling points of all mixtures of *A* and *B*.

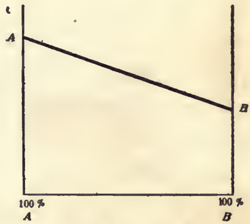


FIG. 29.

To produce the same amount of vapor from solutions of two miscible liquids which can have a minimum vapor pressure, requires a larger expenditure of energy in the form of heat than to produce the same pressure from the pure solvent. So if we take different mixtures of two miscible liquids which manifest minimum vapor pressures and determine the boiling points and plot them on a temperature-concentration diagram, as in Fig. 30, we obtain the curve *EMF*, which shows that as we add the component *F* to the solvent *E* the boiling point is raised, and the rise is greater the greater the concentration within certain limits. The same is true if we use *F* as the solvent, and as we add

E the boiling point of the solutions increases with the increased concentration of E. We obtain the curve EMF which shows a maximum boiling point for mixtures of E

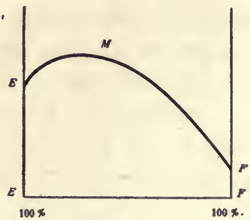


FIG. 30.

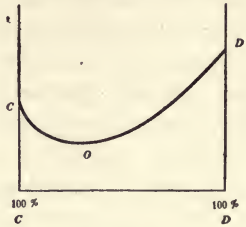


FIG. 31.

and F. Pairs of miscible liquids which have a minimum vapor pressure curve also have a maximum boiling point curve.

Similarly it may be shown, as represented in Fig. 31, that two miscible liquids which have a maximum vapor pressure curve (Fig. 27) have a minimum boiling point curve, COD.

Composition of the Vapor Phase

The vapor phase under constant pressure and temperature will be in equilibrium with the liquid phase, and we have just seen that the pressure of the vapor phase is due to the vapor pressures of the individual components of the vapor, *i.e.* $p = p_1 + p_2$, which is Dalton's Law. The concentrations in a gas are proportional to the partial pressures, and hence we could determine the concentration of the components in the vapor phase if we knew the partial pressures. The determination of the partial pressures is difficult, and satisfactory methods have not been devised. But we can determine the concentration by distilling over fractions, collecting, and analyzing them.

Let us consider a pair of liquids whose mixtures have boiling points intermediate between the boiling points of the two components. In Fig. 32 let A and B represent the two components and AyB represent the boiling points of the mixtures. Let us consider a mixture represented by the point p, the composition of which is, say, 80 per cent A and 20 per cent B. If we heat this mixture and continue to raise its temperature until we intersect the boiling point curve AB at z, the liquid will boil at this temperature, t_z, and the vapor which passes off will be richer in B than in A. The temperature of the liquid in the flask will rise and pass along the line zA, and the concentration of the liquid in the flask will approach the composition of pure A. The distillate which passes off at z is richer in B than the liquid from which it was distilled, and may be represented by some point as x. If the vapor of this composition is condensed and then heated to its boiling point, it will be found to boil at the temperature t_y. This will boil, and the vapor will be richer in B than is represented by the concentration y, *i.e.* some concentration such as w. The vapor w, if condensed, would be found to have a boiling point t_v, and the vapor of this would be richer in B. By this process of redistillation we are obtaining distillates successively richer in B, and it is apparent that if this be continued a sufficient number of times we approach B and thus completely separate it from A. From the liquid remaining in the flask we obtain A and from the distillates pure B, and therefore can completely separate them by this means, which is termed fractional distillation. Any point on the curve $BwxA$ represents the composition of the vapor phase, *i.e.* of the distillates, at the boiling point of the mixture from which it was obtained. This curve is called the *Vapor Composition Curve.*

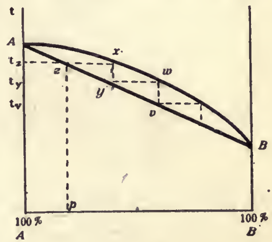


FIG. 32.

In Fig. 33, where we have a maximum boiling point, the vapor composition curve is represented by the dotted curve *CcOdD*. If we take any mixture richer in *D* than the maximum boiling mixture, and fractionate it, the distillate will be richer in *D* than in *C*, and the composition of the liquid in the flask becomes richer in *C*. For mixtures richer in *C* than the maximum boiling mixture, the vapor will be richer in *C* and the composition of the liquid remaining in the flask becomes richer in *D*. For any mixture the concentration of the liquid in the flask tends to become of the concentration as represented by the concentration *O*, at which the boiling point is the highest of any mixtures of *C* and *D*, and the composition of the vapor is the same as that of the distilling liquid, *i.e.* we have a *constant boiling liquid*, and all of the liquid passes over without change in temperature.

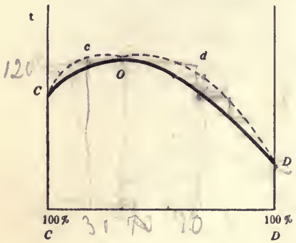


FIG. 33.

This phenomenon is the same as in the case of pure substances. The boiling point is used as a means of determining whether a substance is pure. If the boiling point is constant, we conclude that the substance is a pure one and that the composition of the vapor and of the liquid are the same. If this criterion be applied to this boiling mixture, the conclusion would be that it is a pure chemical compound. For a long time such mixtures were considered as chemical compounds. In the case of pure substances the composition of the liquid and vapor phases is the same, irrespective of the pressure at which the boiling point is determined. If, however, these constant boiling mixtures of pairs of miscible liquids be determined at different pressures, vapors of different composition will be obtained. This proves that they are not chemical compounds but mixtures.

In Fig. 34, *EeMfF* is the vapor composition curve of the distillates from the mixtures of pairs of liquids with a minimum boiling point. The distillates of mixtures whose boiling points are represented by *EM* are richer in *F* than the mixtures from which they were obtained, and as these distillates are continuously fractionated by distillation the composition of the distillate approaches *M*. Similarly, for the liquids whose boiling points are represented by *MF* the composition of the distillates obtained by fractional distillation approaches *M* as the final value. That is, the distillates of all mixtures upon fractionation give as final values the composition represented by *M*, which is that mixture with the lowest boiling point. At this temperature the mixture of this composition distills at constant temperature and the vapor and liquid have the same composition. What was stated with respect to the point *O* of the maximum boiling liquids applies to the point *M* of the minimum boiling liquids; the composition varies with the pressure and therefore they are not pure chemical compounds.

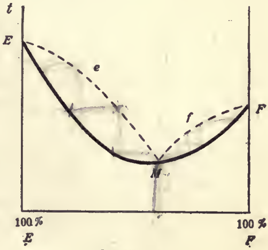


FIG. 34.

Mixtures of the type illustrated in Fig. 32 are not very common. In the case of methyl alcohol-water and acetone-water mixtures, approximate separation by fractional distillation can be obtained.

Mixtures of the type illustrated in Fig. 33 are represented by a number of solutions of acids in water where maximum boiling points are obtained as illustrated in Table XXXII.

Mixtures of the type illustrated in Fig. 34 are common, and a few of the more common pairs of miscible liquids that have a maximum vapor pressure and a minimum boiling point are given in Table XXXIII.

TABLE XXXII

Solvent	Boiling Point	Solute	Boiling Point	Temperature of Maximum Boiling Point	Per cent by Weight of Solvent
Water	100°	Nitric acid	86°	120.5°	32.
Water	100.	Hydrochloric acid	−82.9	110.	79.76
Water	100.	Hydrobromic acid	−68.7	126.	52.5
Water	100.	Hydriodic acid	−35.7	127.0	43.0
Water	100.	Hydrofluoric acid	19.4	120.	63.
Water	100.	Formic acid	99.9	107.1	23.0
Perchloric acid	110.0	Water	100.	203.	71.6
Chloroform	61.2	Acetone	56.4	64.7	80.
Chloroform	61.2	Methyl acetate	56.0	64.5	78.
Propionic acid	140.	Pyridine	117.5	149.	—

TABLE XXXIII

Solvent	Boiling Point	Solute	Boiling Point	Temperature of Minimum Boiling Point	Per cent of Solvent by Weight
Water	100°	Ethyl alcohol	78.3°	78.15°	4.43
Water	100.	Isopropyl alcohol	82.45	80.35	12.10
Water	100.	*n* Propyl alcohol	97.2	87.7	28.31
Butyric acid	159.	Water	100.	99.2	20.
Pyridine	115.	Water	100.	92.5	59.
Benzene	80.2	Methyl alcohol	64.7	58.35	60.
Benzene	80.2	Ethyl alcohol	78.3	68.25	67.64
Tertiary butyl alcohol	82.55	Benzene	80.2	73.95	36.6
Allyl alcohol	95.5	Benzene	80.2	76.5	20.0
Toluene	109.	Allyl alcohol	95.5	91.5	50.0
Ethyl alcohol	78.3	Normal hexane	68.95	58.65	21.0
Carbon tetrachloride	76.75	Methyl alcohol	64.7	55.7	79.4
Ethyl iodide	72.9	Methyl alcohol	64.7	55.0	83.
Ethyl alcohol	78.	Ethyl iodide	72.0	63.0	14.
Acetone	56.4	Carbon bisulphide	46.2	39.25	34.0
Methyl acetate	56.0	Carbon bisulphide	45.6	39.5	29.0

Fractional Distillation with Steam

In the case of a one-component system of a liquid and vapor, the vapor pressure of the pure liquid at the boiling point under atmospheric pressure is equal to 760 mm. pressure. That is, the vapor exerts a pressure of this amount against the tendency of the liquid to vaporize. In the case of two non-miscible or partially miscible liquids, the vapor pressure of these at the boiling point of the mixture will be the sum of the partial vapor pressures of the two liquids. This will be equal to the external or atmospheric pressure, if boiling under atmospheric pressure. If carbon bisulphide boils at 50° C. the vapor pressure at this temperature is balanced by the atmospheric pressure, and if we have water mixed with it at this temperature the vapor pressure of the water is appreciable, as $p = p_{CS_2} + p_{H_2O}$, hence the vapor pressure of CS_2 does not have to equal the atmospheric pressure, as the combined pressures of the carbon bisulphide and of the water are equal to the external pressure. It is, therefore, apparent that the aggregate pressures of the two vapors will equal the atmospheric pressure at a temperature below 50°, the boiling point of the lower boiling liquid. That is, the mixture will boil at a temperature below that of the lower boiling liquid. The quantities of the substances in the vapor phase will, of course, depend upon the vapor pressure of the substances at that temperature. This may be illustrated by a specific case.

In the distillation of nitrobenzene by steam the mixture boils at 99° C. at a pressure of 760 mm. At this temperature the vapor pressure of water is 733 mm. and that of the nitrobenzene would be the difference 760 − 733 or 27 mm. Since 22.4 liters, the gram-molecular volume, would contain 18 grams of water vapor under the standard conditions, an equal volume under 760 mm. pressure and at 0° would contain 123 grams of nitrobenzene. Since the volumes are indirectly proportional to the pressures we would have, as the weights are proportional to the pressures, 18 gr. : x gr. : : 760 mm. : 733 mm. (the vapor pressure of water at 99° C.). This gives $\frac{18 \times 733}{760}$ grams of water which would pass over. In a like manner we find $\frac{123 \times 27}{760}$ grams of nitrobenzene in the distillate. These give us the ratio of $\frac{123 \times 27}{760} : \frac{18 \times 733}{760}$ or 367 : 1466 or 1 : 4 as the relative weights of the distillates. As the water is much lighter than the nitrobenzene, the volume of water is much larger relatively to that of the nitrobenzene that passes over. If the molecular weight of the substance being distilled with steam is not known, it can be readily calculated by measuring the volume of the liquids distilled over, and from their specific gravities the weight could be determined and from this ratio the value of m in place of the molecular weight of nitrobenzene vapor could be calculated.

CHAPTER XVII

PHASE RULE

Since we know that the existence of water in the vapor, liquid, or solid phase depends upon the conditions of temperature and pressure, the limiting value for any particular phase is a question merely of the relation of these factors. In a consideration of the subject of phases and of the problems of equilibrium from this point of view, we practically take into consideration the heat and volume energy and leave out of consideration the force of gravity, electrical strains and stresses, distortion of the solid mass, capillary tension, etc., and thus confine ourselves to those systems wherein there exists only uniform temperature, pressure, and chemical potential.

In a system that contains only one phase, unless we have both the pressure and temperature designated, the concentration is not known. Both of these factors are needed to establish the system. We know that both of these independent variables can be changed within certain limits and the system still be maintained as a one-phase system. Then the question arises: What are the limits to which these independent variables can be varied and yet retain the system as a one-phase system? That is, What are the boundaries of any of these different possible one-phase systems such as water, and what will happen to the system when these limits are exceeded? If the pressure and temperature are varied in the proper direction, a vapor can be made to condense into a liquid, — the greater the pressure the more of the vapor will disappear and the greater the liquid phase will become. The concentration of the system has increased and we have a *two-phase system*. If, on the other hand, the pressure is diminished and the temperature increased sufficiently, it may break up and become disintegrated by the decomposition of the components. So that the boundary limits in all directions are not accessible and hence not easily established experimentally.

By decreasing the temperature of the two-phase system of water — liquid and vapor — a new phase appears. This is the solid (ice). When this occurs we have the system more securely fixed, as it were, for none of the variables can now be changed without causing the disappearance of some of the phases — ice, if the temperature is increased, or liquid, if the temperature is decreased. Every phase of a system has its boundaries or limitations on all sides, that is, its sphere of existence. These boundaries are represented by the independent variables — the temperature, pressure, and concentrations. We see then that every system has a certain amount of freedom in the variation of its variables in so far as the identity of the system is not destroyed, and we have also seen that this sphere of freedom is not necessarily bounded on all sides by other phases. This "sphere of existence" is spoken of as the *number of degrees of freedom* of the system and is defined as "the number of the variable factors — temperature, pressure, and concentration of the components — which must be arbitrarily fixed in order that the conditions of the system may be perfectly defined." — Findlay's *Phase Rule*, p. 16.

A gas would have *two* degrees of freedom because, in order to determine its concentration, we should have to define both the pressure and temperature.

A system, liquid-vapor, has one degree of freedom, while a system, solid-liquid-vapor, has no degree of freedom, because a change of any of the variables would cause one of the phases to disappear and the equilibrium to be disturbed.

In speaking of the amount of variance or variation of the system, we say that the system is nonvariant (invariant), monovariant, divariant, multivariant, etc., when the number of degrees of freedom is respectively zero, one, two, three, etc. This relation between the number of degrees of freedom, the number of independent variables, and the number of components of the system has been expressed by Gibbs in his celebrated Phase Rule, which defines the system completely. This *Phase Rule* may be stated as follows: *The number of degrees of freedom of a system is equal to the number of components plus two, minus the number of phases.* This may be expressed by the following equation:

$$N + 2 - P = F$$

in which N is the number of components, P the number of phases, and F the number of degrees of freedom, or the variance of the system.

The concept of *phases* has been of great importance in aiding the classification and correlation of a large number of isolated facts, in the interpretation of new phenomena, and in guiding us in the discovery of new phenomena and their relations. In this respect the Phase Rule as a system of classification of interrelated phenomena is to chemistry in general what the periodic law is to inorganic chemistry. It is really a basis of classification of the phenomena of chemistry rather than a separate division of the subject.

Ostwald goes even farther and states that it is possible from the principles of chemical dynamics (the theory of the progress of chemical reaction and the theory of chemical equilibrium) to deduce all of the stoichiometrical laws, the laws of constant proportion, the laws of multiple proportions, and the law of combining weights. Through this conception of the phase introduced by Gibbs and amplified by himself and Franz Wald, Ostwald proceeds to deduce these laws in his Faraday Lecture (*Jour. Chem. Soc.*, *85*, 506 (1904)).

System of Water

The *p-t* diagram, Fig. 35, represents the whole range of temperatures and pressures of the system water, and this area is divided into three areas representing the ranges of temperature and pressure at which water can exist as vapor, as liquid, and as solid. Each of these three systems consists of one phase, hence, according to the Phase Rule $N + 2 - P = F$, we have $1 + 2 - 1 = 2$; *i.e.* two degrees of freedom or a *Divariant System*. The three divariant systems then are:

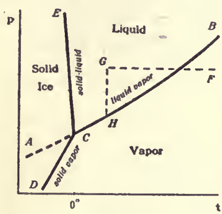


Fig. 35.

1. The area *DCB–t*-axis representing the vapor phase,
2. The area *ECB* representing the liquid phase,
3. The area *DCE–p*-axis representing the solid phase.

It is apparent, as in the case of the liquid phase, that at a point such as *G*, if the temperature be kept constant, there are a large number of pressures to which the liquid can be subjected without introducing a new phase or causing the liquid phase to disappear. Likewise, if the pressure at *G* be kept constant, there are a large number of temperatures at which the liquid phase persists, *i.e.* the liquid phase is capable of existing at various temperatures at the same pressure. This is true of any other phase; each pressure has a number of temperatures and each temperature a number of pressures at which the phase exists.

The boundary between the vapor area and the liquid area is represented by the curve *CB*, which is the *Vaporization Curve* and represents the equilibrium between the liquid and vapor phases. Since we have two phases in equilibrium, according to the Phase Rule we should have $1 + 2 - 2 = 1$, or a *Monovariant System*. The same is true of the equilibrium curve between vapor and solid, represented by the *Sublima-*

tion Curve, *DC*, and the equilibrium between the solid and liquid represented by the *Fusion Curve*, *EC*. Hence we have three *monovariant systems* represented by the following curves:

1. *CB*, representing equilibrium between the liquid and vapor phases,

2. *CD*, representing equilibrium between the vapor and solid phases,

3. *CE*, representing equilibrium between the liquid and solid phases.

The three curves representing the monovariant systems intersect for water at a point known as the *triple point*. This point represents the only temperature and pressure at which the three phases — solid, liquid, and vapor — can exist in equilibrium; for water this is at 4.6 mm. pressure and at $+ 0.0075°$. According to the Phase Rule, since we have three phases present we should have $1 + 2 - 3 = 0$; *i.e.* the system is a *Nonvariant System*.

We have just defined the boundaries of the various phases when in equilibrium, but it is natural to inquire if any particular phase can exist under any other conditions than those represented by the diagram. It is known that if vapor is cooled very carefully, it can be obtained at a temperature much below that at which it should condense and become a liquid. In the diagram, Fig. 35, let *F* represent some temperature and pressure of the vapor. By cooling the vapor very carefully it may be made to follow the conditions represented by the line *FG*, and at *G*, in the liquid area, the vapor phase still exists. That is, the vapor is capable of existing under other conditions than that represented by the area designated *vapor*, but under such conditions the system is said to be in a state of *labile* equilibrium; and if a minute trace of the liquid phase be introduced, some of the vapor will become liquid and assume a condition of stable equilibrium with the vapor represented by a point

H on the equilibrium curve *CB*. If we continue to cool the monovariant system, liquid-vapor, it is possible to continue the curve *CB* into the solid area to *A*, without the appearance of the solid phase. That is, we have undercooled the liquid below its freezing point. If, however, a portion of the solid phase is introduced, the liquid phase will disappear and the system will become a system composed of solid and vapor in equilibrium. We have not been able to obtain the solid phase under such conditions that a liquid or vapor exists, but a liquid can be heated above the temperature at which it is in equilibrium with the vapor phase and be represented in the vapor phase area. It is claimed that water has been heated to about 200° C. and still remained in the liquid phase.

At the triple point *C* we have the three phases in equilibrium. If the system, solid-liquid-vapor, be heated, the solid phase will disappear first and the equilibrium between liquid-vapor will be produced; and if heat be continually added, the system will take the direction represented by the curve *CB*. If the system be cooled, the liquid water will disappear and the equilibrium will be described by the curve *CD*, which represents the equilibrium between ice and vapor.

The triple point *C* for water is not exactly 0° C., as the melting point is defined as 0° under a pressure of 760 mm. This ice is under its own vapor pressure, which is nearly 4.6 mm., or practically one atmosphere less. From Table XXXIV, which gives the fusion pressure of ice for pressure as high as about 2000 atmospheres, it is found that an increase of one atmosphere lowers the melting point of ice 0.0075°, *i.e.* it would require 134 atmospheres to change the melting point 1° C.

TABLE XXXIV — FUSION PRESSURE OF ICE

TEMP.	PRESSURE IN KILOGRAMS PER SQ. CM.	CHANGE OF MELTING PT. PER INCREASE OF 1 KILOGRAM PER SQ. CM.
0° C.	0 (4.6 mm.)	0.0072
− 5	610	0.0087
− 10	1130	0.0102
− 15	1590	0.0118
− 20	1970	0.0135

Polymorphism. — We have been considering the physical forms of matter, *i.e.* the different phases due to the change in pressure and temperature. Whether water exists in the solid, liquid, or vapor phase depends upon the pressure and temperature to which it is subjected. It is known that certain substances exist in only one vapor, one liquid, and one solid phase; but many other substances exist in four or more different phases. For example, sulphur exists in at least four phases: two solid, one liquid, and one vapor. The same is true of a large number of other substances. The solid phases are always different in crystalline form, the melting points are different, as well as the specific gravity and a number of other physical properties. This phenomenon is known as *polymorphism* and was recognized by Mitscherlich as early as 1820 in the cases of disodium hydrogen phosphate and of sulphur. Formerly polymorphism was considered a very rare thing, but so many cases have now been observed that it is considered the rule rather than the exception. When an element exists in more than one form or modification it is said to exhibit *allotropy*, and the forms or modifications are termed *allotropes* or *allotropic modifications*. When compounds exhibit this phenomenon it is termed *polymorphism*, and depending on the number of crystalline forms, the compound is said to be, for two forms, dimorphous; for three, trimorphous; for four, tetramorphous. The term polymorphism is frequently applied to both compounds and elements, but does not include the allotropy of amorphous substances, such as ozone, or of liquid sulphur.

Types of Polymorphism or Allotropy. — The different allotropic modifications of substances have different and distinct physical properties: crystalline form, melting point, rate of expansion, conductivity of both heat and electricity, color, etc.

The transformation of a substance from one phase into another takes place at constant temperature for a given pressure. This is illustrated by the change of liquid water into ice, where we have the appearance of a new phase and the two phases coexisting in equilibrium; or at very high pressures the reverse change may occur. The conditions of temperature and pressure under which the change of one phase into another occurs or where a new phase appears and coexists in equilibrium with the others is termed the *transition point.* The temperature at which this occurs is the transition temperature, and the pressure, the transition pressure, which, however, may vary over wide ranges without appreciably affecting the temperature of equilibrium, and as a result is many times neglected, particularly in the case of such transitions as that of α iron into β iron. The transition point is also called the inversion point.

The three following types of polymorphic or allotropic substances exist:

I. *Enantiotropic substances* are those whose polymorphic forms may be directly transformed one into the other, and the transition point lies below the melting point of each of the forms.

In Table XXXV are listed a few well-marked examples of enantiotropic polymerization among inorganic substances.

TABLE XXXV

SUBSTANCES	FORMS	TRANSITION TEMPERATURE
Fe	$\alpha \rightleftarrows \beta$	780°
	$\beta \rightleftarrows \gamma$	920
S	Rhombic $\rightleftarrows$ Monoclinic	95.5
Sn	Gray $\rightleftarrows$ Tetragonal	18
	Tetragonal $\rightleftarrows$ Rhombic	161
Zn	$\alpha \rightleftarrows \beta$	170
	$\beta \rightleftarrows \gamma$	340
AgI	Hexagonal $\rightleftarrows$ Regular	147
$AgNO_3$	Rhombic $\rightleftarrows$ Rhombohedral	159.5
As_2S_2	Red $\rightleftarrows$ Black	267
Ca_2SiO_4	$\gamma \rightleftarrows \beta$	675
	$\beta \rightleftarrows \alpha$	1420
HgI_2	Tetragonal $\rightleftarrows$ Rhombic	126
KNO_3	Rhombic $\rightleftarrows$ Rhombohedral	129.5
K_2SO_4	Rhombic $\rightleftarrows$ Hexagonal	599
NH_4NO_3	Tetragonal $\rightleftarrows$ α rhombic	−16
	α rhombic $\rightleftarrows$ β rhombic	35
	β rhombic $\rightleftarrows$ Hexagonal rhombohedral	85.4
	Hexagonal rhombohedral $\rightleftarrows$ Regular	125
SiO_2	Quartz $\rightleftarrows$ Tridymite	800
$TlNO_3$	Rhombic $\rightleftarrows$ Rhombohedral	728
	Rhombohedral $\rightleftarrows$ Regular	142.5

II. *Monotropic Substances.* Iodine monochloride is known in two forms: α-ICl which melts at 27.2°, and β-ICl which melts at 13.9°, the α form being the stable form at ordinary temperature. These do not exhibit a transition period nor are they directly transformable one into the other. A number of substances manifest this phenomenon of not being reversibly transformable and polymorphism of this irreversible kind is termed *monotropy.*

III. *Dynamic Allotropy.* It is known that two of the liquid forms of sulphur, S_λ and S_μ, can exist together in definite proportions, which depend on the temperature. This phenomenon is termed *dynamic* allotropy. The various solid polymorphic forms cannot exist together except at the transition point, but those manifesting dynamic allotropy can do so, and this is explained on the basis of the existence of molecules of different complexity.

Smith and his colaborers have shown that the two liquid phases of sulphur, S_λ and S_μ, have different solubilities in a number of different solvents: diphenylmethane, diphenyl, β-naphthol and triphenylmethane; S_λ dissolves in these solvents with an absorption of heat as shown by the ascending curve of solubility, while S_μ dissolves with evolution of heat as shown by the descending curve of solubility.

Many substances that manifest polymorphism have labile modifications that exist at temperatures far below the transition point or inversion temperature as in the case of calcite and aragonite, the two solid modifications of calcium carbonate. On heating, aragonite changes to calcite, but at ordinary temperatures the two forms exist in apparent stable equilibrium. In the case of carbon the three modifications exist together under ordinary conditions of temperature and pressure, which is possibly due to the high inversion temperature. The same is probably true in the case of titanic acid and many others.

One Component System — Sulphur

The *p-t* diagram for sulphur is represented in Fig. 36. Sulphur exists in two solid crystalline forms, the rhombic, stable below 95.5°, and the monoclinic, the stable form, between 95.5° and 120°.

This figure will probably be more readily understood if it is redrawn, first drawing the *p-t* diagram for rhombic sulphur and then drawing the *p-t* diagram for monoclinic sulphur superposed upon this with the melting point of monoclinic sulphur (120°) located upon the vapor pressure curve for rhombic sulphur.

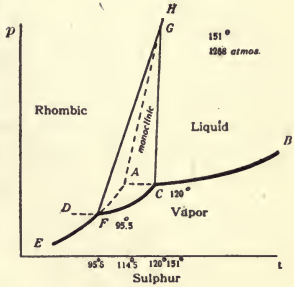


Fig. 36.

Applying the phase rule to the various systems represented by the areas, lines, and points as we did in the case of the *p-t* diagram for water we would have:

I. Fields or areas. Here we have one phase. Then from the Phase Rule, $N - P + 2 = F$, substituting, we have $1 - 1 + 2 = 2$. Therefore the areas represent *divariant systems.* There are four of these:

1. Area under line *EFCB* — sulphur vapor
2. Area to the right of *BCGH* — liquid sulphur
3. Area to left of *EFGH* — rhombic sulphur
4. Area of the triangle *GFC* — monoclinic sulphur

II. Curves. According to the Phase Rule we have, $1 - 2 + 2 = 1$, therefore *monovariant systems:*

1. Curve *EF* — rhombic-vapor
2. Curve *FC* — monoclinic-vapor
3. Curve *CB* — liquid-vapor
4. Curve *CG* — monoclinic-liquid
5. Curve *GH* — rhombic-liquid
6. Curve *FG* — rhombic-monoclinic

III. At the intersection of some of these curves we have three phases in equilibrium, and according to the Phase Rule we have $1 - 3 + 2 = 0$; therefore *nonvariant systems.* These are called *triple* points.

1. Point *F* — rhombic-monoclinic-vapor
2. Point *C* — monoclinic-liquid-vapor

3. Point G — rhombic-liquid-monoclinic

4. Point A — rhombic-monoclinic-vapor is a condition of labile equilibrium and is not readily realized.

The intersection of the two sublimation curves at F represents the transition point 95.5° at which rhombic and monoclinic sulphur are in equilibrium. Below this temperature rhombic sulphur has the lower vapor pressure and is the stable form, while above this temperature monoclinic sulphur is the stable form.

CHAPTER XVIII

SOLUTION OF SOLIDS IN LIQUIDS — I

THE solubility of a solid in a liquid depends upon the nature of the solvent as well as upon the solute. The solubility is also usually greatly affected by the temperature, but the pressure does not have such a marked effect.

In Figs. 37 and 38 we have represented the change in the solubility of solids in water with changes in temperature. These are termed temperature-concentration diagrams.

Generally speaking, the analogous compounds of the elements of the same family, if arranged in the order of their

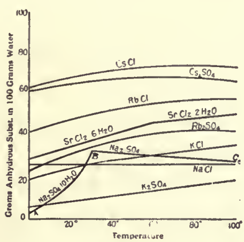


FIG. 37.

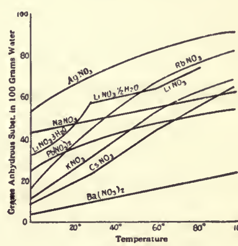


FIG. 38.

solubility, will be found to be in the increasing or the decreasing order of their atomic weights.

Cs, Rb, K, Na, Li, with decreasing order of atomic weights, have increasing solubility of their chlorides and nitrates. This does not hold absolutely.

These solubility curves are equilibrium curves and represent the equilibrium between the solid salt and the solution, which is saturated with respect to the solid phase separating. *A saturated solution is then a solution, at a specified temperature, in equilibrium with the solid phase.*

If we have two curves, as in Fig. 37, *AB* must represent the solubility of one chemical individual and *BC* that of another. That is, along the line *AB* a different solid phase separates than along the line *BC*. Below the curve *AB* we have unsaturated solutions, and on the curve, saturated, and above, supersaturated solutions. In all solubility work we must consider what solid is in equilibrium with the solution, and since many salts separate with water of crystallization, we may have the same solubility at different temperatures. It must be remembered that a solution is saturated with respect to a particular substance only when it is in equilibrium with that particular substance at the specified temperature.

The solubility of organic substances, likewise, depends upon the solvent and the solute, that is, upon the chemical character of both. In water, almost all substances containing the hydroxyl group (OH) dissolve more or less readily, *e.g.* the alcohols. In the case of organic acids, the solubility of the members of a homologous series decreases as the carbon content increases (*e.g.* formic, acetic, propionic, butyric). The solubility of the higher members of the series is small. Benzene, C_6H_6, is insoluble in water; phenol, C_6H_5OH, is soluble to the extent of about two per cent in water; while dihydric phenols, $C_6H_4(OH)_2$, are very soluble, and trihydric phenols, $C_6H_3(OH)_3$, are miscible in all proportions with water. Following the analogy, practically all alcohols are soluble in alcohol and all acids in acetic acid, all hydrocarbons in benzene, etc. An effort has been made by Carnelly and Thomson (*Jour. Chem. Soc.* *53*, 782 (1888)) to formulate some rules for the solubility of substances, and they make the following general statements:

1. That for any series of isomeric organic compounds the order of solubility is the same as the order of fusibility: the most fusible is the most soluble. Taking all solvents into account, 1755 out of 1778 cases hold.

2. In any series of isomeric acids not only is the order of solubility of the acids themselves the same as the order of fusibility, but the same order of solubility extends to all the salts of the second acids, so that the salts of the more soluble and more fusible acids are also more easily soluble than the corresponding salts of the less fusible and less soluble acids. Five exceptions out of 143 cases were found.

3. For any series of isomeric compounds the order of solubility is the same no matter what may be the nature of the solvent. No exception to this was found out of 666 cases.

4. The ratio of the solubilities of the two isomerides in any given solvent is very nearly constant, and is therefore independent of the nature of the solvent.

Pitch of Solubility Curve. — In the pitch of the solubility curve one has some criterion as to the true heat of solution of the particular substance. By inspecting a solubility curve the sign of the heat effect involved in the solution of the substance can be ascertained. If the substance dissolves with an absorption of heat, it will dissolve in greater quantity as the temperature is increased. Most inorganic salts dissolve in water with absorption of heat, and their solubility increases with an increase in the temperature. Examples are NH_4NO_3 and NH_4CNS. A number of salts dissolve with the evolution of heat, and their solubility decreases with increase in temperature; examples are most anhydrous sulphates, calcium isobutyrate, etc. We have a large number of salts, intermediate between these two classes, which dissolve with practically no heat effect, and the solubility of which is nearly constant for wide ranges of temperature. Common salt, NaCl, is an example of this class.

We must not fail to distinguish between the heat of solution usually determined in thermo-chemistry and the true heat of solution, or perhaps it had better be called the *heat of precipitation*, which has the opposite sign. By heat of solution or heat of precipitation we mean the heat effect when the solute is added to an almost saturated solution. The heat of solution in the thermo-chemical sense is the heat effect when the solute is dissolved in a large amount of water and is very much more easily measured than the heat of precipitation. Calcium isobutyrate below 80° dissolves in a large quantity of water with evolution of heat, in a little water with absorption of heat. Cupric chloride dissolves in a large amount of water with evolution of heat, and this heat effect decreases as the quantity of water used is decreased. In nearly saturated solutions the heat of solution changes sign and we have an absorption of heat.

It follows then that there must be some quantity of water in which a definite quantity of the salt will dissolve without either evolution or absorption of heat. This has been verified experimentally in the case of the hydrates of $FeCl_3$. The heat of precipitation of NaCl is very nearly zero, and consequently the change in the solubility of this salt with the increase in temperature is very slight. So one can tell very readily the sign of the heat effect from the solubility curves, providing they are continuous curves. But if a curve has a break in it at some point, a discontinuity, we know that some change has taken place, — probably in the phases in contact with the solution. Hence any such sharp discontinuity will lead us to suspect that there is a change in the phase relations. As we have a number of such cases coming under the head of hydrates we shall defer their treatment.

Theorem of Le Chatelier

We have seen that the results of the determinations of the effect of pressure on the fusion point of ice show that the temperatures at which the solid and liquid are in equilibrium are below the triple point. Ice has a lower density than liquid water, showing that the most dense phase of water is liquid water, hence when the system is subjected to pressure it will tend to compensate for this external pressure by readjusting itself so as to occupy a smaller volume, and if we have ice present this increased pressure will result in liquefying the ice, and the system will occupy a smaller volume. If, however, the temperature at which the solid and liquid are in equilibrium is above the temperature of the triple point, the substance has a greater density in the solid than in the liquid state, and increased pressure will tend to cause the system to pass into the solid state which is the most dense. For substances in general, the solid is the most dense phase. Water is one of the few exceptions to this general rule.

In the case of benzene the most dense phase is the solid. Hence an increase in the pressure will cause the freezing point to rise, and the fusion curve will slant away from the pressure axis toward the right. If benzene is subjected to 3742.7 mm. pressure, the melting point will be raised 0.143°.

This fact, that by means of an increase in pressure the most dense phase of the substance tends to form, represents one of the most fundamental laws. This law has its counterpart in the Law of Motion, that action and reaction are equal and in the opposite direction. This is known in chemistry as the *Theorem of Le Chatelier* and may be expressed as follows: "Any change in the factors of equilibrium from outside is followed by an inverse change inside the system;" *i.e.* there is a change in the factors of equilibrium tending to restore equilibrium.

Hence by increasing the external pressure on a system there would be an increase of that component or phase occupying the least volume; or if heat is added, we have an increase of that component or phase which involves an absorption of heat. Hence a system in equilibrium tends to return to equilibrium by eliminating the disturbing element. Ammonium chloride dissolves with expansion, and the solubility is diminished about one per cent by increasing the pressure to 160 atmospheres. Copper sulphate dissolves with contraction, and the solubility increases 3.2 per cent on increasing the pressure to 60 atmospheres. Sodium sulphate with 10 molecules of water of crystallization dissolves with absorption of heat, hence the solubility increases with an increase in temperature. All of these facts are in accord with the Theorem of Le Chatelier.

If a system is in equilibrium at a specified temperature and heat be applied, there will be a tendency to compensate for this heat added to the system by a readjustment within the system either through a physical adjustment, such as increase of the volume if the pressure remains constant, or by an increase of pressure in order to maintain the volume constant. Or if this addition of heat results in the compensating change through a chemical reaction, such as the formation of ozone from oxygen, or in the preparation of nitric oxide, carbon bisulphide, acetylene, etc., or the dissociation of calcium carbonate, we shall have either an absorption of heat or an evolution of heat, depending upon the particular type of reaction that is taking place under our specified conditions. In most cases of dissociation the increase in dissociation is associated with an absorption of heat, that is, it is an endothermic reaction. For as heat is applied the reaction proceeds, and being accompanied by an absorption of heat, the heat from the outside of the system has to be applied to maintain the system at a constant temperature, so that a rise in temperature favors the formation of the products of the reaction. Ozone is prepared according to the equation $3\,O_2 = 2\,O_3$, and the reaction is accompanied by an absorption of heat. It is an endothermic reaction, and therefore the percentage of ozone formed increases with the rise in temperature. If the reaction evolves heat it is said to be exothermic and takes place best with a decrease in temperature.

The inversion temperature at which the rhombohedral form of NH_4NO_3 can be transformed into the β-rhombic form can be changed from 85.45° under a pressure of one atmosphere to 82.29° by increasing the pressure to 250 atmospheres.

The following geological application of the Theorem of Le Chatelier worked out by Van Hise is a marked confirmation of this principle. In the outer zone of the earth's crust there takes place the metamorphic changes of the minerals, such as the alteration of the silicates by means of hydration, carbonation, and desilicification, which are accompanied by a liberation of heat, decrease in the density, and an increase in the volume. This region is known as the Zone of Katamorphism, and in it the average specific gravity of the minerals is 2.948. In the inner zone of metamorphism, a few thousand feet from the surface of the earth, where there is an increased pressure due to the overlying rocks, there is also a much higher temperature than in the outer zone of metamorphism. This inner region is known as the Zone of Anamorphism, and we have the alteration of the minerals due to dehydration, decarbonation, and silicification, which are accompanied by an absorption of heat and condensation of volume, which are the typical changes. The average specific gravity of the minerals in the Zone of Anamorphism is 3.488, which is about 18 per cent higher than that of the minerals in the Zone of Katamorphism. This is a fair approximation and shows that a given mass of material occupies a much larger volume in the Zone of Katamorphism than in the Zone of Anamorphism.

A few special examples will serve to illustrate this. The change of hematite into limonite may be represented by the equation $2\,Fe_2O_3 + 3\,H_2O = 2\,Fe_2O_3 \cdot 3\,H_2O$. This reaction takes place in the Zone of Katamorphism and is one of hydration. The specific gravity of hematite is 5.225 and of limonite 3.80, which change represents an increase in volume of 60.7 per cent. One of the most common and best known alterations is hematite into siderite. This may be represented as follows:

$$Fe_2O_3 + 2H_2S + CO_2 = FeS_2 + FeCO_3 + 2\,H_2O + k \text{ cal.}$$

If the products of alteration are pyrite (isometric, sp.gr. 5.025) and siderite (sp.gr. 3.855), the increase in volume is 76 per cent; but if marcasite (orthorhombic, sp.gr. 4.875) is formed instead of pyrite, the increase in volume of marcasite and siderite over the hematite is 78.7 per cent. The most marked case known in which minerals are concerned is the alteration of magnetite into siderite. The equation $Fe_3O_4 + CO + 2\,CO_2 = 3\,FeCO_3$ represents the alteration which gives a change of specific gravity from 5.74 for magnetite to 2.83 for siderite, which represents the enormous increase in volume of 101 per cent. These changes all take place with the *liberation of heat, expansion of volume, and decrease in symmetry.*

As a typical example of deep-seated reactions under great pressure and high temperature, the change of calcite into wollastonite is one that is well known, $CaCO_3 + SiO_2 = CaSiO_3 + CO_2 - k$ cal. Here we have a change in specific gravity from 2.713 for calcite and 2.655 for SiO_2 to 2.85 for wollastonite, which represents a decrease in volume of 31.5 per cent provided the silica is solid and the carbon dioxide escapes. We have, as in all other deep-seated reactions, an absorption of heat and condensation of volume as the typical changes in the Zone of Anamorphism.

The same principles are clearly illustrated in the case of the alteration of silicates, which are brought up by means of some orogenic movement to the surface of the earth or near to it. This alteration of the silicates by hydration, carbonation, and desilicification is attended with the concomitant liberation of heat, a decrease in the specific gravity, and a marked increase in the volume. The alteration of garnets into different combinations of the following minerals is well known: serpentine, talc, chlorite, epidote, zoisite, magnesite, and gibbsite.

The following equation, which is typical of these transformations, will suffice to illustrate the marked change which amounts in this case to an increase in volume of 76 per cent:

$$4\,Mg_3Al_2Si_3O_{12} + 15\,H_2O + 3\,CO_2$$

pyrope
sp.gr. 3.725

$$= 3\,H_2Mg_3Si_4O_{12} + 3\,MgCO_3 + 8\,Al(OH)_3 + k \text{ cal.}$$

talc	magnesite	gibbsite
sp.gr. 2.75	sp.gr. 3.06	sp.gr. 2.35

CHAPTER XIX

SOLUTION OF SOLIDS IN LIQUIDS—II

The Solvent and Solute Crystallize Together as a Mixture of the Pure Components

In the two component systems in which we have a liquid solvent, and a solid solute, we assume that the vapor pressure of the solid is so small that it is negligible, so that in the systems we are to consider one of the components is non-volatile and one volatile. There are three general types of such systems:

Type I. The solvent and solute may crystallize together as a mixture of the pure components.

Type II. The solvent and solute crystallize in accordance with the Laws of Definite and Multiple Proportions.

Type III. The solvent and solute crystallize together not in accordance with the Laws of Definite and Multiple Proportions, but as solid solute dissolved in a solid solvent in varying proportions, within certain limits.

Type I—System Water and Sodium Chloride

At the intersection of the vapor pressure and sublimation curves for pure water, the solid, liquid, and vapor phases are in equilibrium, and we designate this the *fusion point* of ice, or the transition point. As these phases are in equilibrium under the pressure of the vapor of the system, it is a pressure of 4.6 mm. and at the temperature $+ 0.0075°$ C. The freezing point of liquids is the temperature at which the solid and liquid phases are in equilibrium under atmospheric pressure, which in the case of water would be under nearly one atmosphere pressure more than at the transition temperature. As an increase in pressure of one atmosphere lowers the melting point of ice 0.0076°, it is apparent that the fusion point, freezing point, and transition point may be considered the same. On the *p-t* diagram, Fig. 39, let us represent the one-component systems by the following dotted lines.

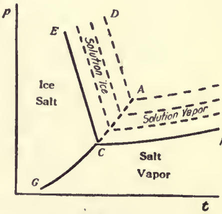


FIG. 39.

AB is the vapor pressure curve

AC is the sublimation curve

AD is the fusion curve

A is the triple point and represents the melting point of ice and the freezing point of water.

If a second component, solid salt, NaCl, be added to water, the vapor pressure of the solution produced is lower than the vapor pressure of the pure solvent water, and the amount of the lowering of the vapor pressure is proportional to the concentration. By adding successive amounts of NaCl the vapor pressures of the solutions would be represented by vapor pressure curves parallel to *AB*, but successively lower until we would reach a concentration representing the maximum amounts of salt that are soluble at the different temperatures, when we would have saturated solutions, the vapor pressures of which we represent by *CF*. This represents the maximum lowering of the vapor pressure of the pure water. If these vapor pressure curves are projected until they intersect the freezing point curve, we have the point *A*, the intersection of the vapor pressure curve and the sublimation curve, passing down successively to the point *C*, its lowest limit. Similarly, the curve *AD*, the fusion curve, would pass over the space to the left of its original position and take up as its final position, *CE*. *A*, the freezing point of pure water, has been lowered from the temperature 0° to the temperature t_c, and the distance along the temperature axis represents the maximum lowering of the freezing point.

The degree of variance of this two-component system may be obtained by applying the Phase Rule as follows:

I. Areas. $(N - P + 2 = F)$, $2 - 2 + 2 = 2$ ∴ Divariant systems:

1. Salt-vapor below *GCF* and above *t*-axis.
2. Solution-vapor between *BACF*.
3. Solution-ice between *DACE*.
4. Ice-salt between *ECG* and *p*-axis.

II. Curves. $(N - P + 2 = F)$, $2 - 3 + 2 = 1$ ∴ Monovariant systems:

1. *CF* Solution-vapor-salt.
2. *CE* Solution-ice-salt.
3. *CG* Ice-salt-vapor.
4. *CA* Solution-ice-vapor.

III. Point *C*. $(N - P + 2 = F)$, $2 - 4 + 2 = 0$ ∴ Nonvariant system.

At point *C* the four phases, solution-salt ice-vapor, are in equilibrium. This is known as *a Quadruple Point.*

If a body in the liquid state be allowed to cool without change of state, and measurement of the temperature be made at different times, and these results plotted on a temperature-time axis, the curve has a regular form — a logarithmic curve when the cooling takes place for constant temperature surroundings. But if a change of state occurs, there is a decided change in the shape of the curve. In all cases observed the passage of a liquid to a solid is accompanied by the evolution of heat. This heat liberated compensates for loss of heat by radiation and maintains the temperature constant, the solid separating and the process continuing until the whole of the liquid has changed to the solid state, when the temperature changes become regular again.

In Fig. 40 we have an illustration of the continuous cooling curve without change of state, while Fig. 41 illustrates the cooling curves of a number of pure substances. These show a marked break at the temperature of the melting point of

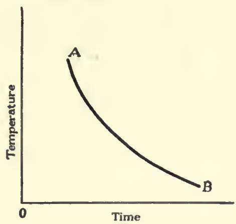


FIG. 40.

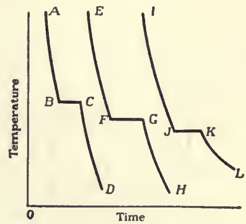


FIG. 41.

the substance; above and below this the temperature falls regularly, but at this point the temperature remains constant until all of the substance has solidified.

The cooling curves for two component systems, such as solutions of sodium chloride in water, differ from that of a pure substance. For when solidification begins, either of the two components may separate, depending upon the concentration of the solution. At the point of solidification we have a marked break in the cooling curve, the separation of the pure component, which results in a change in the concentration of the solution with a lowering of the freezing point. Hence, on a *t-time* diagram for a solution of the concentration of ten per cent of sodium chloride, we should have the regular cooling of the solution, as represented by *ab* in Fig. 42, until

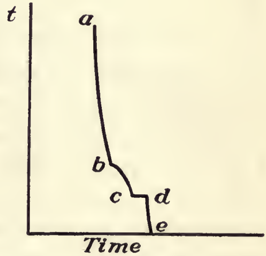


FIG. 42.

at the point *b*, the solid water (ice) begins to separate, and we have a change in the slope of the cooling curve. This separation of the ice continues until the point *c* is reached, when the remainder of the solution solidifies completely.

During the time indicated by *cd*, the temperature remains constant. On further cooling a regular cooling curve is obtained, as represented by *de*.

By this method the cooling curves of solutions over the whole range of concentrations desired may be obtained. The temperature, *b*, at which these solutions begin to solidify has thus been determined. So if these values of the freezing points are plotted on a temperature-concentration diagram against their respective concentrations and the points connected, we obtain the curve represented by a dotted line, the freezing or solidification curve. If on this diagram the cooling curves be superposed so that the freezing points, *b*, are placed on the freezing curve at the point corresponding to their proper concentration, we have the diagram represented by Fig. 43.

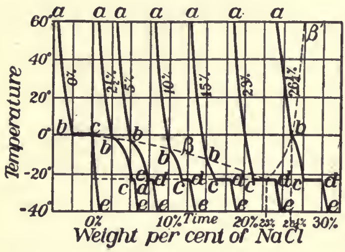


FIG. 43.

The first curve at the left is the cooling curve for pure water, and we have the usual curve for a pure substance, with the break occurring at *b* when it begins to freeze, and the temperature remaining constant until the liquid has all disappeared (*bc*), when the cooling again becomes regular, as shown by the section *ce*. It will be noticed that the cooling curve for a solution containing 23 per cent of sodium chloride is exactly like this and is analogous to the cooling curve of a pure substance as shown in Fig. 41. That is, at the temperature designated t_c, the solidification begins, and the temperature remains constant until the whole mass has solidified. This takes the time indicated by *cd*. This freezing point is different from the freezing point of any of these solutions in so far as the solidification takes place at constant temperature, and the composition of the solid phase separating is the same as that of the solution from which it separates. This temperature is the lowest temperature at which any solution of these two components can exist. It is also the lowest melting point of any mixture of the two components. This temperature is called the *eutectic temperature;* the solid which separates the *eutectic* and the point C, Fig. 44, is called the *eutectic point*. When water is one of the components, this point is also termed the *cryohydric point*, the mixture the *cryohydrate*, and the temperature the *cryohydric temperature*.

For all solutions in which the concentration of the sodium chloride is less than that represented by the point C, the solid phase separating is pure water, while for all concentrations greater than C, the solid phase is pure sodium chloride.

The curve ACB, Fig. 44, represents the temperatures at which solutions of sodium chloride begin to solidify, that is, where the solid phase appears. This is an equilibrium curve, and since it is not a continuous curve, but composed of two branches, it must represent two different conditions of equilibrium, that is, along the curve AC pure water is the solid phase in equilibrium with the solution, and along the curve CB pure NaCl is the solid phase in equilibrium with the solution. The curve AC is termed the *Freezing Curve* and the curve CB the *Solubility Curve*, both of which are also *Solidification* or *Fusion Curves*. The Eutectic Point may also be defined as the intersection of two fusion curves (of a freezing curve and a solubility curve).

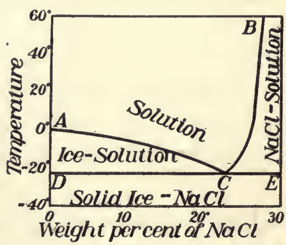


FIG. 44.

That the time required for the solidification of these different solutions is not the same, is shown by the different lengths of the horizontal sections cd, of the *t-time* curves.

This indicates that there are different quantities of the eutectic formed, and consequently the times required for solidification will be different, and we have, therefore, an indication of the relative quantities of the eutectic separated upon solidification of the solutions of different concentrations.

The area above the curve, *ACB*, on the temperature-concentration diagram, Fig. 44, represents solutions of sodium chloride in water; along the equilibrium curve *AC* solid ice separates; along the equilibrium curve *CB* solid NaCl, while at the intersection of these two curves at *C* a mixture of ice and salt separates, consisting of 22.43 per cent of sodium chloride. Connecting the points designated by *C*, we obtain the line *DCE* parallel to the concentration axis. This represents the lowest limit of solidification of all mixtures of the two components. In the area between this line and the freezing curve, *AC*, we have solution and ice, and in the area between *CB* and *CE* there exist solution and salt, while below *DCE* we have solid only existing, which consists of the two crystalline species, ice and salt.

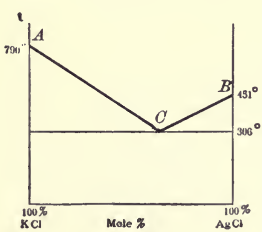


Fig. 45.

The mutual solubility of AgCl and KCl is represented on the temperature-concentration diagram, Fig. 45. The melting point of KCl is 790°. As AgCl is added, the freezing point is lowered, and we obtain *AC* as the equilibrium curve, along which KCl is the solid phase separating, and *AC* is a fusion curve. Similarly, as KCl is added to molten AgCl, the melting point of which is 451°, represented by *B*, the freezing point is lowered, and the curve *CB* represents the freezing points of solutions of KCl in AgCl. The solid phase separating is AgCl, and this is in equilibrium with the solution along the fusion curve *CB*. At the intersection *C* of the two fusion curves, both KCl and AgCl separate in the proportion of 70 per cent of AgCl and 30 per cent of KCl. The mixture of this concentration has the lowest fusion point of all mixtures of these two compounds and is therefore the eutectic, and the eutectic temperature is 306°.

The fusion curves of the alloys of lead and antimony, which show the existence of a eutectic, are represented on the temperature-concentration diagram in Fig. 46. If a melt of the composition represented by *m* be selected and cooled, pure Pb will separate when the curve *AC* is reached and the composition of the liquid will become richer in Sb. On further cooling, the fusion curve will follow the line *AC* until sufficient Pb has been removed to bring the concentration to that indicated by *C*, the eutectic, when the mass will solidify without change of temperature. The same is true of mixtures containing more Sb than indicated by the concentration *C*. When these molten mixtures are cooled, the pure metal Sb separates until the concentration *C* is reached, when the mass solidifies like a pure substance without change of temperature. It is evident that no alloy of these two metals has a melting point lower than 246°, the eutectic temperature, which is represented by the horizontal line *DCE* through the eutectic point *C*. This line also represents the temperature at which any alloy of Pb-Sb would begin to melt.

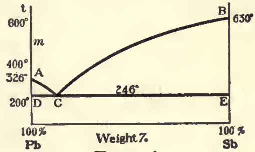


FIG. 46.

The concentration-temperature diagram is divided into the following fields of concentration by the fusion curves and the eutectic horizontal:

1. Above the fusion curve *ACB* is the liquid or melt.

2. In area *ACD*, crystallized Pb is in equilibrium with the liquid.

3. In area *BCE*, crystallized Sb is in equilibrium with the liquid.

4. In the field below *DCE* the homogeneous crystalline mass, composed of the two crystalline solids Pb and Sb,

exists. This field may be divided into two areas by a line parallel to the temperature axis through C. These have differences in structure, recognized microscopically. Hence, the eutectic is regarded as an individual structural element in all metallurgical investigations.

In many cases the fusion curves do not show a marked eutectic point such as we have just been considering, but we have a fusion curve that shows that the fusion point of certain mixtures lies much below the melting point of the lower melting substance, *i.e.* they manifest a minimum freezing point. The temperature-concentration diagram for mixtures of K_2CO_3 and Na_2CO_3 employed in analytical work is given in Fig. 47. A mixture of K_2CO_3 and Na_2CO_3 in about molecular proportions has the lowest fusion point, about 700°, and this is employed in fusions in preference to the pure components, as the reaction with the refractory substances can be carried on at a much lower temperature.

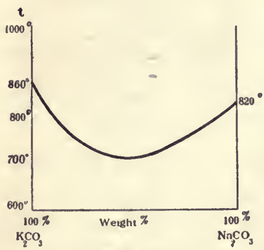


FIG. 47.

In the preparation of explosive mixtures use is made of this same principle in filling shells. It is desirable to introduce the material and handle it in liquid condition. Different explosives are mixed so as to produce a mixture that has a low melting point, thus preventing obnoxious fumes, loss of material, and reducing the hazard to the minimum. In Table XXXVI are given a few explosives with their melting points and also the melting point of their mixture.

The existence of eutectic mixtures is a very common phenomenon. Using water as one of the components, the eutectic (cryohydric) point for a great many substances has been determined, and in Table XXXVII is given a list of some of these, with the eutectic (cryohydric) temperature and the composition of the eutectic (cryohydrate).

TABLE XXXVI

Substance	Melting Point	Melting Point of Mixture
Trinitrophenol	122	49
Nitronaphthalene	61	
Trinitrophenol	122	47
Dinitrotoluene	71	
Trinitrophenol	122	70
Trinitrocresol	107	

TABLE XXXVII

Salt	Eutectic (Cryohydric) Temperature	Per Cent Anhydrous Salt in the Eutectic (Cryohydrate)
Sodium bromide	− 28.0°	40.3
Sodium iodide	− 31.5	39.0
Sodium chloride	− 21.2	22.42
Sodium nitrate	− 18.5	36.9
Potassium iodide	− 23.0	52.2
Potassium nitrate	− 3.0	11.2
Potassium bromide	− 11.5	31.2
Potassium chloride	− 10.64	19.5
Ammonium sulphate	− 19.05	38.4
Ammonium chloride	− 16.00	19.5

From Fig. 44 it is apparent that at the eutectic (cryohydric) temperature for the system NaCl and water, the four phases — salt, ice, solution, and vapor — are in equilibrium. We have a nonvariant system. If we add heat to this system, we obtain different conditions, depending on whether ice is in excess or whether salt is in excess.

1. With ice in excess, on heating, the ice will melt, and the salt will all go into solution. We then have the monovariant system, ice-solution-vapor.

2. With salt in excess, on heating, the ice will melt, the salt will dissolve, and as more heat is added the ice will all disappear and we have the monovariant system salt-solution-vapor.

Ice and salt are not in equilibrium above the cryohydric temperature. If they are mixed above this temperature the ice will melt, and depending upon the relative quantities of salt and ice, we shall get one of the two monovariant systems, represented by CE or CF.

When ice melts heat is absorbed, and when a salt dissolves heat may be either absorbed, evolved, or neither absorbed nor evolved. This can be readily ascertained from the slope of the solubility curve. So that in using a mixture for freezing purposes, the object being to remove heat from the substance we desire to cool, it is evident that the removal of heat is going to be accomplished by (*a*) the melting of the ice and (*b*) the solution of the salt.

If the salt absorbs heat, then the two factors (*a*) and (*b*) are going to work together; but if the salt evolves heat, they will oppose each other; and if the heat of solution of the salt is zero, the whole cooling effect is due solely to the melting of the ice. Such is the case when common salt, NaCl, and ice are used.

If we have a system salt-ice-vapor above the cryohydric temperature, it is not in equilibrium and so will tend to pass into a state of stable equilibrium. The temperature will fall until (1) one or both of the solids disappear or (2) until the cryohydric temperature is reached. This is the lowest temperature attainable at atmospheric pressure with a given freezing mixture, for we then have equilibrium between the solids at and below this temperature. The temperature reached in the laboratory is not always the cryohydric temperature, for the solution that is being continually formed has to be cooled with the rest of the system. There results a temperature at which the heat absorbed by the solution being formed, in unit time, is just sufficient to keep the mass of solution present at a constant temperature. Attaining the minimum temperature, then, depends on (1) the initial temperature, (2) the rate of radiation, (3) quantities of salt and ice used, and (4) the thoroughness of the mixture, since the speed of reaction is proportional to the surfaces of the solids. When the ice is in large pieces, less heat will be absorbed in unit time. Therefore, the equilibrium will be reached at a higher temperature than if the pieces are small.

In order to obtain a low temperature by means of a freezing mixture the following precautions should be observed:

1. Select a mixture with a low cryohydric temperature.

2. Select a mixture such that the heat absorbed per gram of solution formed is as great as possible. This is realized if the solubility increases rapidly with the temperature. (NaCl is not ideal, as heat absorbed is nearly zero, hence the heat absorbed is due practically to the melting of the ice.)

3. Take substances in proportion indicated by the cryohydrate.

4. Remove solution as fast as formed.

5. Use fine material to increase speed of reaction, thus producing maximum absorption in unit time.

CHAPTER XX

SOLUTION OF SOLIDS IN LIQUIDS — III

SOLVENT AND SOLUTE CRYSTALLIZE IN ACCORDANCE WITH THE LAWS OF DEFINITE AND MULTIPLE PROPORTIONS

TYPE II

MANY substances on crystallizing from aqueous solutions are found to contain a considerable amount of the solvent, which is always in a definite ratio to the solute or some multiple of this ratio. The solute is said to crystallize with water of crystallization, *e.g.* $CuSO_4 \cdot 5\,H_2O$; $Na_2SO_4 \cdot 10\,H_2O$, etc. Other solvents than water act in a similar manner, and we may have alcohol of crystallization, benzene, acetone, etc. The compounds containing water of crystallization are known as *hydrates* and have been very extensively studied, while those in which other liquids appear as the solvent have also been studied. It is possible for us to take up the consideration of only a few of the hydrates.

Sodium Sulphate and Water. — From the solubility determinations of sodium sulphate in water, the data of which are represented diagrammatically on the concentration-temperature diagram, Fig. 48, it is apparent that the curves represent the equilibrium between different solid phases and the solution.

The abscissas are the per cent of sodium sulphate, the ordinates the temperature, and the system is supposed to be under its own pressure.

Starting with water at zero degrees, the freezing points of the solutions of increasing concentration are represented by the curve AB, familiarly known as the freezing-point curve. At B, the cryohydric point, the hydrate $Na_2SO_4 \cdot 10\,H_2O$ begins to crystallize out, and we have the inversion point at $-1.2°$ and a concentration of about 40 grams per 100 grams of water. The curve BC represents the solubility curve for the decahydrate and is an equilibrium curve between the solid and the solution. On heating there is a decrease in the solubility, as is represented by the curve CD, which is an equilibrium curve between the anhydrous solid and the solution. The intersection of these two solubility curves at C indicates another transition point, and we have the two solid phases in equilibrium with the solution and vapor. The temperature of this transition point is 32.5° (Richards, 32.379° hydrogen thermometer, 32.482° mercury thermometer) at a concentration of 49.8 grams. Hence, above this temperature the solid anhydrous salt is in equilibrium with the solution, and below, the hydrated salt with ten molecules of water of crystallization. The curve BCD is then not a continuous curve, but the solubility curve shows a break or discontinuity in direction, which is characteristic of the sulphates and indicates that entirely different phases are in equilibrium along the respective curves. The curve BC has not been realized very far beyond the inversion temperature C.

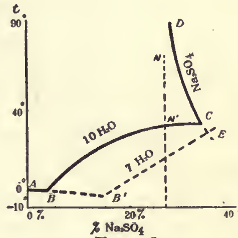


FIG. 48.

There is one other hydrate known, the heptahydrate, which can be very readily obtained in the presence of alcohol. but which also separates out of a solution of sodium sulphate which has been saturated at about 34° and allowed to cool below 17°, having it protected very carefully. The composition of these crystals which separate is $Na_2SO_4 \cdot 7\,H_2O$. The solubility curve for this solid is represented by EB', and its intersection with *DC* continued in the vicinity of 25° represents a labile nonvariant system and of course unstable with respect to $Na_2SO_4 \cdot 10\,H_2O$.

We stated that the solubility curve of the decahydrate had been carried out a little ways beyond the transition point. Above this point the solubility of the decahydrate is greater than that of the anhydrous salt, and so a solution which is saturated with the decahydrate would be supersaturated with respect to the anhydrous salt. Likewise, if we have a concentration and the temperature of a solution as represented by the point N, and this be cooled in a closed vessel, the changing state of the system will be represented by the vertical line NN'. At N' the solid phase decahydrate should appear. If, however, the solution be cooled carefully, it may be possible to get the temperature much below that indicated by N' and prolong the line considerably. The solution contains very much more salt than a saturated solution contains and is said to be *supersaturated*, for if the solid phase of $Na_2SO_4 \cdot 10\,H_2O$ be brought in contact with the solution, the amount of the salt in excess of that contained in a saturated solution at that temperature will be separated out. Hence, our definition of a saturated solution must contain the statement as to the temperature of the solution and the solid phase with which it is in equilibrium. It might be stated, however, that *any substance which is isomorphous with the solid phase will also produce the precipitation.*

This phenomenon of supersaturation is not confined to aqueous solutions, but it may be stated in general that those salts that separate out with water of crystallization form supersaturated solutions much more readily than those that separate in the anhydrous form. This is by no means universal, for many substances which separate in the anhydrous state form supersaturated solutions very readily. This is true for silver nitrate and sodium chlorate in aqueous solutions, while in the case of organic solvents this is very common. It is generally held that those salts that separate with water of crystallization form large crystals and form most easily on crystals already present, while salts that form supersaturated solutions with difficulty crystallize spontaneously in very small crystals.

Pressure-Temperature Diagram of Sodium Sulphate and Water. — The curves *AB*, *AC*, and *AM*, Fig. 49, represent the system for pure water. We saw that upon adding a solid solute to water the vapor pressure of the system was lowered. If Na_2SO_4 is added to water, the resulting solution will have a lower vapor pressure than the pure solvent under the same conditions of temperature. We shall then have the following systems:

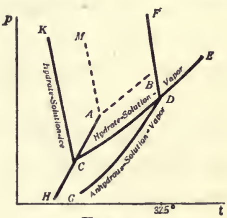


FIG. 49.

Curve *CD*, monovariant system — Hydrate-solution-vapor.

Curve *CA*, monovariant system — Ice-solution-vapor.

Curve *CK*, monovariant system — Hydrate-solution-ice.

Curve *CH*, monovariant system — Hydrate-ice-vapor.

Point *C*, cryohydric point, nonvariant system — Hydrate-ice-solution-vapor.

If under the conditions represented by *C*, the system is heated and the volume kept constant, the ice will disappear first and we shall have the system — solution-hydrate-vapor, which will increase in temperature with increased pressure, and the curve *CD* will represent the equilibrium of the system. At the point *D* the solid anhydrous phase appears, and there results the nonvariant system — anhydrous salt-hydrate-solution-vapor. This point *D* represents the inversion point and is the intersection of four curves *DE*, *DF*, *DC*, and *DG* at the temperature 32.5° and a pressure 30.8 mm. of mercury, representing the four possible monovariant systems:

DE — Anhydrous salt-solution-vapor.
DF — Hydrate-anhydrous salt-solution.
DC — Hydrate-solution-vapor.
DG — Anhydrous salt-solution-vapor.

The vapor pressure curve for anhydrous salt *DG* is below that for the hydrate *DC*, but the stable system below 32.5°, *D*, is the hydrate-solution-vapor, and the labile system is anhydrous salt-solution-vapor. But this is the reverse of what we considered under the sulphur system, where we saw that the stable system was that one which had the lower vapor pressure. The more stable system is the one with the lesser concentration and therefore greater vapor pressure. This is a general condition, as there are two forces acting: (1) the tendency of the vapor to distill from the higher to the lower pressure and (2) the tendency of the solute to precipitate from the more concentrated solutions. The latter is the stronger, but either would bring about equilibrium. This condition depends upon the fact that the less stable form is the more soluble, and as the lowering of the vapor pressure is proportional to the concentration, the result is a much lower vapor pressure for the labile solutions (Bancroft's *Phase Rule*).

Solubility Curves of Hydrates Which Do Not Have a Definite Melting Point. — The following diagrams, Figs. 50, 51, and 52, illustrate the types of solubility curves obtained for salts that crystallize with water of crystallization.

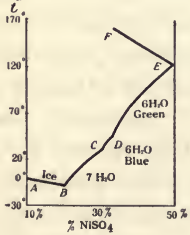


FIG. 50.

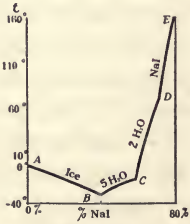


FIG. 51.

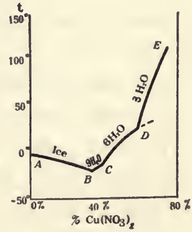


FIG. 52.

Each solubility curve is made up of a number of individual curves, each of which represents the equilibrium between some specific hydrate and solution, and there will be as many different solid phases separating as there are segments. Hence, in determining the solubility of a substance *it is necessary to know the composition of the solid phase in equilibrium with the solution* as well as the temperature at which this equilibrium is established. To establish thoroughly the point of equilibrium it is best to approach it from both a higher and a lower temperature, or by establishing the rate at which it is attained. A saturated solution is a solution in equilibrium with the solid phase (*i.e.* with the pure solute) at a specified temperature. In these cases the pure solutes are the hydrates and the anhydrous salt.

Solubility Curves of Hydrates, Some of Which May Have a Definite Melting Point. — The following solubility curves, Figs. 53, 54, and 55, represent the equilibrium curves of substances, some of the hydrates of which melt without change of temperature and form a liquid of the same composition as that of the crystalline solid hydrate.

It will be noticed that the curves starting from the left of the figure represent first the lowering of the freezing point of water as the concentration of the solute is increased. This is usually designated a freezing-point curve, and it is a cooling curve for the solvent which separates along this curve, as solutions of concentrations up to that represented by B are cooled. It also represents the temperatures at which mixtures of these concentrations, when in the solid state, will have to be heated before they begin to melt; they may also be termed fusion curves. We reach a minimum value for the temperature at which the mixture of the compounds can exist in the liquid state. This temperature is the eutectic temperature, or when water is the solvent, it is termed the cryohydric temperature.

The curve BCD is termed the solubility curve. This is an equilibrium curve, for all along this curve the same solid phase (a hydrate) is in equilibrium with the solutions of various concentrations. The temperature at which this hydrate is in equilibrium with the saturated solution increases with increased concentration until a maximum value, *C*, is reached, when the solid hydrate is of the same concentration as that of the solution from which it separates. In other words, if we had a solution of this specific concentration and cooled it, at the temperature represented by this maximum value the whole solution would solidify without change in temperature, or if we had a solid hydrate of this concentration, it would melt at this temperature without change in temperature, *i.e.* it has a constant melting point, and the solution has a constant freezing point. These are characteristics of pure chemical compounds, and therefore we conclude that such points as *C* represent definite chemical compounds, which in these cases are termed hydrates.

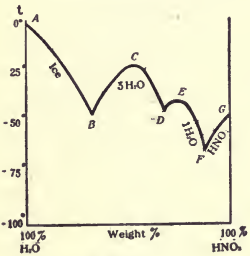


FIG. 53.

The remainder of the curve *CD* shows a decrease in the temperature at which this solid hydrate is in equilibrium with solutions of increasing concentration. This decrease continues until the point *D* is reached, where our solubility curve is intersected by another so-called solubility curve, *DEF*, along which another solid phase of a different hydrate separates and is in equilibrium with a series of still more concentrated solutions. It will be noticed that this portion of the curve is practically a repetition of what we have just explained: the point *E* represents the maximum temperature at which this solid hydrate is in equilibrium with the solution and is the melting point of the hydrate, and melting points of this character are termed *congruent melting points*.

The *retroflex* portion of the curve EF, similar to CD, is really similar to AB, the freezing-point curve, for in all of these cases we have a case of the lowering of the freezing point of the solute by the addition of a second component. This second component in all cases is the anhydrous salt, but the solvent in the first case is pure water, the freezing point of which is A; in the second case the solvent is the hydrate of the composition represented by C, the freezing point of which is the temperature corresponding to C; while the solvent in the third case is the hydrate of the composition E, the freezing point corresponding to the temperature E. It is then apparent that these curves, which we term solubility curves (portions of them at least), are readily recognized as freezing-point curves or fusion curves. It is also apparent that if these values were plotted with the two components interchanged, the portions of the curves we have been designating solubility curves become the portions recognized as the freezing-point curves and the freezing-point curves become the solubility curves. We are, therefore, justified in using the terms fusion curves, solubility curves, and freezing-point curves as synonymous, and subsequently we shall do so. It is evident that the intersection of a fusion and a solubility curve is the eutectic or cryohydric point, or this point could be defined as the point of intersection of two fusion curves.

If at any temperatures between C and D a horizontal line be drawn, it will intersect the solubility curve BCD in two points, which indicates that for the same temperatures there are two solubilities of the hydrate of the composition represented by C. In the weaker solution we have a hydrate separating which is richer in the solute component than the solution, while in the other case the concentration of the solution is richer than the hydrate in the solute component. The hydrate can exist in equilibrium with two solutions of very different concentrations at the same temperature.

In the diagram, Fig. 54, representing the solubility curve of $FeCl_3$ in water, let us draw the line *XY* representing a temperature of about 31.2°. If a solution of ferric chloride is evaporated at this constant temperature, the concentration will increase until the solubility curve *BC* is intersected, when $FeCl_3 \cdot 12\,H_2O$ will crystallize out. This crystallization will continue until all the solution will have disappeared. Liquefaction occurs again where *CD* is intersected and at the concentration on *DF* above *D* solidification again occurs. On further evaporation liquefaction again occurs and at the intersection of *FG* it again solidifies and remains solid. Hence we have successively solution; solidification to dodecahydrate; liquefaction; solidification to heptahydrate; liquefaction; solidification to pentahydrate.

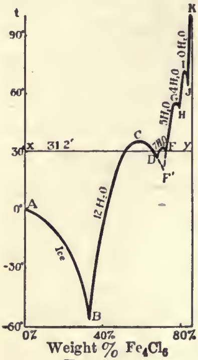


FIG. 54.

In the case of the system H_2O-SO_3, Fig. 55, we have a marked example of the formation of hydrates. Here we have five as represented by the congruent melting points *C*, *E*, *H*, *J*, and *L*.

This type of solubility curve, which exhibits a congruent melting point, is common in aqueous solutions, and when other substances are employed as the solvent, as mixtures of organic substances and in alloys, we find it a very common type of solubility curve. This fact in the latter cases is used as a basis for the establishment of the existence of chemical compounds.

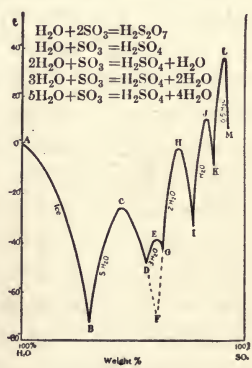


FIG. 55.

Vapor Pressure of Hydrates. — The dehydration of crystalline hydrates is analogous to the dissociation of other substances such as ammonium chloride, which on dissociation gives $NH_4Cl \rightleftarrows NH_3 + HCl$. Similarly we have $Cu(NO_3)_2 \cdot 6\,H_2O \rightleftarrows Cu(NO_3)_2 \cdot 3\,H_2O + 3\,H_2O$; but as we have a two-component system, salt-water, in three phases, we have a monovariant system, and at each specified temperature there will be a certain definite corresponding vapor pressure which is independent of the masses of the phases present.

Hydrated salts give off their water of crystallization as vapor *in vacuo*. This is also true when the substance is heated at other pressures, and for a definite temperature there is a certain pressure of the vapor which is independent of the water given off as vapor. This law has been very thoroughly established, and the vapor pressures of many hydrated salts have been measured. The vapor pressure in millimeters of mercury of a number of hydrates is given in Table XXXVIII, which shows the variation of the pressure with the temperature.

TABLE XXXVIII

Salt	Temperature	Pressure mm. Hg.
$Na_2HPO_4 \cdot 10\,H_2O$	17.28°	10.531
$Na_2HPO_4 \cdot 10\,H_2O$	27.	21.575
$ZnSO_4 \cdot 7\,H_2O$	18.	8.406
$ZnSO_4 \cdot 7\,H_2O$	29.95	22.389
$SrCl_2 \cdot 6\,H_2O$	19.7	5.61
$SrCl_2 \cdot 6\,H_2O$	37.55	19.86
$BaCl_2 \cdot 2\,H_2O$	18.25	2.97
$BaCl_2 \cdot 2\,H_2O$	43.45	21.117

The diagrammatic representation of the different hydrates of copper sulphate is given in Fig. 56.

The vapor pressure curves are:

BA for pure water.

CE for saturated solutions in equilibrium with the pentahydrate.

*O*5 dissociation curve for $CuSO_4 \cdot 5\,H_2O$; $CuSO_4 \cdot 3\,H_2O + 2\,H_2O$

*O*3 dissociation curve for $CuSO_4 \cdot 3\,H_2O$; $CuSO_4 \cdot H_2O + 2\,H_2O$

*O*1 dissociation curve for $CuSO_4 \cdot H_2O$; $CuSO_4 + H_2O$

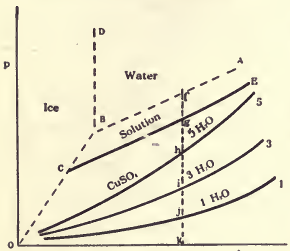


Fig. 56.

If at some arbitrarily selected temperature, as indicated at *k*, water vapor be admitted to the anhydrous $CuSO_4$, the vapor pressure will increase. By the continuous addition of water vapor the vapor pressure will continue to increase, and at various pressures we should have the vapor in equilibrium with the different hydrates represented by the intersection of the vertical line from *k* intersecting the vapor pressure curves at the points *j*, *i*, *h*, *g*, and *f* respectively, when we should obtain an infinitely dilute solution the vapor pressure of which would be practically that of pure water, represented by the intersection *f*.

Pareau measured the values of the vapor pressure of hydrates of $CuSO_4$ by withdrawing the vapor gradually and establishing points of equilibrium of the lower hydrates thus formed. The data in Table XXXIX were obtained by him at 50°.

Table XXXIX

	Pressure
$CuSO_4 \cdot 4.5\,H_2O$	46.3 mm.
$CuSO_4 \cdot 3.5\,H_2O$	47.1 mm.
$CuSO_4 \cdot 2.5\,H_2O$	29.9 mm.
$CuSO_4 \cdot 1.5\,H_2O$	29.7 mm.
$CuSO_4 \cdot 0.5\,H_2O$	4.4 mm.

For compositions between $CuSO_4 \cdot 5\ H_2O$ and $CuSO_4 \cdot 3\ H_2O$ the pressure remains practically constant at 47 mm.; it then drops to 30 mm., at which pressure it stays until there remains only one molecule of water of crystallization, when the pressure falls to 4.4 mm., at which it remains until the salt is completely dehydrated and we have the anhydrous salt.

This may be represented on a pressure-concentration diagram at 50°, as is shown in Fig. 57. The vapor pressure of pure water at 50° is represented by *f*, and as the $CuSO_4$ is added the vapor pressure changes as represented by the line *fg*, when a saturated solution is reached, as shown by curve *CE* in Fig. 56. Now the vapor pressure remains constant until sufficient anhydrous salt has been added to convert the $CuSO_4 \cdot 5\ H_2O$ all into $CuSO_4 \cdot 3\ H_2O$, and then the vapor pressure drops suddenly to 47 mm.

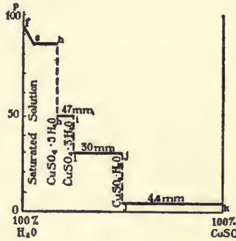


FIG. 57.

If we were to start with the anhydrous salt $CuSO_4$ and add water vapor, the vapor pressure would increase until we reach point *j*, Fig. 57, when the monohydrate will be formed, and we shall have the monovariant system $CuSO_4$-$CuSO_4 \cdot H_2O$-vapor at constant temperature and *constant* pressure (4.4 mm.). By continued addition of vapor there will be a continued formation of the monohydrate from the anhydrous $CuSO_4$ until it has all disappeared, when we have a divariant system represented by line *ji* with increase of pressure until *i* is reached, which represents the formation of the trihydrate, when we have a new monovariant system $CuSO_4 \cdot H_2O$ - $CuSO_4 \cdot 3\ H_2O$-vapor. The pressure on this system will remain constant (30 mm.) until there has been added enough vapor to convert all of the $CuSO_4 \cdot H_2O$ into $CuSO_4 \cdot 3\ H_2O$. As soon as this occurs we have a divariant system, the pressure on which changes as represented by *ih* until *h* is reached, and we have the new monovariant system $CuSO_4 \cdot 5\,H_2O$-$CuSO_4 \cdot 3\,H_2O$-vapor, when the pressure (47 mm.) will remain constant until all of the trihydrate has disappeared, when we have a new divariant system $CuSO_4 \cdot 5\,H_2O$-vapor. The pentahydrate, like the other hydrates, can exist with water vapor at different pressures, and the area $5OCE$ represents the area in which this divariant system may exist. So that if the vapor pressure at this temperature is increased, at *g* the vapor will begin to condense, and we shall have introduced the new phase — solution. The curve CE then represents the equilibrium between $CuSO_4 \cdot 5\,H_2O$-solution-vapor and is the vapor pressure curve of saturated solutions.

Data such as represented for copper sulphate and its hydrates enable us to determine the relation between the vapor pressure of water in the atmosphere under ordinary conditions and that of the hydrates. So that a particular hydrate, such as the pentahydrate $CuSO_4 \cdot 5\,H_2O$, with a vapor pressure represented by curve $O5$, Fig. 56, begins to lose water of crystallization if it is brought into an atmosphere in which the vapor pressure is less than the amount represented by $O5$; it will take on water if the vapor pressure in the atmosphere is greater than the pressure represented by $O5$. This process of crystalline hydrates losing water of crystallization under atmospheric conditions is designated *efflorescence*, and the process of taking on water is designated *deliquescence*. This principle is made use of in the processes of desiccation, and the particular substances employed, such as H_2SO_4, $CaCl_2$, etc., have low vapor pressures and become hydrated by the absorption of the water from the substance to be dried.

CHAPTER XXI

SOLUTION OF SOLIDS IN LIQUIDS—IV

Solvent and Solute Crystallize to Form Solid Solutions or Mixed Crystals

Type III

In the examples of the freezing point of mixtures we have assumed that the solid phases that separated were the pure substances along their respective solubility curves, and at only one point — the eutectic point — did we have the two solids separating together. This is, however, only a special case, for in a large number of binary mixtures the solid phase separating along the fusion curve consists of a mixture of the two components in proportions varying within certain limits. This, as we recall, is our definition of a solution, and these solid phases that separate were termed *solid solutions* by van't Hoff. They are generally termed *mixed crystals* or *isomorphous mixtures.*

It will be recalled that the addition of a solute lowers the freezing point of the solvent, and the greater the concentration the greater the lowering until we reach the maximum solubility in saturated solutions, when we have the eutectic temperature reached.

Let BC, Fig. 58, be the vapor pressure curve and BD the sublimation curve for the pure solvent water. On addition of a solute the vapor pressure is lowered, and as the concentration is increased the vapor pressure curve takes the successive positions indicated by the dotted lines. These, continued until they intersect the curve BD, give the triple point for the successive solutions, with the corresponding lowering of the freezing temperature.

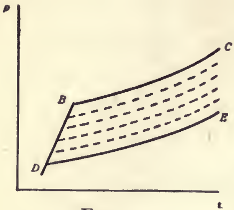


Fig. 58.

Our explicit assumption in this case is that the vapor pressure of the solid phase as represented by the sublimation curve is that of the pure solvent, *i.e.* that the solid phase that separates is pure solvent, and BD is its sublimation curve. Now, if the solute and solvent separate together, the vapor pressure of this solid phase will be different from that of the pure solvent as represented by the freezing curves.

We may represent this in Fig. 59, where the vapor pressure of the solid phase separating varies with the increase of solute, and we have also the vapor pressure curves of these various solid solutions represented by a, b, c. The values of these vapor pressures are higher than they would be were the solid that separates pure solvent. It is evident that the freezing point (represented by the intersection of a, a'; b, b'; c, c') is raised, and it may be higher than that of the pure solvent. We thus have mixtures separating which have many of the properties of ordinary liquid solutions, although they are in the solid state. These are called solid solutions or mixed crystals, and are also termed isomorphous mixtures.

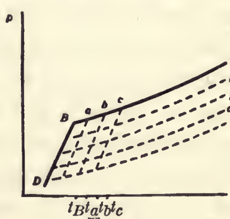


Fig. 59.

If, however, a solution of two metals, M and N, which are miscible at all temperatures, be allowed to cool, we have a somewhat different cooling curve, as illustrated in Fig. 60. The part of the cooling curve, AB, is regular, but at the temperature t_B the solid separating out is a mixture of M and N, richer in M than the mother liquor. The temperature at which more crystals can be separated from it becomes lower and lower, and this may be represented by BC. When the temperature t_C is reached, the whole mass solidifies, and the cooling curve CD then represents the regular cooling of the solid mass.

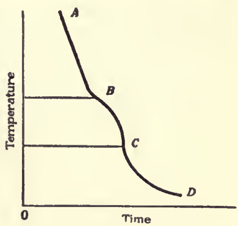


FIG. 60.

Fusibility Curves of Binary Alloys. — If, in the manner which was described on page 207, cooling curves be obtained for alloys of different percentage composition and these results plotted on a temperature-concentration diagram, we have a means of obtaining the fusibility curves or equilibrium diagram for all possible mixtures of these two metals for all ranges of temperature. Figure 61 illustrates the fusibility curves so constructed. Let M and N represent respectively the melting points of the two metals M and N, then the horizontal axis represents all possible mixtures of the metals M and N.

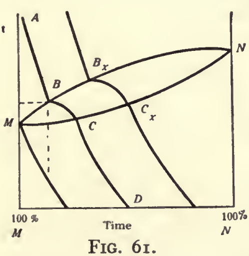


FIG. 61.

The curve $MBB_x\text{–}N$ represents the points of initial solidification and is designated the *liquidus* curve. Now by connecting the points $MCC_x\text{–}N$, we get an equilibrium curve which represents all temperatures at which all mixtures of the two metals M and N completely solidify, and this is designated the *solidus* curve.

Cooling Curves. — By means of the thermoelectric pyrometer, temperature measurements can be readily made and data obtained for determining the heating and cooling curves from which the thermal critical points are determined. In order to emphasize the existence of such critical points and then determine their location more accurately the data are plotted in a number of different ways.

1. *The time-temperature curve.* In this method the coördinates are the time t in seconds and the temperature θ. The ordinates are the successive rises (or falls) of temperature, and the abscissas the corresponding time in seconds when the temperature readings are made counting from the beginning of the observations. The data for a cooling curve

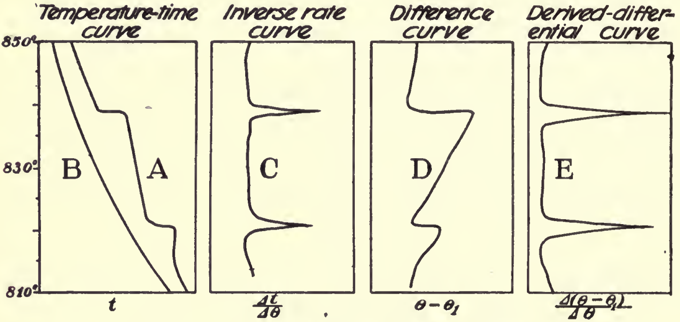


FIG. 62.—TYPES OF *Cooling Curves*—*Desch.*

showing two critical points are represented by this method by curve A in Fig. 62.

2. *Inverse-rate curve.* If the temperatures are plotted against the actual interval of time required for each successive change of 1° C. in temperature, we have what is known as the inverse-rate curve, such as C in Fig. 62. $\frac{\Delta t}{\Delta \theta}$ represents the change in time required for a change in temperature and gives us the time required for cooling through 1°. Plotting these values against the temperatures θ, we have as the coördinates θ and $\frac{\Delta t}{\Delta \theta}$.

The fact that the slight retardation in rate of cooling might be overlooked, owing to the small jogs in the curves, suggested to Osmond the desirability of emphasizing these thermal points by using the inverse-rate curves, the breaks in which are approximately proportional to the amount of heat evolved on cooling or absorbed on heating. To still further overcome the irregularities and effects of the furnace and other surrounding influences, use is made of *neutral bodies*, the cooling of which is compared with that of the sample to be tested. Robert Austen introduced the use of a neutral body and two thermocouples, so that the difference of temperature between it and the sample to be tested could be determined, as well as the actual temperature of the metals. The temperature of the two would be the same if the heat capacities and emissivities were identical, and they would be different, only at the critical points, where heat is evolved on cooling or absorbed on heating. There will always be a little lagging in one of the substances, for they will not have the same heat capacities, but the critical points will be represented by abrupt differences between the temperatures of the two bodies.

3. *Difference curves.* By employing a neutral body that shows no thermal inversion points, and plotting the difference in temperature between the neutral body and the one under examination against the temperatures, we then have as the coördinates the temperature θ and $\theta - \theta_1$. Such a difference curve is represented by D in Fig. 62, while the curve designated B represents the temperature-time cooling curve for a neutral body.

4. *Derived differential curve.* If the slope of the difference curve is plotted against the temperature, we have as the coördinates the temperature θ, and the rate of cooling for each degree of temperature $\frac{\Delta\,(\theta - \theta_1)}{\Delta\,\theta}$. This is the method employed by Rosenhain and is represented by curve E in Fig. 62. This method gives the most pronounced indication of the thermal critical points, as is readily seen from a comparison of these different curves, and thus eliminates more completely the irregularities which are due primarily to the differences of the heat capacities and emissivities of

the neutral body and the sample under examination resulting from their different rates of cooling and heating.

Figure 63 represents a typical fusion curve of binary alloys whose metals form solid solutions. For, if at some concentration, such as 50 per cent of A and 50 per cent of B, we have the liquid at the temperature t represented by the point P, and if we cool the melted mass we reach the *liquidus* curve AlB at the point l temperature t_l. Solidification begins and the crystals that separate must have the composition represented by s on the *solidus* curve, which is obtained by drawing a horizontal line through l until it intersects the *solidus* curve at s. This must represent the composition of the crystals that separate. This is designated a solid solution.

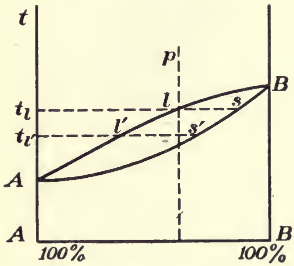


FIG. 63.

Now as the mass continues to cool from t_l to $t_{l'}$, the solid crystals that separate at l' continue to grow and become richer and richer in the metal A, while the remaining mother liquid likewise becomes richer in A and therefore more fusible. The varying composition of the liquid is represented by the part of the curve $ll' \cdot \cdot \cdot A$, and at any temperature the composition of the crystals is designated by s on the *solidus* curve, and at the still lower temperature $t_{l'}$ by s', etc. This means that the crystals that separate out on cooling change in composition from s, through s' to A represented by the *solidus* curve. This means that the crystals first formed increase in size by addition of crystals of different composition, but as the temperature falls diffusion takes place, and the crystals become homogeneous. At the temperature $t_{l''}$ the solidification is complete, and the composition of the last drop of molten liquid to solidify has the composition of nearly pure A.

Diffusion takes place readily in the case of liquid solutions, but to produce homogeneous crystals with solid solutions the solidification and subsequent cooling must be very slow, otherwise the solid solutions will be heterogeneous, that is, the different layers on the crystals may be of different composition, the proportion of the more fusible metal increasing from the inside to the outside. By heating the alloy a long time at a temperature below the melting point, diffusion takes place and destroys the heterogeneous structure of the solid solution. This is designated the *annealing process*.

This will become clearer if we give a specific example. In Fig. 64 we have the temperature-concentration diagram of the fusibility curves for gold and platinum, which are typical of such isomorphous pairs of solids. *AlB* is the *liquidus* curve and *AsB* the *solidus* curve, and in the area between the two the alloys are partially liquid and partially solid. In Fig. 65 for Cu and Ni series, this area is much

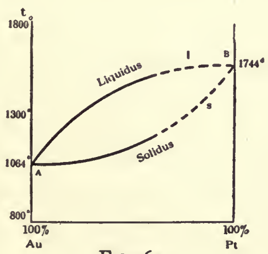


FIG. 64.

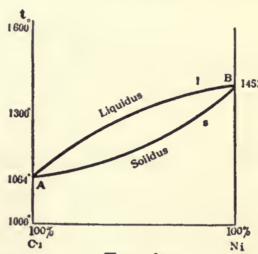


FIG. 65.

smaller than in the Au-Pt series. If a Cu-Ni alloy is rapidly cooled, it will be much more nearly homogeneous than an alloy of Au-Pt when cooled under the same conditions. There is less difference in the composition of the liquid and the solid which separates, and consequently incompleteness of equilibrium has a less influence in the case of Cu-Ni than in the case of Au-Pt. It is conceivable that the *liquidus* and *solidus* curves may be so close together that it would be practically impossible to distinguish them, and then the solid and liquid phases in equilibrium would be identical in composition.

The type of freezing curve depends upon the mutual action of the pairs of liquids selected. In the cases just considered we have systems the components of which form no chemical compounds, and the crystals that separate are miscible in all proportions, forming solid solutions. Now it is conceivable that the restriction that no chemical compound formed by the action of the constituents can be removed, and also that the crystals separating may be nonmiscible or insoluble. It is then possible to classify these various binary systems upon the basis of the freezing-point curves as follows:

I. *The freezing-point curve represents a complete series of mixed crystals or solid solutions which are miscible in all proportions.*

1. The freezing points of all possible mixtures of the two metals A and B in Fig. 66 are intermediate between the freezing point of A and that of B. The curve AlB represents the freezing points of the molten masses and AsB the *solidus* curve which represents the composition of the solid solutions which separate when these mixtures solidify completely. These solid solutions vary in concentration as indicated by the horizontal axis.

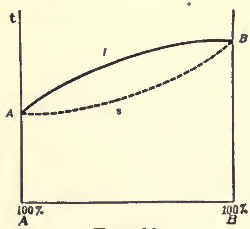


Fig. 66.

2. The freezing-point curve shows a maximum freezing point. That is, by the addition of B to A the freezing point is raised until a certain concentration, C, is reached, when the maximum value is obtained. Likewise when A is added to liquid B the freezing point of the solution is higher than that of the pure solvent B. As the concentration of A increases, the freezing point of the solution increases until a concentration is reached which gives the solution of the maximum freezing point, designated by C in Fig. 67. Now

if a solution of B in A be allowed to cool, at the freezing point t_s, the crystals which separate will be richer in B than the solution from which they separate, as s, and similarly for other solutions, we have a series of points representing the concentrations of the solid solutions separating, and these are represented by the *solidus* curve AsC. At the point C the composition of the solid which separates is the same as that of the solutions, that is, the whole mass solidifies. Similarly the curve $Cl'B$ represents the *liquidus* curve for solutions rich in B, and the corresponding solidus curve is represented by $Cs'B$. The *liquidus* and *solidus* curves coincide at this point, C, and we have an equilibrium when the molten mass solidifies without change of temperature, as in the case of a pure substance, and the structure of an alloy of the composition represented by C will be completely homogeneous.

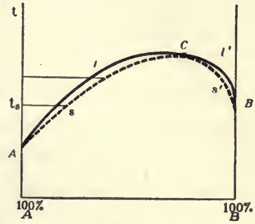


FIG. 67.

No examples of this case are known among alloys, but the system *d*- and *l*-carvoxim shows this type of freezing-point curve.

3. The freezing-point curve shows a minimum freezing point. The curve AlC, Fig. 68, represents the *liquidus* curve of alloys rich in A, and AsC its corresponding *solidus* curve, which shows that the composition of the solid solutions that separate is richer in A than that of the solutions from which they separate. Likewise the curve $Cl'B$ represents the *liquidus* curve of the alloys rich in B; and $Cs'B$ its corresponding *solidus* curve, which shows that the composition of the solid solutions which separate is richer in B than that of the solutions from which they separated. At

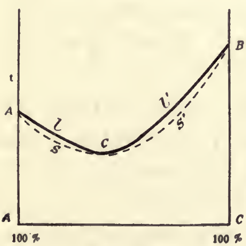


FIG. 68.

the point C the crystals and the liquid from which they separate have the same composition, and the alloy is crystallized at constant temperature and must be homogeneous.

Binary systems of alloys which belong to this type of curves are Mn-Cu and Mn-Ni.

It is conceivable that one or more minimum or maximum points may occur in the same system, and that even a combination of these three types might be present, thus giving rise to a very complicated cooling curve. Such combinations are represented in Fig. 69. In I the addition of B to A raises the melting point, and the addition of A to B lowers the melting point, while at C there is a considerable range of concentration over which the *liquidus* and *solidus* curves are the same, and we have a marked horizontal inflection of the curve. It is possible to overlook such a condition in plotting the experimental determinations of the cooling curve, but the halting of the crystallization interval would be much more pronounced than at other portions of the curve where no such intervals of crystallization take place. The systems Br-I and Mg-Cd are examples of this type of fusion curves. There are no known examples of the curves II and III shown in Fig. 69.

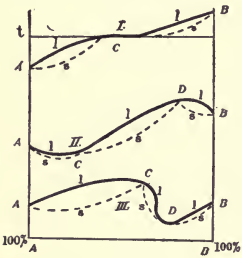


FIG. 69.

By a consideration similar to that employed in connection with fractional distillation it can be readily shown that Type I, 1 represents the only pairs of binary mixtures that can be completely separated by *fractional crystallization.*

II. *Freezing-point curves which do not represent a continuous series of mixed crystals or solid solutions and which are not miscible in all proportions.*

1. The freezing-point curves of a binary system which meet at a transition point form two series of solid solutions.

This type of freezing-point curves is represented by the system Hg-Cd, Fig. 70. The two *liquidus* curves for this system are AB and BC.

The solid solution richer in Hg separates along the *solidus* curve AD, and the solid solution richer in Cd separates along the *solidus* curve EC, and at the point of intersection, B, of the two *liquidus* curves we have the two solid solutions in equilibrium. At this temperature, 188° C., the two solid solutions separating have the composition represented by D (62.7 atomic per cent of Cd) and E (65.2 atomic per cent Cd) and are in equilibrium with the liquid of the composition represented by B (51 atomic per cent Cd). B is a transition point, where we have the transition of one series of crystals into the other taking place at constant temperature, as represented by the horizontal line BDE. Along the liquidus curve BC we have crystals of one solid solution (b) separating, and along AB crystals of another solid solution (a). So we may divide our diagram into the following areas:

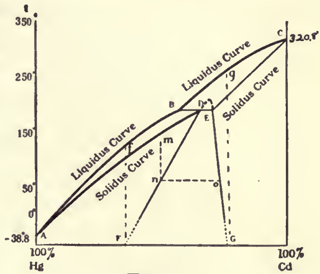


FIG. 70.

Above the freezing-point curve ABC the alloys of Hg-Cd are liquid. All alloys of which AB is the *liquidus* solidify with the separation of crystals of the solid solution a, and the area inclosed between the *liquidus* curve AB and the *solidus* curve AD contains crystals of this solid solution and the liquid, and at temperatures below that represented by the *solidus* curve we have only solid solution a.

All alloys with a Cd concentration greater than represented by E consist of crystals of the solid solution b, and those between concentrations designated by D and E consist of a mixture of crystals of two solid solutions, a and b, and the solid alloy is a mixture of a and b, as represented by the area marked *FDEG*. That is, we have a solution of the one in the other, and as the solubility is dependent upon the temperature, the curves *DF* and *EG* represent their mutual solubility, decreasing with decrease of temperature. This is the area where we have the crystals *a* and *b* existing together. It is analogous to the system aniline and water, Fig. 16, wherein the area inclosed within the equilibrium curve represents the area of mixtures which separate into two liquid layers, the compositions of which are represented by some points on the two limbs of the equilibrium curve. If a mixture of a composition intermediate between that represented by the lines *fF* and *gG* be cooled sufficiently low, say to about $-40°$, they will eventually separate into the two types of solid crystals *a* and *b*, but if the composition is richer in Hg than indicated by *fF*, only *a* crystals will appear, and if richer in Cd than indicated by *gG*, the crystals will be *b*.

If, however, a solution of the composition as represented by *m* be solidified, it will consist wholly of the solid solution whose crystals are *a* only; but if this be cooled, the curve *FD* will be intersected and the solid solution will separate into two nonmiscible isomorphous mixtures which are represented by *n* and *o* respectively. The curves *DnF* and *EoG* represent the change in concentration of the two sets of mixed crystals which are in equilibrium at different temperatures. That is, we have a change in the composition of the mixed crystals with a change in temperature, which is again our annealing process, and in the production of alloys this is of very great importance, as the physical properties depend upon the type of mixed crystals present.

The freezing-point curves of liquid solutions of $MgSiO_3$ and $MnSiO_3$ are represented in Fig. 71. We have in this case the melting point of all mixtures of $MgSiO_3$ and $MnSiO_3$ intermediate between that of the two components. Along one part of the freezing-point curve *AB* one set of solid solutions separate, and along *CB* another set of solid solutions separate, and at their point of intersection, *B*, we have a marked discontinuity represented. For this pair of binary mixtures this is at 1328° and is known as the *transition point.* The composition of the two solid solutions that separate at the transition point *B* is designated by *D* and *E*.

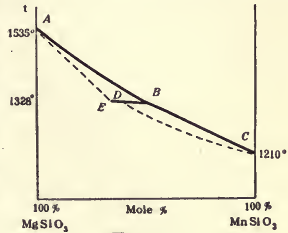


FIG. 71.

2. The freezing-point curves show a eutectic point and the crystals separated are partially miscible (Roozeboom's Type 5).

The binary system Cu-Ag is an illustration, Fig. 72, of this type of fusion curve, which has been worked out very carefully. Along the *liquidus* curve *CB* the crystals of the solid solution *a*, which is a solution of Cu in Ag, separate. The composition of this solid solution varies, as indicated by the curve *CE*. Likewise along the *liquidus* curve *AB* the solid solution *b* separates, and at the intersection *B* of the two *liquidus* curves the concentration of the two solutions which separate is designated by *D* and *E*. These represent saturated solutions which are in equilibrium at the point *B*. This is designated a eutectic point and indicates a marked arrest during which the temperature remains constant while the mass solidifies. The eutectic is then composed of a saturated solid solution of Cu in Ag, represented by *E*, and of a saturated solid solution of Ag in Cu, represented by *D*. Just as any two partially miscible liquids have different solubilities at different temperatures, so these partially miscible solid solutions have a solubility curve analogous to that of liquids such as aniline and water.

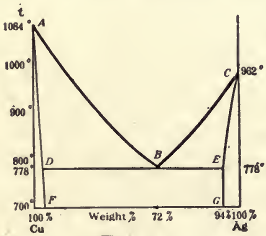


FIG. 72.

We may then consider the curves *DF* and *EG* portions of the solubility curves of these partially miscible solid solutions.

Figure 73 represents the freezing-point curves for Li_2SiO_3 and $MgSiO_3$. *AC* and *CB* are the freezing-point curves, and *C* is the eutectic point. If any liquid solution of these two substances be selected at a temperature and concentration represented by *P*, and if this be cooled to the temperature at which we meet the freezing curve *CB* at *D*, the solution will freeze, and the solid phase will separate; as the solid in this particular case is a mixture of Li_2SiO_3 and $MgSiO_3$, its concentration may be represented by some such point as *E*, richer in Mg than the solution from which it was separated, and the liquid will become richer in the other component. We can obtain the composition of the other solids separating, which we represent by the curve *BEG*, while similarly *AF* represents the solids separating along the curve *AC*. *AC* and *CB*, representing the freezing points of liquid solutions, are designated the *liquidus* curves, and *AF* and *BG*, representing the melting points of the solid solutions, are termed the *solidus* curves.

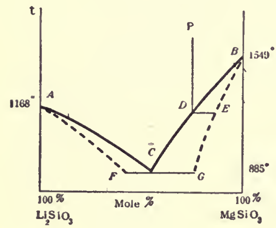


FIG. 73.

At the eutectic point *C* the solid phase separating is a *eutectic* consisting of two solid solutions of the concentrations represented by *F* and *G*. The area between the *liquidus* and *solidus* curves represents both liquid and solid.

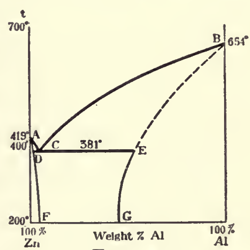


FIG. 74.

In the case of Zn-Al alloys, Fig. 74, it will be noted that the saturated solutions of Zn contain but a small quantity of Al, whereas solutions of Al contain a very much larger quantity of Zn. The eutectic *C* is composed of these two solid solutions, *D* and *E*, and the concentration *D* of the solid solution of Al-Zn is nearly over to the pure zinc concentration.

III. *The components of the binary system form chemical compounds and the freezing-point curves show one or more chemical compounds.*

It is conceivable that a conglomerate consisting of mixed crystals may not only melt at constant temperature, as in the case of eutectic mixtures, but also that they may be in such a proportion as to conform to the laws of definite and multiple proportions, when we should have a pure chemical compound separating, which would also be characterized by the liquid solution solidifying completely without change of temperature. In Fig. 75 we have represented the freezing-point curves for solutions of K_2SO_4 and $MgSO_4$ above 700° C. Along *AB* the solid phases separating are solid solutions, and along *ED* pure $MgSO_4$. At *B* and *D* we have two eutectic points at 747° and 884° respectively. The curve *BCD* represents

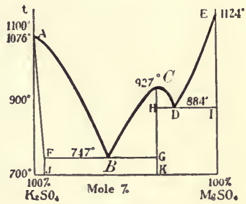


FIG. 75.

the solubility or freezing-point curve of the chemical compound of composition *C*, which is $K_2SO_4 \cdot 2\ MgSO_4$ and known as the mineral Langbeinite, with a melting point of 927°. Along the curve *CB* the solid phase which crystallizes is this mineral, and the liquid becomes richer in K_2SO_4 until the concentration *B* is reached, when the whole mass solidifies into the conglomerate, the solid solution *F* and $K_2SO_4 \cdot 2\ MgSO_4$, without change of temperature. Along *CD*, the solid phase which separates is $K_2SO\ \cdot 2\ MgSO_4$; the liquid solution becomes richer in $MgSO_4$ until the concentration of the eutectic is reached, when it will solidify without change of temperature at 884°, and the mixed crystals will be a conglomerate of the mineral $K_2SO_4 \cdot 2\ MgSO_4$ and pure $MgSO_4$.

The complete concentration-temperature diagram for Mg-Sn is given in Fig. 76, in which the curve *ABCDE* represents the fusion curve. It is composed of three branches, *AB*, *BCD*, and *DE*, along each of which there is a separate definite crystalline variety in equilibrium with the

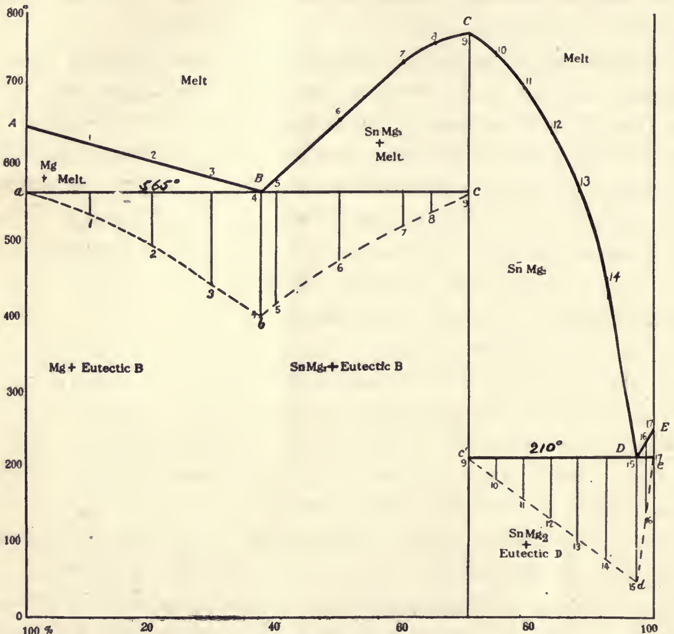


FIG. 76.

liquid. Along curve *AB* the pure α (Mg) is in equilibrium; along *DE*, the pure β (Sn); while along the fusion curve *BCD*, which shows no discontinuity at *C* and is to be considered a single continuous fusion curve, the chemical compound $SnMg_2$ separates out along the whole range of temperatures. That is, in melts richer than about 70 per cent Sn and those richer in Mg than about 30 per cent Mg to about 60 per cent, we have for temperatures above the eutectic temperature *B*, about 565°, this chemical compound existing in equilibrium with melts of two different concentrations at the same temperature. The point *C* is a maximum temperature and corresponds to the melting point of the pure chemical compound $SnMg_2$. At points *B* and *D* we have two marked breaks in the fusion curve and these represent the two eutectic points known for this alloy. The two eutectic horizontals, *aBc* and *c′De*, are at different temperatures, and their components, which are represented by the ends of the lines, are nonmiscible. The eutectic *B* separates into pure magnesium and the pure chemical compound $SnMg_2$, and the eutectic *D* separates into pure $SnMg_2$ and pure Sn.

The method of obtaining a cooling curve is represented by Fig. 77, in which we have represented on a temperature-concentration diagram the temperature-time cooling curves

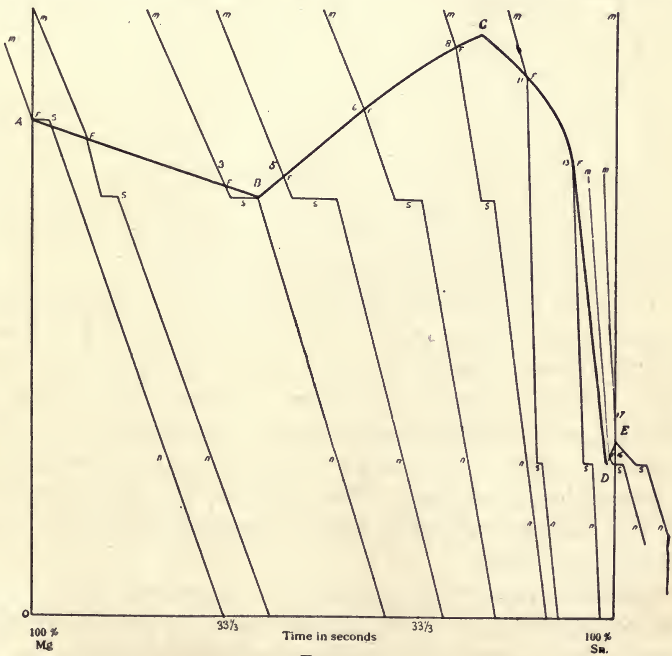


FIG. 77.

for a number of alloys of different concentrations, represented by the numbers on the fusion curve in Fig. 76. We have the pure metal Mg, the cooling curve of which is represented by mA; the molten metal cools regularly until the temperature represented by A is reached, when its temperature is arrested for the time Fs, during which the metal solidifies completely, and then the cooling proceeds regularly as represented by sn. A melt containing approximately 90 per cent is cooled, and we have the curve mF; when the point F is reached, the melt begins to solidify with the separation of pure Mg, and the solidification continues until the temperature of the eutectic B is reached, when we have another arrest in the rate of cooling, as designated by s, at which the temperature remains constant until the remaining liquid has completely solidified. In a similar manner the temperature-time curves illustrating the rates of cooling are determined for alloys representing the whole range of concentration, and the points F, representing the initial freezing, are all connected, giving us the heavy line representing the freezing-point or fusion curve $ABCDE$ for the alloys composed of Mg-Sn. The horizontal portions designated by s represent the eutectic temperature, or the lowest temperature at which these constituents can exist in the liquid state.

It will be noticed that the time required for the solidification of these different alloys is not the same, and this is shown by the different lengths of the horizontal sections represented by s. This indicates that there is more of the eutectic present, and consequently more time is required for its solidification, and the temperature therefore remains constant for a greater length of time. We therefore have an indication of the relative quantities of the constituents present with the eutectic alloy.

Methods have been employed to represent graphically the per cent of the eutectic present in any particular solidified melt. This is shown by the dotted portion of the diagram in

Fig. 76. Draw the line *Bb* of a length representing 100 per cent, and since at *B* the melt all solidifies to eutectic, then this is the maximum quantity of the eutectic that can be produced from the melt, since all of the melt goes over into the eutectic without change of temperature. At *a*, which represents pure Mg, there would be no eutectic, hence the quantity would be zero per cent; the same is true for *c*, which represents all pure $SnMg_2$ and no eutectic. Connecting these points with *b* we have the percentage of the eutectic in the solidified melt of any specified concentration, such as 1, 2, 3, 5, 6, etc., represented by the distances from the base line *aBc*. If the distance from this line to *b* were divided into 100 parts, the percentage of the eutectic alloy in the solidified melt could be readily ascertained. The same is true for the eutectic *D* and the per cent it is of any melts above approximately 70 per cent Sn, the structural composition of the solidified melt being represented by the curve *c′de* drawn upon the base *c′De*. Many times, these are drawn with the base line the same as that of the concentration axis, and a convenient distance on the vertical axis taken as 100 per cent for the eutectic *D*. These different solidified melts have their characteristic microscopic appearance, and the different mixed crystals are readily distinguished and the different components thus recognized.

CHAPTER XXII

APPLICATIONS OF THE PHASE RULE

THE number and nature of the phases possible to any system when in equilibrium depend on the composition and the temperature, and it is due largely to the application of the Phase Rule to the study of alloys that such marked progress has been made in the last few years. So we shall confine our consideration of the application of this rule to the study of alloys primarily.

COPPER-ZINC ALLOYS

In Fig. 78 we have reproduced Shepard's freezing-point curve for alloys of copper and zinc. This cooling *liquidus* curve consists of six branches, thus showing the existence of six different solid solutions; but there are no chemical compounds of copper and zinc such as we found in the case of magnesium and tin. There is a distinct solid solution in equilibrium with each of the six branches of the freezing-point curve.

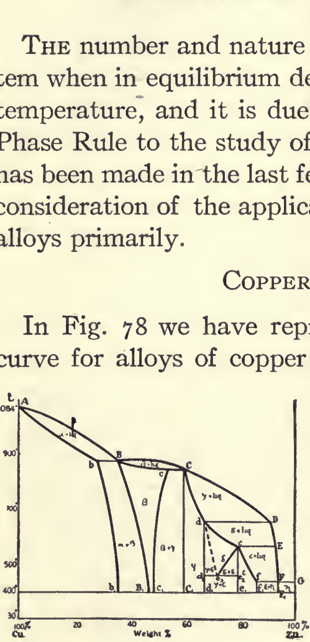


FIG. 78.

Along the section of the *liquidus* curve designated AB homogeneous α crystals separate, the composition of which is represented by the *solidus* curve Ab, thus showing that the left-hand portion of the diagram from the Cu axis over to the line bb_1, which represents about 65 per cent of copper, consists of α crystals. The area between the *solidus* curve

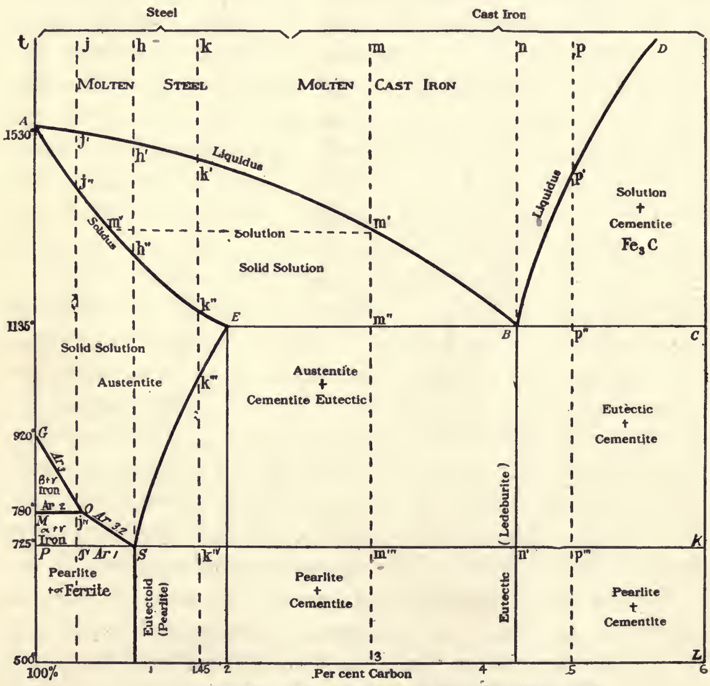
Ab and the *liquidus* curve AB represents α crystals with the mother liquor. The area Bbb_1B_1 is occupied by α and β crystals, the latter being stable along the freezing curve BC, and the area cBB_1c_1 gives the limits of the solid solution, the composition of which varies greatly with the change in temperature. At the lower temperature the β crystals break down along the line BB_1 with the formation of the homogeneous α crystals, while along the line cc_1 they break down with the formation of γ crystals. The existence of α and γ crystals in the same ingot has not been discovered; β and γ exist in the area Ccc_1C_1, while γ is in equilibrium along the portion of the *liquidus* curve designated CD, and the area CC_1d_1d is the field of pure γ crystals. δ crystals form from the melt along DE, while at lower temperatures these break down, forming δ and ϵ crystals or ϵ and γ crystals. The transformation of ϵ-δ into ϵ crystals is so marked that it can be accurately observed to 29 per cent of copper. The exact position of de_3 is not definitely known, but it lies between 20 and 31 per cent of copper. Below $d_2e_3e_2$ the alloy consists of the mixed crystals of γ and ϵ. The ϵ crystals separate out along the *liquidus* EF, and these solid solutions vary in concentration from 13 to 20 per cent of copper. Alloys of copper and zinc containing from 2.5 to 14 per cent of copper when solid consist of the mixed crystals ϵ and η, the η crystals being stable along that part of the cooling curve designated FG. Below concentrations less than 2.5 per cent of copper, the solid alloy consists of homogeneous solid solutions of η.

Muntz's metal, which contains 60 per cent copper, is composed at ordinary temperatures of the α and β crystals, but if quenched above 750° it will consist of homogeneous β crystals, which make the brass ductile at temperatures above 750° so that it may be rolled hot. β crystals are less ductile at lower temperatures than the α crystals. Quenched from temperatures above 750°, Muntz's metal is harder and stronger but less ductile than the annealed alloy.

These different mixed crystals are readily recognized under the microscope, and by means of micro-photographs the heat treatment of brass has been carefully studied.

IRON-CARBON ALLOYS

Among the binary alloys, that of iron and carbon is perhaps the most important. The complexity of the system is much increased by the fact that iron exists in three allotropic modi-



Metastable or Cementite-Austentite Carbon-Iron Diagram (Howe)

FIG. 79.

fications: α, β, and γ forms. Howe's carbon-iron equilibrium diagram is given in Fig. 79. The melting point of pure iron is 1530°. The three allotropic modifications of iron all crystallize in the regular system, and as there are decided energy and volume changes at their points of transformation, there are evidences of discontinuity in the cooling curve of pure iron, and consequently proof of the different physical modifications. The γ-iron is the stable form above 920°, where it passes on cooling into β-iron with the evolution of heat and a considerable expansion of volume. γ-iron has a marked solvent power for carbon, and AB, the *liquidus* curve, represents the freezing points of solutions of carbon in iron, while AE, the *solidus* curve (melting point curve), "represents the temperature at which the alloys have just completed their freezing process, that is, have just become completely solid; or conversely it represents the temperature of incipient fusion on heating" (Rosenhain). "The method of determining the *solidus* was to take small pieces of steel of known composition, heat these, and suddenly cool them from successively higher temperatures; afterwards, each specimen was examined by means of the microscope. It is easy, as the photographs show, to determine what is the particular point at which you have reached a temperature where there was a small quantity of liquid metal present at the moment of quenching."

Critical Thermal Points of Pure Iron. — When pure iron is cooled from a high temperature (1000° or above), the cooling proceeds slowly and regularly, then it is arrested for a considerable time while the temperature remains constant, and in some instances the temperature of the cooling sample of iron actually rises; the metal becomes hotter, it *recalesces;* hence the name *recalescence* is given to this particular critical thermal point. This recalescence or glow of the steel may be readily seen if the experiment is conducted in a darkened room. Eschernoff designated such critical points by A, and to distinguish those obtained on cooling from those on heating, it has been agreed to designate the former by Ar (from the French *refroidissement*, meaning cooling) and the latter by *Ac* (from the French *chauffage*, heating). These critical points *Ar* and *Ac* do not occur at exactly the same temperature, and for steel are as much as 25° to 50° apart. This lagging of the critical point on cooling behind the critical point on heating is the physical phenomenon known as *hysteresis* and is due to the delayed transformation. The equilibrium temperature at which the transformations actually occur, designated by *Ar* and *Ac*, is distinguished from the equilibrium temperature *Ae*, at which they are due to occur.

If a molten steel of low carbon content (less than about 0.4 per cent carbon), represented by the line *j*, be cooled, it will begin to freeze with the formation of crystals of the solid solution termed *austenite*, the composition of which is poorer in carbon than the solution from which they separated, and these crystals are represented in composition by the *solidus* curve $Aj''E$, while $Aj'B$ is the *liquidus* curve. On further cooling there is no change in the austenite until about 805° is reached, when the transformation into β-iron occurs, which consists in the separation of pure β-iron. The concentration of the austenite remaining is represented by the curve Ar_3 (*GO*) until the temperature 780° is reached at j_{iv}, when α-ferrite appears, and as the temperature is further lowered more of this is separated from the austenite, the composition of which is represented by the curve $Ar_{3\cdot2}$ (*OS*). On reaching the temperature 725° at the point j_v, the composition of the residual austenite is represented by *S*, which is pearlite of a carbon content of 0.9 per cent. This point is analogous to a eutectic point, but we do not have the lowest point at which the particular mixture is a liquid, but it is the lowest transformation point for austenite, which is a solid solution. We have a eutectoid substance which consists of a mixture of α-ferrite and pearlite. So below a temperature of 725° and up to a carbon content of 0.9 per cent the solid steel when slowly cooled consists of pure α-ferrite and pearlite.

On cooling a mixture containing 4.3 per cent of carbon, represented by the line *n*, the molten mass of cast iron remains liquid until the temperature 1135° is reached at the eutectic point *E* with the formation of the eutectic Ledeburite. This eutectic is a conglomerate consisting of a mixture of a honeycomb structure of eutectic cementite filled in with the darker masses of eutectic austenite. Cementite is the carbide of iron, Fe_3C, while the austenite is iron saturated with carbon. On further cooling the chemical compound cementite does not change, but the austenite changes over into pearlite and cementite at 725°, as represented by Sn_1K.

In an analogous manner the various concentrations such as are represented by *h*, *k*, *m*, and *p* could be discussed, but this would lead us too far and the student can work the changes out as an exercise.

Applications to Analytical Chemistry

In the analysis of multiple component systems the properties of the individual constituents are often so nearly alike that the usual methods of analysis fail. So that in order to determine the quantities of the constituents it is necessary to do this by some method wherein the separation of the components of the system is not necessary. This method of procedure is dependent on the relationship established under conditions of equilibrium and by means of equilibrium diagrams obtained experimentally.

In the case of the determination of alcohol in alcoholic beverages we have one of the principal applications of this method. It is known that if to a solution of alcohol in water certain salts, such as K_2CO_3, NaF, etc., be added, the single liquid solution breaks into two liquid phases. The equilibrium is established between the two saturated solutions, and this equilibrium can be obtained at the point at which the components are in equilibrium *just before* the separation into two liquid layers occurs.

This equilibrium is dependent on the reduction of the degrees of freedom of the system by the introduction of the second liquid layer in this case, or the solid phase in others. For at a given temperature a definite solution of alcohol and water will dissolve a definite quantity of the salt (K_2CO_3), and if we know the amount of salt, we then know the amount of alcohol in the alcohol-water mixture. This will become more apparent after the following consideration of the special cases.

By a method similar to that described for obtaining the equilibrium curve for the system water-alcohol-ether, page 163, the equilibrium curve for the system water-alcohol-salt may be constructed on a triangular diagram. These data may be expressed on a rectangular diagram by calculating the amounts of the alcohol and of salt (K_2CO_3) in a constant quantity of water and plotting the results. It is evident then that if the amount of salt is known, the percentage composition of alcohol and of water can be calculated.

The actual determination is made in the following manner: If we employ the system water-acetone-K_2CO_3, the actual experimental data are obtained by the general method just described. Weigh out 100 grams of the solution of acetone and water to be analyzed. Add K_2CO_3 as a solid, or in the form of a solution of known strength, until the solution breaks into two liquid layers. Determine the amount of K_2CO_3 added. Render the solution homogeneous by the addition of water, then titrate back and forth with acetone and water until the correct end point is ascertained. Weigh again and determine the amounts of the solvents added. Now from these weights and the amount of the carbonate added compute the grams of K_2CO_3 in 100 grams of the solvent (water). Referring to the acetone-K_2CO_3 curve the amount of acetone can be obtained and from this the percentage composition of the mixture.

CHAPTER XXIII

OSMOTIC PRESSURE

By placing in pure water a bladder filled with alcohol Nollet (1748) observed that the bladder became greatly distended, but it was not until many years later that this phenomenon was rediscovered and explanations offered. Dutrochet (1822–) observed that there were two currents connected with the passage of liquids through membranes during such phenomena as that just described: (1) the principal current inward through the membrane, which he termed the *endosmotic* current, and (2) the secondary one outward, the *exosmotic* current; while the phenomena were called respectively *endosmosis* and *exosmosis*. Later the term *osmosis* was applied to the phenomenon as a whole and is the one now employed.

Graham (1854) employed septa of different kinds and demonstrated that, depending upon the character of the membranes employed and of the solute present, both the solvent and the solute would pass through the membrane; while in the case of certain solutes they would not pass through. He utilized this method, which he termed *dialysis*, for the separation of substances into two general classes — those which passed through the membrane, *crystalloids*, and those which did not pass through, *colloids*. Therefore it is necessary to distinguish between *dialysis*, wherein the solute passes through the membrane, and *osmosis*, where only the solvent passes through the membrane. In this latter case the membrane is said to be semipermeable, being pervious to only one of the constituents of the solution, that is, to the solvent.

It was recognized in the process of osmosis that some of the solute also appeared on the side of the septum opposite where the solution was placed, and many explanations have been offered to account not only for this small trace of the solute passing through, but also for the membrane being pervious to the solvent particularly. The conception of the sieve construction of the membrane supposes it to be composed of numerous small openings of such size that only substances with molecules of small dimensions can pass through, while those substances with large molecules are prevented from going through. The passage of small quantities of some solutes, such as sugar, through animal or vegetable membranes was explained by assuming the openings to be of such size that in the passage of the solvent the inflowing current would pass along the walls of the openings, while through the central channel the outflowing current would be located. When the thickness of the solvent layer was such as to remove the particles of the solute a distance from the walls of the opening in the membrane greater than that represented by their molecular dimensions, they would slip through and thus pass out into the pure solvent.

Lhermite (1854) showed, however, that if a layer of chloroform be placed on top of water in a large test tube, and then ether placed on top of the chloroform and the vessel closed by means of a stopper and allowed to stand for a day or two, there would be only two liquid layers. The ether passes through the chloroform and appears in the water layer. That is, the ether dissolves in the chloroform, but being more soluble in water it is extracted by the water, and most of it appears in this layer. The ether is distributed between the chloroform and the water layers and the chloroform is the *semipermeable septum.*

Flusin (1898–1900) showed that by using vulcanized caoutchouc as the semipermeable membrane and employing numerous liquids in pairs of all possible combinations, the main current was from the liquid which is the more readily absorbed (imbibed) by the rubber, through the membrane into the liquid less readily absorbed. The combination of liquids included carbon bisulphide, chloroform, toluene, benzene, xylene, benzyl chloride, turpentine, nitrobenzene, ether, methyl alcohol, ethyl alcohol, and acetic acid. By using as the membrane hog's bladder and having ethyl alcohol on one side, he placed on the other side water, methyl alcohol, amyl alcohol, amyl acetate, chloroform, benzene, and many others, and in each case found the direction of the main current always toward the ethyl alcohol. Raoult, by employing a rubber septum, found the current to be from ether through the membrane to methyl alcohol, and by using hog's bladder as septum the main current was reversed.

Kahlenberg (1906) by employing a rubber septum has collected a large amount of data confirmatory of the solvent action of the semipermeable membrane and concludes: "that whether osmosis will take place in a given case or not depends upon the specific nature of the septum and the liquids that bathe it; and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed. The motive power in osmotic processes lies in the specific attractions or affinities between the liquids used, and also those between the latter and the septum employed."

The mechanism of osmosis will be further discussed in Chapter XXXV on Colloid Chemistry.

By fastening a parchment membrane over the end of a thistle tube, filling this with a solution of cane sugar, and placing the bulb of the tube in pure water, the solvent will pass into the solution, which becomes diluted. The passage of the water into the solution will continue until the hydrostatic pressure of the dilute solution in the tube is such that it prevents any more of the water from going through the membrane into the solution, *i.e.* the tendency of the water to pass in is balanced by this hydrostatic pressure, and the osmotic cell is in a state of equilibrium. The pressure thus developed can be measured, and it is the pressure measured by such a device that is termed *the osmotic pressure of the solution*. This pressure is also conceived to be due to the bombardment of the membrane by the molecules of the solute present in the solution, and, as will be shown later, is considered analogous to the pressure of gaseous molecules on the walls of the containing vessel.

Precipitation Membranes. — In addition to the numerous materials that have been given as examples of semipermeable membranes, such as platinum, palladium, red-hot iron, vegetable membranes (begonia leaf), animal membranes (bladder), parchment paper, caoutchouc, zeolites, etc., there is another class termed *precipitation membranes*, which are colloidal gelatinous precipitates such as ferric hydroxide, calcium phosphate, gelatine, tannates, etc.; but the one most successfully employed is copper ferrocyanide, discovered by Traube.

It was this type of membrane that Pfeffer (1877), the botanist, used in his classic experiments. In order to obtain a strong membrane firmly attached, he precipitated the membrane in the interstices of a porous unglazed porcelain cup. He prepared these cells by soaking them first in water, then in a three per cent copper sulphate solution, then filling the cell with a three per cent solution of potassium ferrocyanide and immersing this in the three per cent copper sulphate solution. The solutions diffuse into the walls of the cell, where they meet with the formation of the gelatinous precipitate of copper ferrocyanide.

$$2\ CuSO_4 + K_4FeCN_6 = Cu_2FeCN_6 + 2\ K_2SO_4.$$

After standing some time the cell is removed and the excess of salts carefully washed off. It is essential that the precipitate be deposited in the interstices of the wall, and that the deposit be thin, adherent, and absolutely continuous. These conditions are very difficult to obtain.

These membranes are pervious to the solvent water but not to the dissolved substances. Pfeffer found that when these cells containing salt solutions were immersed in pure water, that water entered through the semipermeable wall and diluted the solution. The tendency of the water to dilute the solution was measured by the pressure exerted or the height to which the liquid would rise in a tube against the atmospheric pressure and the force of gravity. Pfeffer found that these pressures against the walls of the membrane were enormous — amounting to many atmospheres.

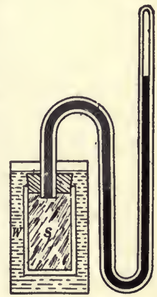


Fig. 80.

The simple device Pfeffer used for measuring these pressures is illustrated in Fig. 80. It consisted of an unglazed porcelain cell, *C*, in the interstices of which the copper ferrocyanide membrane was precipitated. To this cell was attached a manometer, *M*, by means of which the pressures could be determined. Table XL contains Pfeffer's data and illustrates the effect of concentration on this pressure, which is termed osmotic pressure.

Table XL

Per Cent Concentration, c	Osmotic Pressure in cm. Hg., p_O	Ratio, $\frac{p_O}{c}$
1	53.8	53.8
1	53.2	53.2
2	101.6	50.8
2.74	151.8	55.4
4	208.0	52.0
6	307.0	51.3
1	53.5	53.5

The pressure, p_o, which is expressed in centimeters of mercury, is directly proportional to the concentration, *i.e.* $\frac{p_o}{c} = k$.

The effect of temperature on the osmotic pressure of sugar solutions is illustrated by the data in Table XLI.

TABLE XLI — SUGAR AS SOLUTE

TEMP.	p_o CM. HG.
6.8°	50.5
13.2	52.1
13.8	52.2
14.2	53.1
22.0	54.8
36.0	56.7

That is, the osmotic pressure, p_o, is directly proportional to the absolute temperature.

Van't Hoff from a consideration of Pfeffer's data saw that, as in the case of gases, the pressure was proportional to the concentration (Boyle's Law), and also directly proportional to the absolute temperature (Charles', Gay Lussac's Law). Expressing these we have

$$p_o = kcT \qquad (1)$$

The concentration, c, Pfeffer expressed as per cent, but it can be expressed in any way we choose, as we have previously seen. If we state the amount of solute, g, grams in volume, V, then $c = \frac{g}{V}$, or for n gram-molecules of the solute we have $c = \frac{n}{V}$. Substituting this value for c in (1) we have

$$p_o = k\frac{n}{V}T, \text{ or}$$

$$p_oV = nkT$$

which, when $n = 1$, becomes

$$p_o V = kT. \qquad (2)$$

Van't Hoff recognized this as similar to the Gas Law Equation $pV = RT$ and inquired if k were the same as R. This was readily ascertained by calculating the value of k from Pfeffer's data as follows:

A one per cent sugar ($C_{12}H_{22}O_{11}$) solution at 13.8° C. gave an osmotic pressure of 52.2 cm. of mercury.

Since $$p_o V = nkT$$

solving for k we have $k = \frac{p_o V}{nT}$.

Substituting in this equation the following values: p_o = 52.2 cm. of mercury, or 710 grams per square centimeter; a one per cent solution contains 10 grams per liter (assuming the density = 1); and since the molecular weight of sugar is 342, we have $\frac{10}{342}$ gram-molecules in 1 liter, or 1000 cc.

$$\therefore\ n = \tfrac{10}{342} \text{ and } V = 1000 \text{ cc.}$$
$$T = 273° + 13.8° \text{ or } 286.8°$$

we have

$$k = \frac{710 \times 1000}{\frac{10}{342} \times 286.8} = \frac{710 \times 1000 \times 342}{10 \times 286.8}$$

or $$k = 84600 \text{ gram-centimeters per degree.}$$

But R, the gas constant, equals 84,700 gram-centimeters per degree, and van't Hoff concluded, since these values were experimentally the same, that $k = R$, and that we can apply the Gas Law Equation to solutions in which the osmotic pressure of a dilute solution is the same value as the gaseous pressure of an equivalent mass of solute would be at the same temperature, and occupying the volume of the solution.

This application of The Gas Law to solutions is one of the great contributions of van't Hoff to the development of chemistry.

Osmotic Pressure of Solutions

Confirmatory data have been published by numerous workers, including Ladenburg, Adie, Tammann, Ponsot, and particularly Naccari (1897), whose results are among the few marked duplications of Pfeffer's work. A four per cent glucose solution at 0° C. should give an osmotic pressure of 37.6 cm., and Naccari found the following values: 37.0, 37.8, 37.8. For a four per cent mannite solution the calculated value is 38.3 cm. at 0°, and Naccari found 37.3, 37.6, 37.9, 37.5, 37.5, 36.3, 36.4, which is an excellent agreement.

More recently, however, we have the excellent work of Morse and his collaborators (1908–13). This shows a marked confirmation of van't Hoff's generalization, as Table XLII illustrates.

Table XLII

Ratio of observed osmotic pressure to calculated gas pressure at the same temperature, the volume of the gas being that of the solvent in the pure state.

Weight Normal Concentration	Cane Sugar				Glucose	
	Series I		Series II		Series I	
	Temperature	Ratio	Temperature	Ratio	Temperature	Ratio
0.1	18.71°	1.017	24.23°	1.049	25.10°	0.996
0.2	20.91	0.998	21.38	0.996	24.93	0.981
0.3	19.28	1.001	21.67	1.004	22.20	0.986
0.5	20.84	0.993	22.67	1.000	21.86	1.003
0.7	20.14	0.993	23.64	1.000	22.26	0.998
0.8	19.56	1.012	23.69	1.002	23.28	0.991
0.9	19.84	1.006	24.79	0.998	23.80	0.993
1.0	23.32	1.012	23.56	1.010	22.20	1.002

The value of the ratios in this table is approximately unity, and Morse concludes from his results: "That in the vicinity of 20° the osmotic pressure exerted by both cane sugar and glucose is equal to that which a molecular equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to the volume of the solvent in the pure state."

Lord Berkeley and E. G. J. Hartley (1906), instead of measuring the pressure developed in an osmotic cell by the passage of the solvent into the cell, as is usually done, separated the solution from the solvent by a semipermeable membrane and then subjected the solution to a gradually increasing pressure until the solvent which first flowed into the solution reversed its direction and flowed out. The pressure, which was just sufficient to produce this reversal of the current and to prevent the solvent from flowing into the solution, was taken as the equivalent of the osmotic pressure of the solution.

By this new dynamic method Lord Berkeley and Hartley determined the osmotic pressure by measuring the rate of flow of the solvent into the solution. By assuming that this rate of flow is the same as that which would occur if the solvent were caused to pass through the semipermeable membrane under a mechanical pressure equal to the osmotic pressure of the solution, they find that if only the *initial* rate of flow is considered, the values for the osmotic pressure, in the case of dilute solutions, agree well with those obtained by the direct measurement. In concentrated solutions the discrepancy is greater than by the other method, yet it may have wide application.

De Vries, the botanist, worked on the osmotic pressure of plant cells. He found that if a plant cell is placed in a strong sugar solution the cell will shrink, while in a weak solution it will swell up. By the introduction of a cell into other solutions the same results were obtained. The cell wall is permeable to water and impervious to the dissolved substances.

De Vries determined the strength of various solutions that caused the plant cell wall to be just separated from the protoplasm. This process of the separation is designated *plas-*

molysis, and the cell is said to be plasmolyzed. Those solutions of the strength just sufficient to produce plasmolysis are equal in osmotic action. Solutions, such as these, which have the same osmotic pressure, contain equimolecular quantities of the dissolved substances and are called *isotonic* solutions. These results are designated as normal; but another class of compounds gave values for the plasmolysis that were abnormal, and the osmotic pressure values for these solutions were likewise abnormal. The binary substances (uni-univalent) such as KNO_3, NaCl, KBr, $KC_2H_3O_2$, etc., gave practically twice the osmotic action they should have from the gram-molecular content of the solution. Salts (uni-bivalent) of diacid bases and of dibasic acids gave values approximately three times what they should have.

Hamburger obtained, with red blood corpuscles, results which were in accord with the other animal and vegetable organisms employed as semipermeable membranes.

Hence in dilute solutions of different substances we find that the osmotic pressure conforms to all the gas laws, being proportional to the concentration, that is, inversely proportional to the volume (Boyle's Law); the coefficient of variation of the pressure with the temperature is the same for all substances (Gay Lussac's Law); equimolecular solutions have the same osmotic pressure, or conversely, solutions that have the same osmotic pressure contain the same number of moles in a given volume (Avogadro's Law).

The absolute value of the osmotic pressure is the same as the gaseous pressure of the dissolved substance would be if we could allow it to remain at the same temperature and occupy the volume of the solution but remove the solvent.

The laws of gases we have seen hold only for ideal gases; so too we shall see that the application of these to solutions holds only for ideal solutions, but in the case of dilute solutions the variations are not so pronounced as in more concentrated solutions.

CHAPTER XXIV

LOWERING OF VAPOR PRESSURE

In the discussion of one and two component systems it will be recalled that the vapor pressures of these systems were represented on pt diagrams. In Fig. 81 we may represent the vapor pressure on the vertical axis and the temperature on the horizontal axis. Then the vapor pressure of the system water may be represented by the following curves:

CB = the vaporization curve.
CD = the sublimation curve.
CA = the fusion curve.

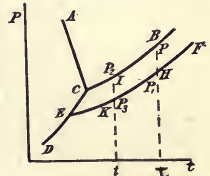


Fig. 81.

As a second component (a nonvolatile solute) is added, the vapor pressure of the solvent is lowered, and for a specified concentration the vapor pressure of the solution would be represented by the curve EF. At a specified temperature, t, the vapor pressure of the solvent has been lowered by the addition of the solute from p to p_1. That is, at the temperature t the vapor pressure of the solvent p_1 is equal to Bt, and the vapor pressure of the solution at the same temperature t is Ht, then the vapor pressure has been lowered $p - p_1$ or BH. At any other temperature, t_1, the lowering of the vapor pressure is IK or $p_2 - p_3$. The ratio of the lowering to the original vapor pressure of the pure solvent is $\frac{p - p_1}{p} = \frac{BH}{Bt}$ and $\frac{IK}{It_1} = \frac{p_2 - p_3}{p_2}$. But von Babo showed that the ratio of the lowering of the vapor pressure of the solvent to the vapor pressure of the pure solvent is not a function of the temperature, hence

$$\frac{p - p_1}{p} = \frac{BH}{Bt} = \frac{IK}{It_1} = \frac{p_2 - p_3}{p_2}$$

therefore $$\frac{p - p_1}{p} = k\,.$$

We have seen that the amount of lowering of the vapor pressure of the solvent is proportional to the concentration. This is known as *Wüllner's Law*, which is expressed as follows: The ratio of the change in the vapor pressure of the solvent to the vapor pressure of the solvent is proportional to the concentration, *i.e.*

$$\frac{p - p_1}{p} = kc.$$

If we express the concentration in terms of the number of moles of the solvent and of the solute, we have

$$\frac{p - p_1}{p} = k\frac{n}{N}$$

in which n = the number of moles of the solute and N the number of moles of the solvent. This is known as *Raoult's Law*.

Employing ether as a solvent, Raoult showed that the ratio of the vapor pressures of solvent and solution is independent of the temperature, which is a confirmation of von Babo's Law. This is evident from Table XLIII.

TABLE XLIII

(After Jones)

16.482 Grams Oil of Turpentine in 100 Grams of Ether				10.442 Grams Aniline in 100 Grams Ether			
Temperature	Vapor Pressure		Ratio $\frac{p_1}{p}\times 100$	Temperature	Vapor Pressure		Ratio $\frac{p_1}{p}\times 100$
	of Solvent p	of Solution p_1			of Solvent p	of Solution p_1	
1.1°	199.0	188.1	91.5	1.1°	199.5	183.3	91.9
3.6	224.0	204.7	91.4	3.6	223.2	204.5	91.6
18.2	408.5	368.7	91.0	9.9	289.1	264.0	91.3
21.8	472.3	430.7	91.2	21.8	472.9	432.7	91.5

Raoult selected a number of substances with a low vapor pressure, such as oil of turpentine, aniline, nitrobenzene, ethyl salicylate, etc., the boiling points of which ranged between 160° and 222°, and dissolved these in ether, which has a high vapor pressure as compared with the solutes. In Table XLIV are given the solutes, the molecular weights, n, the number of moles of the solutes, $\frac{p - p_1}{p}$, the ratio of the change in the vapor pressure of the solvent, caused by addition of the solute, to the vapor pressure of the solvent, *i.e.* the fractional lowering of the vapor pressure, and in the next column, $\frac{p - p_1}{np}$, the fractional lowering produced by one mole when dissolved in 100 moles of ether. K is the molar lowering of the vapor pressure when 100 grams of the solvent are employed.

TABLE XLIV

SOLUTES	MOLECULAR WEIGHT	n	$\frac{p-p_1}{p}$	$\frac{p-p_1}{np}$	K
Turpentine	136	8.95	0.0885	0.0099	0.71
Methyl salicylate	152	2.91	0.026	0.0089	0.71
Methyl benzoate	136	9.60	0.091	0.0095	0.70
Benzoic acid	122	7.175	0.070	0.0097	0.71
Trichloracetic acid	163.5	11.41	0.120	0.0105	0.71
Caprylic alcohol	130	6.27		0.0110	0.73
Aniline	93	7.66	0.081	0.0106	0.71
Cyanic acid	43				0.70
Benzaldehyde	106				0.72
Cyanamide	42				0.74
Antimony trichloride	228.5			0.0087	0.71
Carbon hexachloride	237			0.0100	0.71

From Raoult's Law $\frac{p - p_1}{p} = k\frac{n}{N}$, we have $\frac{p - p_1}{np} = \frac{k}{N}$, which is the value given in the next to the last column. The mean value of fourteen substances employed by Raoult was

0.0098, which is practically 0.01, that is, one mole of any substance dissolved in 100 moles of the solvent (ether) lowers the vapor pressure of the solvent one one-hundredth of its value. And since $N = 100$ and $\frac{p - p_1}{np} = 0.01$, we have on substitution $0.01 = \frac{k}{100}$ or $1 = k$. That is, the constant of Raoult's Law is *unity* for ether, and so the expression for the law becomes $\frac{p - p_1}{p} = \frac{n}{N}$ in general. From the data presented in Table XLV the mean value of the constant for a large number of solvents is 0.0105, which is virtually one one-hundredth. Therefore, one mole of a nonvolatile substance

TABLE XLV

(After Jones)

Solvents	Mol. Weight	K	$\frac{K}{M}$
Water	18	0.185	0.0102
Phosphorus trichloride	137.5	1.49	0.0108
Carbon bisulphide	76	0.80	0.0105
Tetrachlor methane	154	1.62	0.0105
Chloroform	119.5	1.30	0.0109
Amylene	70	0.74	0.0106
Benzene	78	0.83	0.0106
Methyl iodide	142	1.49	0.0105
Ethyl bromide	109	1.18	0.0109
Ether	74	0.71	0.0096
Acetone	58	0.59	0.0101
Methyl alcohol	32	0.33	0.0103
		Average value	0.0105

dissolved in 100 moles of any volatile liquid lowers the vapor pressure of this liquid by a nearly constant fraction approximately 0.01 of its value. We are therefore justified in expressing Raoult's Law thus, $\frac{p - p_1}{p} = \frac{n}{N}$, remembering that the proportionality factor is unity.

For concentrated solutions, in the equation $\frac{p - p_1}{p} = \frac{n}{N}$, the right-hand member may become $\frac{n}{N} = 1$, when the solution is so concentrated that the number of moles (n) of the solute is equal to the number of moles (N) of the solvent. Then $\frac{p - p_1}{p} = 1$, and this may be written $\frac{p}{p} - \frac{p_1}{p} = 1$, which becomes $\frac{p_1}{p} = 0$, which is an impossibility, for the vapor pressure of a concentrated solution will always have some numerical value. Raoult therefore changed the formula to read $\frac{p - p_1}{p} = \frac{n}{N + n}$, which expresses the ratio of the number of moles of the solute to the *total* number of moles present, and this holds for concentrated solutions.

If we obtain the relative lowering of the vapor pressure of $\frac{p - p_1}{p}$ when we have a specified weight, g, of the solute dissolved in a constant quantity of the solvent, then $\frac{p - p_1}{gp}$ is the relative lowering for one gram of solute, and $\frac{(p - p_1)\,m}{gp}$ is the lowering for one mole of the solute. That is, $\frac{(p - p_1)\,m}{gp}$ is the fractional *molecular lowering of the vapor pressure.* Values of K for 100 grams of the solvent are given in Table XLV.

The lowering of the vapor pressure can be utilized as a means for the determination of the molecular weight of substances. By definition

$n = \frac{g}{m}$, in which g is the grams of the solute and m the molecular weight, and $N = \frac{S}{M}$, in which S is the grams of the solvent and M is its molecular weight.

Substituting in the modified Raoult formula, which is

$$\frac{p - p_1}{p} = \frac{n}{N + n},$$

we have

$$\frac{p - p_1}{p} = \frac{\frac{g}{m}}{\frac{S}{M} + \frac{g}{m}}.$$

This equation may be used for calculating the molecular weight of the solute, or if this is known, the vapor pressure, p_1, of the solution can be ascertained providing the other terms of the equation are known.

Relation of the Lowering of the Vapor Pressure to Osmotic Pressure

The vapor pressure of a solution is intimately related to the osmotic pressure of the solution. Suppose that an aqueous solution of a nonvolatile solute and the pure water be placed in separate vessels under a bell jar and the air exhausted until the liquids are virtually under the pressure of the vapor of the pure solvent. Since the vapor pressure of the solution is less than that of the pure solvent, distillation will take place from the pure solvent to the solution, where condensation will occur with an increase in the volume of the solution and a resulting decrease in the volume of the solvent. By keeping the solution stirred, the dilution will continue until the liquids are in equilibrium with the vapor directly above and in contact with them.

If we have two isotonic solutions, A and B, separated by a semipermeable membrane and contained in an inclosed vessel, and if the saturated vapor above the solutions be not the same, there will be a passage of the vapor from the one solution, A, to the other, B, resulting in the dilution of B and a corresponding concentration of A. This change in concentration would cause the passage of the solvent through the semipermeable membrane from B to A, which would result in the production of a condition for a perpetual motion. It therefore follows that in the case of isotonic solutions the vapor pressures are equal.

By a simple proof Arrhenius has shown the relation between the vapor pressure and osmotic pressure without the use of thermodynamics.

In Fig. 82 is illustrated an osmotic pressure cell in which the solution within the cell has come to rest at the height h, and all is inclosed under the bell jar from which the air has been removed, leaving the system under the pressure of the vapor of the pure solvent. At equilibrium the solvent does not pass by distillation either into the solution or out of it. But the vapor pressure, p, of the solvent is greater than the vapor pressure, p_1, of the solution by the weight of the column of vapor represented by the difference between the height h of the two surfaces. Therefore, the vapor pressure of the solution must be less than the vapor pressure of the pure solvent by the amount equivalent to the weight of the column of vapor of unit area of the height h. That is,

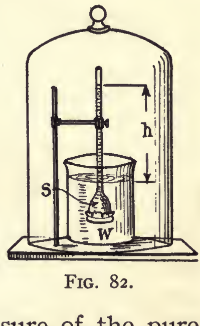


FIG. 82.

if p = vapor pressure of solvent
p_1 = vapor pressure of solution
h = height of the osmotic column
ρ = density of the vapor of solvent

then
$$p - p_1 = h\rho. \qquad (1)$$

The osmotic pressure of the solution is equivalent to the weight of the column of the solution per unit area of the height *h*. Hence the change in the vapor pressure is to the osmotic pressure as the weight of any volume of vapor is to the weight of the same volume of the liquid, which gives

$$\frac{p - p_1}{p_o} = \frac{\rho}{\rho_1} \qquad (2)$$

in which ρ_1 is the density of the solution. Now, since $\rho = \frac{nM}{V}$, substituting in the Gas Law Equation, $pV = nRT$, we have $\rho = \frac{pM}{RT}$. Similarly, since $\rho_1 = \frac{g}{V}$, in which g is the weight of the solution and V its volume, substituting in van't Hoff's equation for osmotic pressure, $p^oV = nRT$, we have $\rho_1 = \frac{gp_o}{nRT}$. Then $\frac{\rho}{\rho_1} = \frac{pnM}{p_o g}$. Substituting this value in equation (2) we have $p - p_1 = \frac{pnM}{g}$. As g is the weight of the solvent (of an infinitely dilute solution) and M the molecular weight as determined from the vapor density (no assumption is made concerning its molecular weight in the liquid state), $\frac{M}{g} = \frac{1}{N}$, the reciprocal of the number of moles of the solute. The equation then takes the form

$$p - p_1 = \frac{pn}{N} \text{ or } \frac{p - p_1}{p} = \frac{n}{N}$$

which is *Raoult's Law.*

CHAPTER XXV

FREEZING POINTS AND BOILING POINTS OF SOLUTIONS

It will be recalled that the freezing point is the temperature at which the three phases — solid, liquid, and vapor — are in equilibrium, and is represented by A in Fig. 83. On the pt diagram, AB is the vapor pressure curve of pure water, and AC is the sublimation curve. The intersection, A, is the triple point and represents the temperature and pressure at which the three phases — ice, liquid, and vapor — are in equilibrium. The pressure is, however, the vapor pressure of the pure substance and is, as we have previously seen, 4.6 mm., while the temperature is not 0° C., since the freezing point is designated as the temperature of equilibrium under atmospheric pressure. The freezing point is then not quite the same as the triple point A, but at 760 mm. pressure differs from it slightly, the freezing point being 0.0075° lower than the transition point. As the change for one atmosphere pressure is small, for a few millimeters difference in pressure the differences are negligible, and no serious error is introduced in practice if we consider the two points identical, remembering, however, that to obtain the true transition point correction for the pressure must be made.

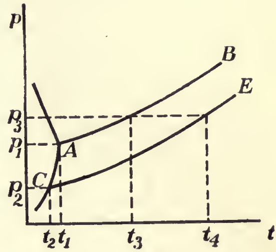


FIG. 83.

For the solution, the vapor pressure is lower than the vapor pressure of the pure solvent, and at some specified concentration we shall assume that the line CE represents the vapor pressure of the solution. The intersection, C, of the vapor pressure curve, *CE*, of the solution, and the sublimation curve, *AC*, represents the equilibrium between ice, solution, and vapor, and is the freezing point of the solution. The freezing point then has been lowered from the temperature t_1, to the temperature t_2, *i.e.* the lowering of the freezing point is $t_1 - t_2$, and at the same time the vapor pressure has been lowered from p_1, that of the pure solvent, to p_2, the vapor pressure of the solution, or $p_1 - p_2$.

It is therefore apparent that the lowering of the freezing point bears an intimate relation to the lowering of the vapor pressure of solutions, and there must be a way of expressing this lowering of the freezing point in terms of the lowering of the vapor pressure of the solvent.

It should be remembered that we are assuming that the solid phase separating from the solution is pure solvent, otherwise we might get a rise of the freezing point, as in the case where solid solutions or isomorphous mixtures are separated out. In the case of the separation of eutectic mixtures the simple relation will not hold.

As early as 1788 Blagden showed that the freezing points of aqueous solutions of a given substance are lower than that of the pure substance, and that this lowering of the freezing point is proportional to the concentration. But it was not until the work of Rüdorff (1861) and of Coppet (1871) that attention was given to the freezing point of solutions. It was, however, the work of Raoult, published in 1882, that presented the fundamental facts. He showed that the lowering of the freezing point is proportional to the concentration, and that the lowering of the freezing point of solutions for various solutes is nearly the same when one mole of the solutes is dissolved in the same amount of the solvent. He found that this is true not only for water but also for a large number of organic solvents as well. This is illustrated in Table XLVI, which contains some of Raoult's extensive data. The molecular lowering represents the lowering of the freezing point produced by one mole of solute dissolved in 100 grams of the solvent.

Table XLVI

Solvent: Water

Solute	Molecular Lowering in Degrees C.	Solute	Molecular Lowering in Degrees C.
Acetamide	17.8	Hydrochloric acid	39.1
Acetic acid	19.0	Nitric acid	35.8
Aniline	15.3	Sulphuric acid	38.2
Cane sugar	18.5	Potassium hydroxide	35.3
Ether	16.6	Sodium hydroxide	36.2
Ethyl alcohol	17.3	Barium chloride	48.6
Ethyl acetate	17.8	Calcium chloride	49.9
Glycerine	17.1	Potassium chloride	33.6
Phenol	15.5	Sodium chloride	35.1
Urea	17.2	Potassium nitrate	30.8

Solvent: Benzene

Solute	Molecular Lowering in Degrees C.	Solute	Molecular Lowering in Degrees C.
Anthracene	51.2	Acetic acid	25.3
Aniline	46.3	Benzoic acid	25.4
Carbon disulphide	49.7	Amyl alcohol	39.7
Chloral	50.3	Ethyl alcohol	28.2
Chloroform	51.1	Methyl alcohol	25.3
Ether	49.7	Phenol	32.4
Methyl iodide	50.4		
Naphthalene	50.0		
Nitrobenzene	48.0		
Nitroglycerine	49.9		

Solvent: Nitrobenzene

Solute	Molecular Lowering in Degrees C.	Solute	Molecular Lowering in Degrees C.
Benzene	70.6	Acetic acid	36.1
Chloroform	69.9	Benzoic acid	37.7
Ether	67.4	Ethyl alcohol	35.6
Stannous chloride	71.4	Methyl alcohol	35.4

Solvent: Acetic Acid

Solute	Molecular Lowering in Degrees C.	Solute	Molecular Lowering in Degrees C.
Benzoic acid	43.0	Hydrochloric acid	17.2
Chloroform	38.6	Sulphuric acid	18.6
Chloral	39.2	Magnesium acetate	18.2
Ether	39.4		
Ethylene chloride	40.0		
Ethyl alcohol	36.4		
Glycerine	36.2		
Nitrobenzene	41.0		
Stannic chloride	41.3		
Water	33.0		

From the above tables it will be observed that the substances on the left hand give for the same solvent approximately the same molecular lowering of the freezing point. In the case of water the solutes listed in the right-hand side of the table give molecular lowerings approximately twice, in some cases three times, as great as the normal values listed in the other column of the table. These abnormally high values for the molecular lowering are attributed to the *dissociation* of the solute, analogous to the abnormal values of the density of certain vapors which we attribute to the increased number of parts or molecules resulting from the dissociation of the substance. We shall refer to this type of abnormal values later for a full discussion. In the case of benzene, nitrobenzene, and acetic acid, when used as solvents, we observe that the values for the molecular lowering in the left-hand column are approximately twice the values in the right-hand column. The normal values are considered to be those in the left-hand column, while the smaller values are designated the abnormal values, and these abnormally small lowerings are explained upon the basis of the *association* of some of the solute molecules. The lowering of the freezing point is proportional to the number of dissolved molecules, and as shown from the values given in the above table, it is independent of their nature. We have previously seen that some substances in the liquid state have molecules which are aggregates of the molecules of the substance when it is in the gaseous state, *i.e.* they are said to be associated. These abnormal values of the molecular lowering can be accounted for by assuming that there is a decrease in the number of molecules of the solute due to association, while in the case of some solutes in water the increase in the number of molecules of the solute is due to the dissociation of the solute molecules.

Molecular Weight Determinations

Freezing Point Method. — Let

g = the number of grams of solute

m = the molecular weight in grams of solute

S = the weight in grams of the solvent

Δ = the lowering of the freezing point produced by g grams of solute in S grams of solvent.

Then

$\frac{\Delta}{g}$ = lowering of freezing point produced by one gram of solute in S grams of solvent.

$\frac{S\Delta}{g}$ = lowering of freezing point produced by one gram of solute in one gram of the solvent.

$\frac{mS\Delta}{g}$ = lowering of freezing point produced by one mole of solute in one gram of the solvent, *i.e.* the molecular lowering.

$\frac{mS\Delta}{100\,g}$ is the molecular lowering for 100 grams of the solvent.

But we saw that for a specified solvent the molecular lowering is constant, hence we have

$$\frac{mS\Delta}{100\,g} = K_F.$$

And solving for m we have

$$m = \frac{100\ K_F g}{S\Delta}$$

in which $K_F g$ is the molecular lowering when one mole is dissolved in 100 grams of solvent; then 100 K_F would be the molecular lowering when one mole is dissolved in one gram of solvent.

From this equation we have a method for calculating the molecular weight of a substance from the freezing point lowering, for it is only necessary to determine Δ, the lowering produced when g grams of solute are dissolved in S grams of the solvent, and the constant K_F is known for the solvent.

We have seen that Raoult determined the value for K_F experimentally. Subsequently a very large amount of work has been done in order to obtain this value with a high degree of accuracy. Nernst and Abegg discussed the theory of the freezing point determinations, and Beckmann has devised the common form of apparatus employed in these determinations. We define the freezing point as the temperature at which the liquid and solid solvent are in equilibrium at atmospheric pressure.

In Beckmann's apparatus, Fig. 84, we have an inner vessel, in which a thermometer and a stirrer are placed, containing an isolated mass of liquid to be frozen. This is surrounded by another tube forming an air jacket, which in turn is surrounded by the freezing mixture. In this determination it is assumed that when the liquid freezes a small quantity of ice is formed, and this is in equilibrium with the liquid at a fixed temperature, which is taken as the true freezing point of the liquid. But as Nernst and Abegg have shown, this isolated mass of liquid and ice is at a higher temperature than the surrounding freezing mixture and will therefore radiate heat, which would result in the establishment of some intermediate equilibrium temperature below the true freezing point of the liquid under investigation. Then, too, the rate of stirring will affect the equilibrium temperature as well as the amount of ice which separates at the time of freezing the solution. Hence it is evident that unless this equilibrium temperature does not coincide with the freezing point, the reading of the thermometer will not record the true freezing point of the liquid.

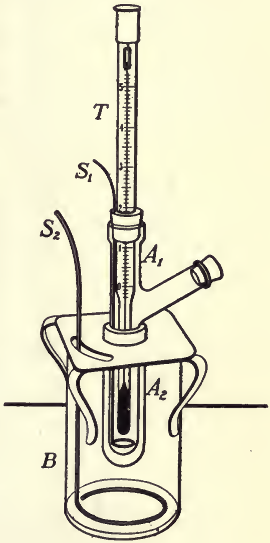


FIG. 84.

Recent investigators have aimed to produce conditions such as to eliminate as many of these sources of error as possible, with the result that the values of K_F for a large number of solvents are fairly accurately known. For water the accepted value of K_F is 18.6. That is, one mole of the solute when dissolved in 100 grams of the solvent will lower the freezing point of water 18.6°; if one mole is dissolved in one liter (1000 grams) the constant becomes 1.86, *i.e.* the freezing point is lowered 1.86°. If one mole could be dissolved in one gram of solvent, the freezing point would be lowered 1860°, *i.e.* the freezing point constant is 1860. Various authors use these different values for K_F, and hence more or less confusion may arise. In Table XLVI we saw that in one of the columns are given abnormal values for the molecular lowering of the freezing point; an explanation of these will be taken up subsequently.

Boiling Point Method. — By referring to Fig. 83 it will be observed that if p_3 represents the vapor pressure of the pure solvent and is one atmosphere, then the boiling point is t_3, and for a solution of such concentration that its vapor pressure curve is represented by CE, the boiling point would be represented by t_4. The boiling point of the solvent has been raised by the addition of the solute from t_3 to t_4, that is, the rise of the boiling point is $t_4 - t_3$, while the pressure has remained constant.

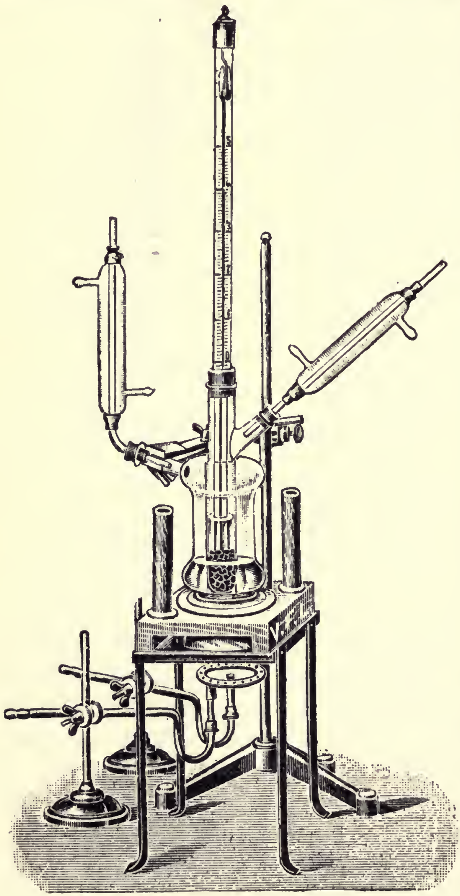


FIG. 85.

That the rise of the boiling point of solutions is proportional to the concentration was emphasized by Raoult and has been confirmed subsequently. Raoult devised a method by means of which these small changes can be measured accurately; in Fig. 85 is represented the general form of the apparatus. As in the freezing point method so in the boiling point method a constant quantity of the solvent is employed, S, in which g grams of the solute are dissolved, and a rise of the boiling point of Δ degrees is obtained. A formula similar to that obtained by the freezing point method may be obtained, from which the molecular weight of the solute may be calculated, that is, $m = \frac{100\ K_B g}{S\Delta}$, in which K_B is the molecular rise when one mole of the solute is dissolved in 100 grams of the solvent.

An additional discussion of these two methods and the significance of the constants will be presented in the following chapter.

CHAPTER XXVI

THERMODYNAMIC CONSIDERATIONS

ABOUT 1798 Count Rumford's experiments on the boring of cannon convinced him that heat is nothing more than energy of motion. Heat had been termed caloric, an igneous fluid, and this new view received but slight attention until the determination of a numerical relation between the quantity of work and quantity of heat made by Robert Mayer (1842) and by James Prescott Joule (1843) were published. Various experiments in this field have been performed, such as the heat effects produced by the friction of liquids, by the compression of gases, heating effect of electric currents; and the agreement between the results is as close as the errors of experimentation justify. These lead to the formulation of the Principle of Equivalence, familiarly known as the First Law of Thermodynamics or the Mayer-Joule Principle:

"*When heat is transformed into work, or conversely when work is transformed into heat, the quantity of heat gained or lost is proportional to the quantity of work lost or gained.*"

The old fundamental notion that a body or system "contains so much heat" necessitates obtaining a clear conception of the terms heat, work, and energy.

If we have a given mass of a gas under specified conditions of pressure and temperature, it will occupy a certain volume. If this gas be brought into contact with a body at a higher temperature and the pressure remain constant, the volume will increase, which, under suitable conditions, would result in doing mechanical work. The system receives heat energy from an external source and in turn does mechanical work. The relation between the heat energy imparted and the mechanical energy obtained is represented in the statement that the total energy gained by a body is equal to the energy supplied to it in the form of heat, and in any other form of energy, *i.e.* the energy supplied in the form of heat can be obtained in the form of work, and energy supplied as work is withdrawn as heat. These are statements of the law of Conservation of Energy.

It is only under perfect conditions that one form of energy can be completely transformed into another, and the reverse transformation accomplished. Such a process is termed reversible. All processes are actually irreversible. The maximum quantity of heat that can be converted into work by any machine depends upon the Principle of Carnot-Clausius and is known as the Second Law of Thermodynamics or the Law of Degradation of Energy. "*Heat cannot pass from a colder to a warmer body without some compensating transformation taking place*," or "*It is impossible by means of a self-acting machine unaided by any external agency to convey heat from one body to another at higher temperature*," or "*No change in a system of bodies that can take place of itself can increase the available energy of the system.*"

Availability of Energy. — Mechanical energy as well as electrical energy can be completely transformed into heat energy, but heat energy cannot be completely converted into mechanical energy.

It is not the actual amount of energy a system possesses, but the amount that can be utilized in any special transformation desired, that is of importance; that is, it is the part of the energy present that is available and that can be utilized in any particular transformation.

Let dU represent the increase of the intrinsic energy of a system when the work, dW, is done by the addition of the *quantity of heat*, dQ. Then,

$$dQ = dU + dW.$$

This is the quantity of heat absorbed by the system, which increases its intrinsic energy and does external work. In this equation Q, U, and W are measured in the same units of energy. If Q is measured in heat units and U and W in mechanical units, Joule's equivalent, J, must be used on the left-hand side. We consider dQ positive when the system absorbs heat, negative when it gives out heat; dW is positive when work is done *by* the system, dU is positive when the intrinsic energy is increased during the transformation.

Carnot's Cycle. — Since it is impossible to obtain work from the heat of a system unless there is another system at a lower temperature, Carnot showed that it is possible to obtain work continuously from the two systems at different temperatures by employing a third intermediate system and causing it to undergo a series of cyclic transformations known as Carnot's Cycle.

Suppose we have two systems, S, a source, and R, a refrigerator, at the constant temperatures t_1 and t_2, respectively, with $t_1 > t_2$. If they are placed in contact, heat will flow from S to R and no work will be done; but if they are kept separated and a third system, M, used to convey the energy, work can be obtained.

1. The system M at the temperature t_2 is brought by some convenient mechanical means, without gain or loss of heat, to the temperature t_1 (for a gaseous system, by compression). This is called *adiabatic* action.

2. It is now placed in contact with the system S and receives from it a certain quantity of heat, Q_1, while its temperature remains constant and equal to t_1. The system M also expands and does work. This is called *isothermal* action, as there is no change of temperature.

3. The temperature is now allowed to fall to t_2 without the medium receiving or parting with heat (by expansion of a gas). Adiabatic action.

4. The system M is brought in contact with the refrigerator R and is allowed to return to the initial state. During this change a certain quantity of heat, Q_2, is given up to the refrigerator. Isothermal action.

This may be represented diagrammatically by the p-V diagram, Fig. 86.

1. At the volume and pressure designated by A at the temperature t_2, by adiabatic compression the volume will change as indicated by the line AB without gain or loss of heat.

2. Along the isothermal line BC we have the change of volume indicated, while the quantity of heat, Q_1, is being absorbed by the system at the constant temperature t_1.

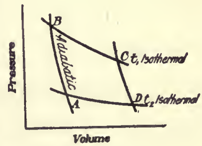


FIG. 86.

3. During the fall in temperature the adiabatic line CD represents the change in volume through expansion while cooling to the temperature t_2.

4. The isothermal DA at temperature t_2 represents the change during which the quantity of heat Q_2 has been given up to the refrigerator.

This is known as the *Carnot Cycle*, and the work done in the cycle is represented by the area $ABCD$. The difference $Q_1 - Q_2$ is the heat transformed into work. This process could be reversed. Then we should have the same area, $ABCD$.

By this perfectly *reversible* process, the Carnot Cycle, work can be derived indefinitely from a single source and refrigerator maintained at given constant temperatures, but since this cannot be exactly obtained on account of resistance, friction, velocity, etc., the resulting cycle in practice is irreversible, and consequently the maximum work cannot be obtained.

Efficiency is defined as the ratio between what is obtained to that which might be obtained. The quantity of heat Q_1

is the amount that is supplied, but $Q_1 - Q_2$ is the amount that is transformed, or it is the part of Q_1 that is actually available; then the ratio $\frac{Q_1 - Q_2}{Q_1}$ is called the efficiency, or the availability of Q_1 for transformation into work.

If reversible cycles are operated between the same source and refrigerator, they have the same efficiency. This is seen as follows: Let

$$\frac{Q_{1a} - Q_{2a}}{Q_{1a}} > \frac{Q_{1b} - Q_{2b}}{Q_{1b}}.$$

If the more efficient cycle be used as an engine moving directly to drive the less efficient cycle in a reverse direction, the numerators which represent the work would be equal, and hence $Q_{1b} > Q_{1a}$. This means that the cycle *b* returns more heat to the source than cycle *a* takes from the source; or, heat flows from a point of low temperature to a point of high temperature. This is impossible, and hence cycle *a* cannot be more efficient than *b*. In the same way *b* cannot be more efficient than *a*. The efficiencies, therefore, are equal. If *a* were a non-reversible cycle, the above proof would show that it could not have a higher efficiency than that of *b*, but we could not prove that it was less. In other words, no cycle can be more efficient than a reversible cycle when acting between the same source and refrigerator. The reversible cycle therefore has the maximum efficiency.

The absolute temperature is sometimes defined by the statement that the absolute temperatures of two bodies are proportional to the quantities of heat given up by one body to the medium and rejected by the medium to the other in the Carnot cyclic transformation in which the bodies play the part of source and refrigerator. Using this concept, we have

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \quad \text{then} \quad \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

would be the value of the efficiency of the Carnot Cycle. The portion of the heat energy available for work between the two temperature limits, T_1 and T_2, would be $\frac{T_1 - T_2}{T_1}$ which is designated the *availability*. So if Q_1 is the quantity of heat absorbed by a system at the temperature T_1, then if T_2 is the temperature of the refrigerator, $\left(\frac{T_1 - T_2}{T_1}\right) Q_1$ is the quantity available for useful work, and $\left(\frac{T_2}{T_1}\right) Q_1$ is the quantity unavailable, or the waste; or the Available Work = $Q_1 \frac{\Delta T}{T}$.

Applications to Solutions. — The following is van't Hoff's proof of the application of The Gas Law to dilute solutions, and is virtually his own presentation: By means of a reversible cyclic process carried out at a constant temperature, T, one mole of the dissolved substance is to be removed from an aqueous solution in the form of a gas and restored to it again. By raising the pistons A and B, Fig. 87, remove the solute through ac, a semipermeable membrane impervious to the solvent. Remove the pure solvent to the outside through the walls ab and cd, which are impervious to the dissolved substance, so as to maintain a constant concentration. By the two pistons, A and B, the equilibrium is to be maintained between the gas pressure and the osmotic pressure. At the temperature T_1 and pressure p_1 one mole of the solute will occupy a volume V_1 as a gas. The absorption of the gaseous solute is such that the gas is in equilibrium with a solution that contains one mole of the solute in volume V_O, the osmotic pressure of which is p_O.

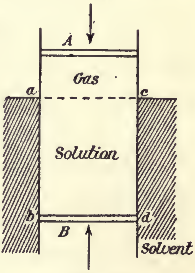


Fig. 87.

The action desired includes the following steps:

I. If both pistons be moved upward, one mole of the solute may be removed reversibly and at constant pressure from the solution, and the amount of work done by it on A is p_1V_1. By The Gas Law

$$p_1V_1 = RT_1 \qquad (1)$$

An amount of work is performed by B against the constant osmotic pressure, which will be expressed with a negative sign as

$$-p_OV_O \qquad (2)$$

II. By a second process restore the solute to the solution. First let the gas expand isothermally to an infinite volume, V_∞, and in so doing perform work

$$\int_{V_1}^{V_\infty} p\,dV = RT_1\int_{V_1}^{V_\infty}\frac{dV}{V} = RT_1 \log_e \frac{V_\infty}{V_1}. \qquad (3)$$

This infinitely diluted gas may now be brought into contact with the volume V_O of solvent, and under these circumstances the solvent would not absorb any of the gas because the gas pressure is zero.

III. Now let the piston be lowered so that the solute is brought into solution, as the pressure rises. The expenditure of work is

$$-\int_0^{V_\infty} p\,dV.$$

Here, however, p has not the value given by $pV = RT$, but a smaller value, because a part of the vapor has gone into solution, as the pressure rises. This part is exactly one mole when the pressure has increased to p_1, and consequently if Henry's Law be true, when the pressure is p, the quantity of gas absorbed amounts to p/p_1 moles: the undissolved part remaining is therefore $(1 - p/p_1)$ moles and p may be calculated from

$$pV = (1 - p/p_1)\,RT_1 = RT_1 - pV_1$$

so that

$$p = \frac{RT_1}{V + V_1}.$$

Consequently the work done is

$$-\int_o^{V_\infty} p\,dV = -RT_1\int_o^{V_\infty}\frac{dV}{V + V_1} = -RT_1\log_e\frac{V_1 + V_\infty}{V_1}$$

since V_∞ is infinitely great, in comparison to V_1, the expression becomes

$$-RT_1\log_e\frac{V_\infty}{V_1}. \tag{4}$$

Since the total work done in a reversible cyclic process at constant temperature must be zero because the cycle of Fig. 83 would have no area,

$$(1) + (2) + (3) + (4) = 0$$

and

$$RT_1 + (-p_0V_0) + RT_1\log_e\frac{V_\infty}{V_1} + \left(-RT_1\log_e\frac{V_\infty}{V_1}\right) = 0$$

or

$$p_0V_0 = RT_1.$$

But

$$p_1V_1 = RT_1$$

since T_1 is constant we see that for equal values of V_1 and V_0 we must have

$$p = p_0.$$

From this we see that for any dissolved body which conforms to Henry's Law, for the same temperature and concentration the gas pressure and the osmotic pressure of its solution must be equal.

Assuming that a gas dissolving according to Henry's Law has the same molecular character in the solution and in the gas, we may consequently draw all the conclusions as to the osmotic pressure of dissolved bodies that have been drawn as to gas pressure or vapor pressure, *i.e.* we may apply Avogadro's Law to solutions, making use of the osmotic pressure instead of the gas pressure. It follows that The Gas Law can be applied to solutions.

Relation between Lowering of Vapor Pressure due to the Solute and the Osmotic Pressure

By making use of the fundamental conceptions of thermodynamics van't Hoff showed by the following isothermal reversible cyclic process the relation between the osmotic pressure and the lowering of the vapor pressure of the solvent due to the presence of a non-volatile solute.

Let us assume that we have a solution containing a non-volatile solute, the vapor pressure of the solution being p_1 and that of the solvent p. Then, as shown above, $p > p_1$. Let p_O be the osmotic pressure of the solution.

The following order in the cyclic process is taken:

I. By means of a semipermeable membrane as a piston, remove through the piston osmotically and reversibly the amount of the solvent containing one gram-molecule of the solute, *i.e.* $\frac{mS}{g}$ grams. Then $V_O = \frac{mS}{g\rho}$. The work done is $p_O V_O$ where V_O is the volume in which one mole of the solute is dissolved and p_O the osmotic pressure.

II. Now restore reversibly this quantity of solvent by distilling it, expanding isothermally to pressure p_1, condensing, and returning this solvent to the solution.

At the temperature T and pressure p we gain a quantity of work done by the reversible evaporation.

By expanding this vapor (which is considered to be a gas) at the temperature T to the pressure p_1, an additional quantity of work is gained. For one mole of the vapor of the solvent the work gained would be

$$RT \log_e \frac{p}{p_1}$$

and for the mass containing one gram-molecule of the solute, it would be

$$\frac{mS}{gM} RT \log_e \frac{p}{p_1}.$$

Finally, the vapor is to be condensed in contact with the solution at p_1 and T, in which process the work gained by evaporation is used up. The heats required for evaporation and obtained from condensation are assumed equal. Since this cyclic process has been carried out at constant temperature, the net work is zero as before, and the osmotic work spent must equal the work of expansion gained,

$$p_O V_O = \frac{mS}{Mg} RT \log_e \frac{p}{p_1}.$$

Substituting for V_O its value above, we obtain

$$p_O \frac{mS}{g\rho} = \frac{mS}{Mg} RT \log_e \frac{p}{p_1}$$

from which we get

$$\log_e \frac{p}{p_1} = \frac{Mp_O}{\rho RT}$$

which is the relation sought. In dilute solutions $p_O V_O = nRT$ where n = number of molecules dissolved in volume V_O. From this, since $\frac{p_O}{RT} = \frac{n}{V_O}$, substituting we have

$$\log_e \frac{p}{p_1} = \frac{M}{\rho} \frac{n}{V_O}.$$

This is an accurate form of Raoult's Law. If the difference between p and p_1 is small one may substitute in place of $\log_e \frac{p}{p_1}$, $\frac{p - p_1}{p}$ and obtain

$$\frac{p - p_1}{p} = \frac{M}{\rho} \frac{p_O}{RT}$$

or

$$\frac{p - p_1}{p} = \frac{M}{\rho} \frac{n}{V_O}.$$

Since $\frac{M}{\rho} = V_{(\text{mole})}$, the volume of one mole of the solvent and V_O is the volume of the solution which when very dilute becomes the volume of the solvent, hence $Vo/V_{(\text{mole})} = N$, the number of moles of the solvent. This is the reciprocal of what we have in the formula, hence we have

$$\frac{p - p_1}{p} = \frac{n}{N}.$$

This is the form of Raoult's Law previously used.

Relation between the Osmotic Pressure and the Lowering of the Freezing Point of the Solvent due to a Non-volatile Solute

The following cyclic process showing the relationship between the osmotic pressure of solutions and the lowering of the freezing point of the pure solvent when the non-volatile solute is present cannot be carried out at constant temperature and hence involves the Second Law of Thermodynamics.

Let us assume that we have a large mass of a very dilute solution such that when the amount of the solvent that contains one mole of the solute is removed the concentration of the solution remains practically constant. Since the solution is very dilute, the change in the freezing point is very small; and when the volume of solvent containing one mole has been removed, the volume change is very small.

Let us suppose that we have this solution so inclosed that by means of a frictionless semipermeable piston we can remove the desired quantity of solvent, at the temperature of the freezing point, T, of the pure solvent. Allow this to freeze; cool the whole system to the freezing point of the solution $T - \Delta t$. Bring the ice in contact with the solution and allow it to melt and become part of the solution. Finally warm the whole system up to its original temperature, then we shall be back to the initial state, having completed the cyclic transformation. We have the following stages in this reversible process:

I. At the temperature of the freezing point, T, of the pure solvent we have done work in removing osmotically by means of the semipermeable piston the quantity of the solvent containing one mole of the solute. There have been removed $\frac{Sm}{g}$ grams of the solvent at this temperature.

The external work done against the osmotic pressure p_0 is $p_0 V_0$ mechanical units or $Ap_0 V_0$ calories, where V_0 is the volume of solvent removed and A is the conversion factor.

II. Now allow these $\frac{Sm}{g}$ grams of the solvent to freeze isothermally and in doing so there will be liberated $L_F \frac{Sm}{g}$ calories of heat at the temperature T, where L_F is the latent heat of fusion of one gram of the solid solvent.

III. Now cool adiabatically the solution and also the $\frac{Sm}{g}$ grams of the solvent which is now ice, to the temperature $T - \Delta T$.

IV. At this lower temperature $(T - \Delta T)$ we place the ice in contact with the solution, allow it to melt and to become a part of the solution again. In melting, the heat absorbed at this lower temperature is $L_F' \frac{Sm}{g}$ calories.

V. Now raise the temperature of the whole system adiabatically to the original temperature T, during which no heat is given out or absorbed.

This is a reversible cyclic process, and the sum of the work terms is zero. The work in III is equal and opposite in direction to that in V, and therefore they may be neglected. We shall then have

$$p_0 V_0 - L_F \frac{Sm}{g} + L_F' \frac{Sm}{g} = 0$$

or

$$p_0 V_0 = L_F \frac{Sm}{g} - L_F' \frac{Sm}{g}.$$

But $L_F \frac{Sm}{g}$ is the heat absorbed by the system at the higher temperature, T_1. Let us designate this by Q_1 and the heat, $L_F' \frac{Sm}{g}$, given up at the lower temperature, we will designate by Q_2. On substitution we have

$$p_0 V_0 = Q_1 - Q_2.$$

But from the equation $\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$, page 286, we should have on substitution, since $T_1 - T_2 = \Delta T$

$$p_0 V_0 = \frac{\Delta T}{T_1} Q_1,$$

or

$$p_0 V_0 = L_F \frac{Sm}{g} \frac{\Delta T}{T}.$$

We assumed that The Gas Law for ideal gases holds in the case of infinitely dilute solutions. Hence for the osmotic pressure at the freezing point T_1 of the pure solvent we will have upon the basis of this assumption $p_0 V_0 = RT_1$. Substituting in the above the value of $p_0 V_0$, we have

$$RT_1 = \frac{L_F\, Sm}{g} \frac{\Delta T}{T_1}.$$

Solving for the slight temperature difference ΔT which we will designate as Δ, we have

$$\Delta = \frac{RT_1^2 g}{L_F Sm}$$

which gives us

$$\frac{m\Delta}{g} = \frac{RT_1^2}{L_F S}$$

the *gram-molecular lowering*, since it is the lowering of the freezing point of a solution of one mole of the solute contained in S grams of the solvent. It is customary to take

100 grams of the solvent, then $S = 100$, which on substitution gives

$$\frac{m\Delta}{g} = \frac{RT_1^2}{100\ L}.$$

We have previously seen (page 26) that the gas constant, R, is equal to 84,780 gram-centimeters per degree.

1 calorie is 4.186 Joules, and 1 Joule is $\frac{10^7}{981}$ gram-centimeters.

1 calorie $= \frac{4.186 \times 10^7}{981}$ or 42,670 gram-centimeters.

Then $\frac{84780}{42670} = 1.987$ calories per degree as the value of R, or $R = 2$ calories per degree approximately.

Substituting, the equation takes the form

$$\frac{m\Delta}{g} = \frac{2\ T^2}{100\ L} \qquad (1)$$

as the expression for the gram-molecular lowering of the freezing point when T is the freezing point of the pure solvent expressed on the absolute scale.

The left-hand member $\frac{m\Delta}{g}$ is the form of the expression used by Raoult, which he stated was equal to a constant K_F. $\frac{m\Delta}{g} = K_F$ is the empirical formula obtained by him and subsequently confirmed by numerous experimenters. It states that the lowering of the freezing point, when one mole of various solutes is dissolved in the same arbitrarily selected quantity (100 grams) of a solvent, is a constant quantity. Hence it is evident that the right-hand member of equation (1) must also represent this same constant. Therefore, knowing T, which is the temperature of the freezing point of the pure solvent, and L_F, which is the latent heat of fusion of the pure solvent, the value of $\frac{2\ T^2}{100\ L_F}$ can be readily ascertained, which is the value of the gram-molecular lowering of the solvent. There is no term in this expression which relates to the dissolved substance, hence the character of the solute should not affect the value, and we are justified in drawing the conclusion that the gram-molecular lowering of the freezing point is a constant and independent of the solute, *i.e.* $\frac{2\,T^2}{100\,L_F} = K_F = \frac{m\Delta}{g} =$ *gram-molecular* lowering.

We have then two experimental methods by means of which the value of this constant, K_F, can be determined: (1) as Raoult did, by determining the lowering produced by the freezing point method, (2) as van't Hoff did, by calculating the value of K_F from the latent heat of fusion of the solvent. The agreement between the two methods is very close, as the values in Table XLVII show, wherein the quantity of the solvent, S, employed is 100 grams.

TABLE XLVII

Substance as Solvent	Freezing Point	Latent Heat of Fusion, Calories per Gram	Freezing Point Constant	
			Determined Experimentally $K_F = \frac{m\,\Delta}{g}$	Calculated from van't Hoff's Formula $K_F = \frac{RT^2}{100\,L_F}$
Water	0°	79.7	18.6	18.58
Acetic acid . .	17	43.7	39	38.2
Benzene . . .	5.5	30.4	51.2	50.7
Naphthalene . .	80.1	35.6	69	69.5
Nitrobenzene . .	6.0	22.5	70	68.4
Phenol	38	24.9	74	78
Thymol . . .	48.2	27.5	80	74.5
Benzophenone .	48.1	23.7	98	86.4

The value for the latent heat of fusion, L_F, for nitrobenzene had not been determined, and van't Hoff calculated it from the value of K_F, obtained experimentally and found it to be

22.1 calories per gram. Pettersson subsequently determined the latent heat and found it to be 22.3 calories. Similarly for ethyl bromide, from the value of K_F the latent heat was calculated and found to be 13, and Pettersson's subsequent determination was 12.94. So it is evident that the freezing point constant can be employed to calculate the latent heat of fusion by van't Hoff's formula.

The equation for the lowering of the freezing point then takes the form

$$\frac{m\Delta}{g} = K_F$$

in which Δ is the lowering when g grams of the solute are dissolved in 100 grams of the solvent,

or
$$\frac{m\Delta}{g} = \frac{100\ K_F}{S}$$

in which Δ is the lowering when g grams of solute are dissolved in S grams of the solvent.

Solving for m, we have

$$m = \frac{100\ K_F g}{S\Delta}$$

as the general *Freezing Point Equation*.

Relation between the Osmotic Pressure and the Elevation of the Boiling Point of the Solvent due to a Non-volatile Solute

By evaporation at the boiling point of the solution, $T + \Delta T$, remove from a large mass of a very dilute solution a quantity of the solvent that would contain one mole of the solute without materially changing the concentration of the solution; cool the vapor separated and the solution to the temperature of the boiling point of the pure solvent, T; condense the vapor and introduce it osmotically into the solution again; raise the temperature of the solution to the boiling point of the solution. By such a cyclic process similar to that employed in the case of the lowering of the freezing point relationship, we derive an expression for the elevation of the boiling point analogous to that obtained for the lowering of the freezing point, *i.e.*

$$\frac{m\Delta}{g} = \frac{2\,T^2}{100 \cdot L_V}$$

in which the terms have the same significance as in the molecular loworing of the freezing point equation, except that T refers to the boiling point of the pure solvent at atmospheric pressure on the absolute scale, L_V is the latent heat of vaporization of one gram of the pure solvent at the temperature T, and Δ is the rise of the boiling point. This gram-molecular elevation is a constant quantity and we have

$$K_B = \frac{2\,T^2}{100\,L_V}$$

which can be calculated from the boiling point and latent heat of the pure solvent. As in the case of the lowering of the freezing point we may obtain

$$m = \frac{100\,K_B g}{S\Delta}$$

the general *Boiling Point Equation*, in which Δ is the rise of the boiling point when g grams of the solute are dissolved in S grams of the solvent.

Similarly the constant for the boiling point can be obtained by each of these two methods and the experimental values agree well with those calculated by the use of van't Hoff's formula, as is seen from the values given in Table XLVIII, wherein the quantity of the solvent, S, employed is 100 grams.

TABLE XLVIII

SUBSTANCE AS SOLVENT	BOILING POINT	LATENT HEAT OF VAPORIZATION CALORIES PER GRAM	BOILING POINT CONSTANT	
			Determined Experimentally $K_B = \frac{m\Delta}{g}$	Calculated from van't Hoff's Formula $K_B = \frac{RT^2}{100 L_V}$
Chloroform . .	61.2°	58.45	38.80	38.00
Acetonitril . .	81.3	170.6	13.00	14.60
Ethyl alcohol .	78.8	205.1	11.50	11.98
Ether	35.0	90	21.10	20.9
Acetone . . .	56.3	125.3	17.25	17.2
Acetic acid . .	118	97	30.7	31.2
Benzene . . .	80.3	93	26.7	26.7
Nitrobenzene .	205	79.2	50.1	57.3
Aniline	184	113.9	34.1	36.4
Pyridine . . .	115	101.4	29.5	29.5
Water	100	535.8	5.2	5.15

Eykmann confirmed the use of van't Hoff's formula for calculating the latent heat of vaporization, as the following results show:

SUBSTANCE	L_V BY DIRECT MEASUREMENT	L_V CALCULATED BY VAN'T HOFF'S FORMULA
Thymol	27.5	27.9
Diphenyl	28.5	29.4
Azobenzene	29.0	29.4

Significance of K. — The symbol K then represents the change in the freezing point (K_F) or in the boiling point (K_B) of the solvent produced by one mole of the solute dissolved in the arbitrarily selected quantity (100 grams) of the solvent. This value is dependent only on the nature of the solvent and is theoretically independent of the solute. Hence the value of K_F is designated the *gram-molecular lowering* of the freezing point and can be determined either from the freezing point measurements or calculated from the latent heat of fusion of the pure solvent. Similarly the value of K_B is designated the *gram-molecular rise* of the boiling point and can be obtained experimentally from boiling point determinations or calculated from the latent heat of vaporization of the pure solvent.

In Table XLV are given the values for the freezing point constant and in Table XLVI the boiling point constant of a number of the most common solvents used in making molecular weight determinations when 100 grams of solvent are employed.

CHAPTER XXVII

ELECTRICAL CONDUCTANCE

VOLTA recognized two different types of conductors of electricity and upon this basis divided them into Conductors of the First Class and Conductors of the Second Class. Conductors of the First Class include those substances in which the passage of the electric current is not accompanied by a simultaneous motion of matter itself. The metals belong to this class as well as some other good conductors, such as certain metallic sulphides and oxides. To the Second Class belong those conductors in which the passage of the electric current is accompanied by the corresponding motion of the matter composing them. These comprise solutions that conduct the electric current. This is the classification that is also recognized to-day.

Many theories have been proposed in order to explain the mechanism by which the electric current passes through a conductor as well as the various phenomena observed. Among the first efforts was Davy's Electrochemical Theory, wherein he assumed that chemical affinity is essentially electrical. That is, that the atoms possess electrical charges, and when atoms possessing electrical charges of different sign come near one another there results a decomposition and a recombination depending upon the relative strength of the charges of the same sign, the stronger uniting with the atoms having the charge of opposite sign, thus producing a new compound. He also supposed that a large number of atoms of small charges of the same sign might unite and form a unit with a greater charge than that of some single atom. This theory of Davy was not very generally accepted.

Berzelius, from his work on the decomposition of numerous solutions by means of an electric current obtained from a Voltaic Pile, concluded that the compounds in solution were electrically decomposed into two parts, a basic oxide and an anhydride. Copper sulphate, $CuSO_4$, for example, he considered as electrically decomposed into the basic oxide, CuO, and the anhydride, SO_3, which were respectively positively and negatively electrified. In order to explain such reactions Berzelius assumed that each atom when in juxtaposition with another atom possesses two poles, one electropositive and the other electronegative. When in contact, one of these poles is much stronger than the other, and the atom reacts as though it were "unipolar." Hence, the chemical affinity of an element depends upon the amount of the electrical charge of its atoms — positively charged atoms reacting with negatively charged atoms, and the electricities of opposite signs neutralizing each other, resulting in the formation of a compound electrically positive or electrically negative, depending upon which is in excess. This may result from the direct union of the elements, and two such compounds may in turn combine, forming a still more complex substance. The formation of the so-called double compounds is thus explained. SO_3 is the union of negatively charged S with three negatively charged oxygen atoms, resulting in the formation of the strongly negative residue SO_3. The union of two negatively charged atoms is accounted for by assuming that every atom possesses two charges, positive and negative, and that in each case the negative charge predominates. The negative charge of the oxygen neutralizes the positive charge of the sulphur, giving a negatively charged compound, SO_3.

This theory of Berzelius, known as the Dualistic Theory, met with general acceptance and had a very pronounced influence upon chemistry. Particularly in quantitative analysis and mineralogy, in which lines Berzelius was a pioneer, has he left the imprint of the Dualistic Theory in the methods adopted in writing the formulæ of minerals and in reporting the analysis of substances. The mineralogists employ this idea in writing the formulæ of minerals; for example, the formula for feldspar, $K_2Al_2Si_6O_{16}$, is written $K_2O \cdot Al_2O_3 \cdot 6\ SiO_2$. The chemist reports his analysis, not as the percentage of the particular element, but as the oxide; thus, calcium is reported as CaO, phosphorus as P_2O_5, sulphur as SO_3, etc. In this way the imprint of the Dualistic conception of Berzelius is very marked even to-day, although many are making an effort to get away from it, *e.g.* the agricultural chemists in their methods of reporting their analytical data.

Many objections to Berzelius' Dualistic Theory arose, and among them were two which he could not explain. At that time all acids were supposed to contain oxygen, but with the discovery of the halogen acids and their salts there was presented a large group of compounds that could not be conceived as being composed of a basic oxide and an anhydride, and consequently presented a most serious obstacle to the general application of the theory. Liebig called attention to the replacement in organic compounds of the positively charged H by the negatively charged Cl, such as the formation of the chloracetic acids, $CH_2ClCOOH$, CCl_3COOH from CH_3COOH. These acids all have properties similar to those of acetic acid.

Recently J. J. Thomson has shown that when hydrogen gas is electrolyzed, positive H appears at one pole and negative H at the other, from which he concluded that the hydrogen molecule is probably made up of a positive and a negative part molecule and that hydrogen is not always positive. He called attention to the fact that we have negative chlorine replaced by positive hydrogen without altering the type of the compound. For example; from CH_4 we may obtain CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. From $CHCl_3$ vapor, as well as from a study of the spectra of the vapor of methylene chloride, ethylene chloride, and even CCl_4, Thomson concluded that "it would appear that the chlorine atoms, in the chlorine derivatives of methane, are charged with electricity of the same sign as the hydrogen atoms they displace."

Faraday, after having convinced himself that there is only one kind of positive and one kind of negative electricity, showed experimentally that the chemical or magnetic effects produced in any circuit are proportional to the amount or quantity of electricity passing through the circuit. By arranging a number of solutions so that he could pass the same quantity of electricity through them, he demonstrated that "*the quantities of the substances separating at the electrodes in the same time are in the proportion of their equivalent weights*," or as Helmholtz states it, "*the same quantity of electricity passing through an electrolyte either sets free or transfers to other conditions always the same number of valencies*." This is known as Faraday's Law, and the constant 96,540 coulombs, one *faraday*, means that 96,540 coulombs of electricity will deposit one gram-equivalent of a metal or do other chemical work equivalent to this.

Faraday (1839) called those parts which migrate through the solution under the electrical stress and conduct the electricity, *ions*. He also emphasized the fact that it is not easy to tell what the ions are, as frequently they are not the same as that which separates out on the electrodes. In the case of the decomposition of solutions of sodium hydroxide and sodium sulphate, there appear at the electrodes in both cases, hydrogen and oxygen; but the parts which migrate through the solution of NaOH are undoubtedly not hydrogen and oxygen ions, but are supposed to be Na and OH ions. In the case of Na_2SO_4 solution, Daniells said if the ions are

Na and SO_4, the sodium reacts with the water, liberating hydrogen at one electrode, while the SO_4 reacts with water at the other electrode, forming sulphuric acid and liberating oxygen. The ions which migrate toward the cathode are designated *cations*, and those which migrate toward the anode are the *anions*. This process of migration occurs only in conductors of the Second Class, and substances which yield solutions that conduct electricity in this way Faraday termed *electrolytes*, and the process of decomposing the substances (electrolytes) by the electric current he called *electrolysis*.

It was, however, previous to this time that Nicholson and Carlisle (1800) decomposed water by means of the electric current, and many attempts were made to explain the process by means of which this occurred. In 1805 Grotthus presented the first complete theory for this phenomenon of the conduction of a current through the solution and also for the decomposition of water. His theory satisfied the scientific world and was universally accepted until recent times. According to the theory one electrode is positively charged and the other electrode is negatively charged by the electric current, and these charges are communicated to the molecules of water, which become polarized and oriented so that the positive part of the molecules, the hydrogen atom, all face in one direction and the negative part, the oxygen atom, in the opposite direction. This is illustrated in Fig. 88. The current enters the solution through the anode, and the positively charged parts of the molecules are all in the direction of the negative electrode or cathode, by which they are attracted and arrange themselves as represented.

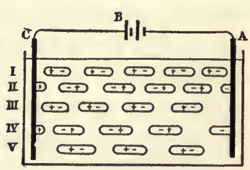


FIG. 88.

If the charges on the electrodes (*i.e.* the Electromotive Force) are large enough, the extreme hydrogen and oxygen atoms nearest the electrodes are liberated and go to neutralize the electrical charge on the electrodes where the hydrogen and oxygen appear as gases; the condition is represented by II in the figure. This leaves the other parts of the molecules free. These immediately combine with the free parts from the adjacent molecules, and this decomposition and recombination pass on throughout the liquid between the electrodes. These new molecules become oriented as shown in III, when the process just described is repeated. In making these transfers of parts of the molecules some would have to move over a considerable distance.

This theory of Grotthus calls for a decomposition of the molecules. To accomplish the decomposition of the molecules would require a good deal of energy. Then a recombination would take place, but before this takes place some time would elapse, during which the particles would be free. The question arose as to what would inaugurate the second decomposition, and the third, and, in fact, where would the energy come from for the *n*th decomposition. The question was asked whether it was the molecules of water or the molecules of the dissolved substance that were decomposed and conducted the electric current. This was a point of controversy for a long time, opinion was divided, and such evasive expressions as the following were used: "water which by the addition of sulphuric acid has become a good conductor."

In order to electrolyze a solution the electromotive force has to reach a certain value — a value below which no decomposition takes place and the affinity of the atoms would not be overcome. Experimentally it has been found that the electric current can be made to pass when the electromotive force is very small. For example, if a solution of silver nitrate is placed between two silver electrodes, the decomposition of the silver nitrate with the deposition of silver on one electrode and the dissolution of silver from the other can be shown to take place. We have merely the transfer of silver from one electrode to another, and this holds for all differences of potential however small.

It was Clausius, about fifty years later, who first pointed out this contradiction, and he stated that any theory which requires the decomposition of the substance must be abandoned. Using Faraday's definition of terms, Clausius concluded that the individual ions are not bound together, but must exist uncombined and free to move in the solution. Employing the conception of the Kinetic Theory of Gases, which was being emphasized by the scientific world at the time, Clausius assumed that a few part molecules or ions are free in so far as they are in independent motion or vibration, but are kept close together by their chemical affinity. This affinity is overcome by the rapid vibrations, and the molecules get into such positions that it is more convenient for one part of the molecule to unite with the other part of another molecule than to recombine with its original partner. He imagined a continual exchange taking place between the parts of the molecules. So when an electric current passes, this simply guides the exchanges, which become much more frequent under the electrical stress. If we consider a cross section at right angles to the direction of the current, more positive ions would move in the direction of the cathode than toward the anode, and more negative ions would move in the direction of the anode. As a result there would be a certain number of positive ions going in one direction and negative ions in the opposite direction. This motion of the two parts of the molecules in the solution causes the conduction of the electricity. Hence, according to Clausius' Theory, the current does not cause a decomposition of the molecules but guides those part molecules which are momentarily free. Clausius in his conclusion declares "every assumption is inadmissible which required the natural condition of a solution of an electrolyte to be one of equilibrium in which every positive ion is firmly combined with its negative ion, and which, at the same time, requires the action of a definite force in order to change this condition of equilibrium into another differing from it only in that some of the positive ions have combined with other negative ions than those with which they were formerly combined. Every such assumption is in contradiction to Ohm's Law."

As we shall see subsequently, this theory of Clausius, which was very generally accepted, is the basis of the present theory as presented by Arrhenius; but before we take up a consideration of this it is necessary to present some of the experimental work of Hittorf on the migration of ions, and on the electrical conductance of solutions by Kohlrausch, which led to the theory of free ions as shown by Arrhenius and by Planck.

Transference Number. — In the electrolysis of a solution equivalent quantities of the substances appear at the two electrodes. If a solution of HBr be electrolyzed, for one gram of hydrogen separating on the cathode, 80 grams of bromine will appear at the anode; and if a solution of HCl be employed and electrolyzed until one gram of hydrogen is obtained, the equivalent of chlorine, 35.5 grams, is liberated at the anode. In order for these quantities to appear at the electrodes, it is necessary that they come from different parts of the solution, and as Faraday said, the parts of the electrolyte migrate through the solution and conduct the current. A current of one *faraday* flowing through a solution liberates one gram-equivalent of hydrogen (1.008 grams) and at the same time there is liberated at the anode one gram-equivalent of some other substance. Hence both of these quantities of material must have migrated through the solution to their respective electrodes and consequently have transported their respective shares of the quantity of electricity that passed through the solution. It was thought that equal quantities of electricity moved through the solution in opposite directions. This is not necessary, for it is conceivable that in order to cause a definite quantity of electricity to pass through a given cross section of the solution we could imagine all of the electricity to be transported by the ions moving toward the anode, or that it could be divided in any ratio we might choose. If the ions migrating toward their respective electrodes moved at the same speed, they would carry the same quantities of the current, but if one traveled twice as fast, the proportions of the current transported by each would be 2 : 1.

Let us assume that we have a solution of HCl and that the vessel, Fig. 89, containing it is divided into three compartments, *A*, *B*, and *C*, each of which contains 10 gram-equivalents of hydrogen and of chlorine. Let us electrolyze until there has been separated one gram of hydrogen and 35.5 grams of chlorine. Then there should be left in compartment *C*, 9 gram-equivalents of hydrogen, and in *A* 9 gram-equivalents of chlorine. But some chlorine ions have migrated over to *A*, and some of the hydrogen ions have wandered into *C*. The question arises, how much of these have migrated? If we assume that $\frac{1}{2}$ gram-equivalent of hydrogen has wandered from *A* to *B* and from *B* to *C*, then there has been removed from *C* $\frac{1}{2}$ gram-equivalent of hydrogen more than there migrated into *C*, hence there is a change in concentration of the hydrogen contents of *C* as well as of *A*, while there migrated into *B* just the same quantity that migrated out, and the concentration remains constant. Let us assume that the hydrogen ions move five times as fast as the chlorine, then $\frac{5}{6}$ of the transportation of the electricity should be done by the hydrogen and $\frac{1}{6}$ by the chlorine. In this case, *A* should have lost $\frac{5}{6}$ gram-equivalent of chlorine, or there should remain $9\frac{1}{6}$ gram-equivalents. As one gram-equivalent of hydrogen was deposited from *C* and $\frac{5}{6}$ was transferred from

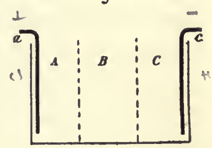


FIG. 89.

A to B and from B to C, there must be remaining in C, $9\frac{5}{6}$ gram-equivalents. The loss in C, the cathode chamber, is $\frac{1}{6}$ gram-equivalent, and the loss from the anode chamber A is $\frac{5}{6}$ gram-equivalent. The ratio of these losses,

$$\frac{\text{Cathode chamber loss } \frac{1}{6} \text{ gram-equivalent}}{\text{Anode chamber loss } \frac{5}{6} \text{ gram-equivalent}}$$

is $\frac{1}{5}$, or the ratio of the rates of migration of the anion and of the cation, *i.e.*

$$\frac{\text{Rate of migration of anion}}{\text{Rate of migration of cation}} = \frac{1}{5} = \frac{\text{Loss at the cathode}}{\text{Loss at the anode}}.$$

Hittorf carried out (1853–57) a large number of experiments in which he determined the ratio of the losses in concentration of the solution about the electrodes after electrolysis and from these determined the ratios of the rates of migration of the ions. He found that it was not necessary to electrolyze until one gram-equivalent had been separated, but passed the current a sufficient length of time to get a marked change in concentration in the electrode chambers. The type of apparatus frequently employed is illustrated in Fig. 90. After electrolyzing a solution of silver nitrate, it was found that 1.2591 grams of Ag had been deposited in the electrolytic cell and the same amount in the coulometer. A unit volume of the solution contained before electrolysis the equivalent of 17.4624 grams AgCl; and after electrolysis 16.7694 grams AgCl, which represents a loss equal to 0.5893 gram of silver. If no silver had come into the cathode liquid, then there should have been a loss in concentration the same as the amount of silver deposited, 1.2591 grams, but there was a change in concentration of only 0.5893 gram, hence

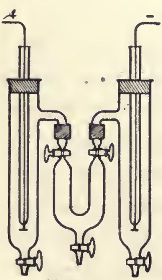


FIG. 90.

the difference, 1.2591 − 0.5893, or 0.6698 gram, represents the amount of silver that migrated into this part of the solution. If as much silver had migrated as was precipitated, all of the current would have been transported by the silver, and its share in transporting the current would have been 100 per cent or unity, and the NO_3 would not have assisted. But only 0.6698 gram migrated, so the share of the current that deposited 1.2591 grams of silver must have been $\frac{0.6698}{1.2591} = 0.532$; or 53.2 per cent of the electricity was transported by the silver, and the difference, 100 − 53.2 = 46.8 per cent, was transported by the NO_3. Or, representing this on the basis of unity, the part carried by the silver is 0.532 and that by the NO_3 is 0.468.

In general, then, if

n_c = transference number of the cation
n_a = transference number of the anion

then $n_c + n_a = 1$. It was seen above that

$$\frac{\text{the change in concentration at the cathode}}{\text{the total change the current would produce}} = n_a$$

and
$$\frac{\text{the change in concentration at the anode}}{\text{the total change the current would produce}} = n_c.$$

Dividing the second by the first we have

$$\frac{\text{the change in concentration at the anode}}{\text{the change in concentration at the cathode}} = \frac{n_c}{n_a}.$$

The transference number which is proportional to the speed of the ions through the solution varies with the temperature and with the concentration, as Table XLIX illustrates.

Table XLIX — Transference Numbers of the Cations

So-called Best Values Compiled by Noyes and Falk

	Temp. Degrees C.	Gram-equivalents per Liter of Solution								
		0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	1
NaCl	0°	0.387	0.387	0.387	0.386	0.385				
	18	0.396	0.396	0.396	0.395	0.393	0.390	0.388	0.382	0.369
	30	0.404	0.404	0.404	0.404	0.403				
	96				0.442	0.442	0.442			
KCl	0	0.493	0.493	0.493	0.493	0.492	0.491			
	10		0.495	0.495	0.495	0.495				
	18	0.496	0,496	0.496	0.496	0.495	0.494			
	30	0.498	0.498	0.498	0.498	0.497	0.496			
LiCl	18		0.332	0.328	0.320	0.313	0.304	0.299		
NH_4Cl	0		0.489	0.489						
	18		0.492	0.492	0.492					
	30		0.495	0.495						
NaBr	18	0.395	0.395	0.395						
KBr	18		0.495	0.495						
$AgNO_3$	18		0.471	0.471	0.471	0.471				
	25		0.477	0.477	0.477					
	30	0.481	0.481	0.481	0.481	0.481	0.481	0.481	0.481	
HCl	0	0.847	0.846	0.844	0.839	0.834				
	18	0.832	0.833	0.833	0.834	0.835	0.837	0.838	0.840	0.844
	30		0.822	0.822	0.822					
	96			0.748						
HNO_3	20	0.839	0.840	0.841	0.844					
$BaCl_2$	0	0.439	0.437	0.432						
	16					0.420	0.408	0.401	0.391	
	25				0.438	0.427	0.415			
	30	0.445	0.444	0.443						
$CaCl_2$	20	0.440	0.432	0.424	0.413	0.404	0.395	0.389		
$SrCl_2$	20		0.441	0.435	0.427					
$CdCl_2$	18	0.430	0.430	0.430	0'430	0.430				
$CdBr_2$	18	0.430	0.430	0.430	0.430	0.429	0.410	0.389	0.350	0.222
CdI_2	18	0.445	0.444	0.442	0.396	0.296	0.127	0.046	0.003	
Na_2SO_4	18		0.392	0.390	0.383					
K_2SO_4	18		0.494	0.492	0.490					
	25				0.496	0.494	0.493			
Tl_2SO_4	25				0.478	0.476				
H_2SO_4	20			0.822	0.822	0.822	0.820	0.818	0.816	0.812
	32			0.808	0.808	0.808				
$Ba(NO_3)_2$	25				0.456	0.456	0.456			
$Pb(NO_3)_2$	25				0.487	0.487				
$MgSO_4$	18	0.388	0.385	0.381	0.373					
	30		0.388	0.386	0.380					
$CdSO_4$	18		0.389	0.384	0.374	0.364	0.350	0.340	0.323	0.294
$CuSO_4$	18			0.375	0.375	0.373	0.361	0.348	0.327	
NaOH	25				0.201					

The limiting value of the transport numbers with an increase in temperature seems to be 0.5, which indicates that the current is transported by the cation and anion equally. This applies to all combinations of cations and anions.

In the case of a number of electrolytes the transport numbers are abnormal and vary greatly with the concentration as well as with the temperature. Hittorf found for aqueous solutions of cadmium iodide values greater than unity for solutions more concentrated than normal; for 3-normal the value for cadmium is 1.3, and for 0.03-normal the value is 0.61. These abnormal values are explained primarily upon the basis of the formation of complexes in solution with or without the combination of the solute with the solvent. It is further assumed in the determination of the transference number that there is no movement of the water with the electric current, and in the case of concentrated solutions this is no longer the case. By the introduction of a substance which will remain stationary and will not take part in the conduction of the current, methods have been devised in order to determine the amount of water transferred with the current and consequently the amount associated with the different ions.

Kohlrausch's Law. — By employing the principles that Wheatstone used in measuring the resistance of conductors of the first class, Kohlrausch devised a method for measuring the conductance of solutions. The apparatus, illustrated in Fig. 91, consists of a wire, *AB*, provided with a scale so that the sections *a* and *b* can be measured; the known resistance *R*, and the electrolytic cell, *C*, into which the solution, the resistance of which is to be measured, can be placed (the Arrhenius

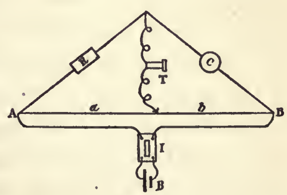


FIG. 91.

type of cell is illustrated in detail in Fig. 92); a battery, B, and induction coil, I, or some means of producing an alternating current. T represents the telephone by means of which the adjustment of the contact point can be correctly made. By introducing a known resistance into R and moving the point k along the wire until the minimum sound is obtained, the resistances in the four parts or arms of the apparatus will be in the ratio, $R : R_c = a : b$. Solving, we have $R_c = \frac{R \times b}{a}$, which gives the resistance of the solution in the electrolytic cell. The conductance is the reciprocal of the resistance, then the conductance, $c = \frac{1}{R_c} = \frac{a}{R \cdot b}$.

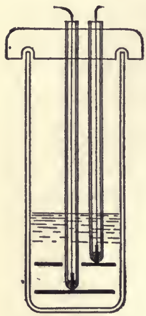


FIG. 92.

Electrical resistance is expressed in ohms and conductance in reciprocal ohms or *mhos*. The unit of conductance is the reciprocal ohm, the *mho*. The *specific* conductance, κ, is the conductance of a cube of the solution having sides 1 cm. long. The conductance of the solution containing one gram-equivalent of the solute when placed between two electrodes 1 cm. apart and of such size as to contain the specified volume of the solution is designated the *equivalent conductance* and is represented by Λ. Then $\Lambda = \kappa V$, in which V is the volume in cubic centimeters which contains one gram-equivalent. It is customary to employ a subscript to designate the volume of the solution that contains one gram-equivalent of the solute, *i.e.* Λ_V, which is the equivalent conductance at volume V, and Λ_∞ is the equivalent conductance at infinite dilution. The molecular conductance μ is the conductance of a solution containing one mole of the solute placed between two electrodes 1 cm. apart and of sufficient size to include the volume of the solution, $\mu = \kappa V$. In many texts and journals it is customary to use λ to represent the equivalent conductance.

It is more convenient to prepare the electrolytic cells so that the electrodes are not exactly 1 cm. apart, are not exactly 1 sq. cm. in area, and do not inclose a volume of exactly one cubic centimeter of solution. Consequently, it is necessary to employ some factor, K, such that the value of the conductance of the solution, as obtained by this cell, multiplied by K will give the *specific conductance*, that is, the conductance of a cube of the liquid one centimeter on a side. We then have, the conductance of the solution c times K equals the specific conductance, *i.e.* $cK = \kappa$, and since $c = \frac{a}{Rb}$, we have $\kappa = \frac{Ka}{Rb}$, or solving, we obtain $K = \frac{\kappa Rb}{a}$. The value of K, which is termed the *Cell Constant*, may be readily determined experimentally by employing in the cell a specified solution, the specific conductance of which is known, determining the value of R, a, and b by the Kohlrausch method, substituting, and solving for K. Then knowing K for the particular cell, the equivalent conductance of other solutions can be readily determined from the relation $\Lambda = \kappa V$ which on substitution of the value of κ becomes $\Lambda = \frac{KaV}{Rb}$.

Kohlrausch (1873–80) by the above method made the measurements of the conductance of a very large number of solutions of different strength. By dissolving one gram-molecule and making it up to one liter we have a molar solution, and if the quantity representing one gram-equivalent be dissolved, we have a gram-equivalent solution. In the case of KCl, NaCl, NaOH, etc., these two kinds of solutions are the same; but with H_2SO_4, $BaCl_2$, etc., one half a mole is required for a gram-equivalent solution, and hence these are one half the strength of molar solutions. In Table L is compiled the equivalent conductance Λ of aqueous solutions at 18° C. of many of the common acids, bases, and salts. The headings of the columns are self-explanatory.

TABLE L — EQUIVALENT CONDUCTANCE OF INORGANIC ACIDS, BASES, AND SALTS IN AQUEOUS SOLUTIONS AT 18° C. (Landolt-Börnstein *Tabellen*)

GRAM EQUIVALENTS PER LITER	0	0.0001	0.0002	0.005	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1
LITERS PER GRAM EQUIVALENT	∞	10000	5000	2000	1000	500	200	100	50	20	10	5	2	1
1. HCl					(377)	376	373	370	367	360	351	342	327	301
2. HNO_3					(375)	374	371	368	364	357	350	340	324	310
3. H_2SO_4				(368)	361	351	330	308	286	253	225	214	205	198
4. CH_3COOH		107	80	57	41	30.2	20.0	14.3	10.4	6.48	4.60	3.24	2.01	1.32
5. KOH					234	(233)	230	228	225	219	213	206	197	184
6. NaOH						204.5		203.4		199.0	195.4		174.1	157.0
7. NH_4OH		(66)	53	38.0	28.0	20.6	13.2	9.6	7.1	4.6	3.3	2.30	1.35	0.89
8. KCl	130.10	129.07	128.77	128.11	127.34	126.31	124.41	122.43	119.96	115.75	112.03	107.96	102.41	98.27
9. NaCl	108.99	108.10	107.82	107.18	106.49	105.55	103.78	101.95	99.62	95.71	92.02	87.73	80.94	74.35
10. LiCl	98.88	98.14	97.85	97.19	96.52	95.62	93.92	92.14	89.91	86.12	82.42	77.93	70.71	63.36
11. $CaCl_2$		115.17	114.55	113.34	111.95	110.06	106.69	103.37	99.38	93.29	88.19	82.79	74.92	67.54
12. $BaCl_2$				117.01	115.60			106.67	102.53	96.04	90.78	85.18	77.29	70.14
13. KNO_3	126.50	125.50	125.18	124.44	123.65	122.60	120.47	118.19	115.21	109.86	104.79	98.74	89.24	80.46
14. $NaNO_3$	105.33	104.55	104.19	103.53	102.85	101.89	100.06	98.16	95.66	91.43	87.24	82.28	74.05	65.86
15. $LiNO_3$	95.18	94.46	94.15	93.52	92.87	91.97	90.33	88.61	86.41	82.75	79.19	75.01	67.98	60.77
16. NH_4NO_3		126.1	126.0		124.5	123.0		118.0		110.0	106.6		94.5	88.8
17. $AgNO_3$	115.80	115.01	114.56	113.89	113.15	112.08	110.04	107.81		99.51	94.33		77.5	67.6
18. CH_3COOK		100.0	99.6	98.9	98.3	97.5	95.7	94 0	91.5	87.7	83.8	79.2	71.6	63.4
19. CH_3COONa		(76.8)	76.4	(75.8)	(75.2)	74.3	(72.4)	70.2	67.9	64.2	61.1	57.1	49.4	41.2
20. K_2SO_4		130.71	130.03	128.53	126.88		120.26	115.80	110.38	101.93	94.93	87.76	78.48	71.59
21. Na_2SO_4		110.5	109.6	108.3	106.7	10.48	100.8	9.68	91.9	83.9	78.4	71.4	59.7	50.8
22. $CuSO_4$		109.95	107.90	103.54	98.54	91.91	80.95	71.72	62.40	51.16	43.85	37.66		25.77
23. $MgSO_4$		(110.1)	(108.1)	103.15	98.40	(92.8)	(82.5)	72.75	(64.5)	(53.4)	45.34	(39.7)		(26.6)

1. From the data in this table it will be observed that the equivalent conductance of all these solutions increases with the dilution, and it is found that the difference of the conductance for the first dilutions is very marked, while for high dilutions the differences are small, showing that the values for the equivalent conductances are reaching a limiting maximum value. That is, at infinite dilution, which is approximately 1000 liters and above, the value for Λ becomes constant. This is shown in the following numbers for NaCl, the difference being with increased dilution: 6.69; 4.29; 3.69; 3.91; 2.33; 1.83; 1.77; 0.94; 0.79; 0.64; 0.28. This shows that the value for the equivalent conductance is approaching a limiting value.

2. The additive property of the equivalent conductance is illustrated by the values given in Table LI, which are obtained from Table L for dilution of 10,000 liters, which we may take as Λ_∞.

TABLE LI

Electrolyte	Λ_∞	Difference K–Na
KCl	129.07	20.97
NaCl	108.10	
KNO_3	125.50	20.95
$NaNO_3$	104.55	
K_2SO_4	130.71	20.21
Na_2SO_4	110.5	
CH_3COOK	100.0	23.2
CH_3COONa	76.8	

The difference of the equivalent conductances for KCl and NaCl should be the same as the difference for the nitrate solutions. This we find to be true, as we obtain 20.97 in one case and 20.95 for the other. We obtain practically the same value for the sulphates. In the case of the acetates the agreement is not so marked.

From a consideration of the data he obtained, Kohlrausch found that the equivalent conductance at infinite dilution could be represented by the sum of the equivalent conductances of the cations and of the anions. That is, the migrations of the ions in solution are independent of each other, and their combined effect results in the conductance of the solution. Hence we have the formulation of Kohlrausch's *Dilution Law of the independent migration of the ions* in the expression $\Lambda_\infty = \Lambda_c + \Lambda_a$, which, stated in words, is: the equivalent conductance of a solution at infinite dilution is the sum of the equivalent ionic conductances, *i.e.* the equivalent ionic conductance of the cations, Λ_c, plus the equivalent ionic conductance of the anions, Λ_a.

3. The ratio of the current carried by the cations to the total current is termed the transference or transport number of the cation, and similarly we have the transference number of the anion. These transference numbers are dependent on the velocities of the ions, and we have the relation $\frac{n_c}{n_a} = \frac{u_c}{v_a}$, in which u_c is the velocity of the cation and v_a is the velocity of the anion. As the total equivalent conductance is the sum of the equivalent ionic conductances, it follows that the relation $\frac{u_c}{v_a} = \frac{\Lambda_c}{\Lambda_a}$ holds, and therefore $\frac{n_c}{n_a} = \frac{\Lambda_c}{\Lambda_a}$. Adding unity to both sides of the equation we obtain $\frac{n_c}{n_a} + 1 = \frac{\Lambda_c}{\Lambda_a} + 1$, which becomes $\frac{n_c + n_a}{n_a} = \frac{\Lambda_c + \Lambda_a}{\Lambda_a}$, and remembering that $n_c + n_a = 1$, and $\Lambda_c + \Lambda_a = \Lambda_\infty$, we have on substitution $\frac{1}{n_a} = \frac{\Lambda_\infty}{\Lambda_a}$. Solving for Λ_a we have $\Lambda_a = n_a\Lambda_\infty$, and similarly we may also obtain $\Lambda_c = n_c\Lambda_\infty$.

We may now apply this to a specific problem as an illustration.

The equivalent conductance Λ_∞ at infinite dilution of NaCl is 109 *mhos*, and this for NaCl is also the molar conductance, μ_∞. The transport number, n_a for the anion, the chlorine ion, is 0.615. Substituting these values in the equation we have $\Lambda_a = 0.615 \times 109$, or $\Lambda_a = 67$, the equivalent ionic conductance of chlorine. The equivalent ionic conductance of the sodium ion is $109 - 67 = 42$, or substituting in the equation above, $\Lambda_c = n_c\Lambda_\infty$, is $\Lambda_c = (1-0.615)\ 109$, and $\Lambda_c = 42$. It is apparent that if the transference number of one ion is known, then the ionic conductance of it and of the one with which it is associated may be readily calculated. Above we have determined the equivalent ionic conductance for Na and Cl. Now if we determine experimentally the equivalent conductance, Λ_∞, for $NaNO_3$, we have from Kohlrausch's Law, $\Lambda_\infty = \Lambda_{Na} + \Lambda_{NO_3}$, and since we know Λ_∞ and Λ_{Na}, we can solve for Λ_{NO_3}, the equivalent ionic conductance of NO_3. By the proper combinations it is possible to determine the ionic conductance for any of the ions. These values of the equivalent conductances of the separate ions at 18° C. have been accurately determined, and the values compiled by Noyes and Falk are given in Table LII.

From the values of the equivalent conductances of the ions and assuming that Kohlrausch's Dilution Law holds, it is then possible to calculate the equivalent conductance at infinite dilution, Λ_∞, for any electrolyte. This gives us, then, the equivalent or the molecular conductance at infinite dilution, and Ostwald has proposed that the conductance at any moderate dilution could be represented by $\Lambda = \alpha\,(\Lambda_c + \Lambda_a)$ where α is the fractional part the equivalent conductance at any dilution is of the equivalent conductance at infinite dilution. Since $\Lambda_\infty = \Lambda_c + \Lambda_a$, then $\Lambda = \alpha\Lambda_\infty$, or solving for α we have $\alpha = \dfrac{\Lambda}{\Lambda_\infty}$.

Table LII — Equivalent Ionic Conductances of the Separate Ions

(Noyes and Falk — Jour. Am. Chem. Soc., *34*, 479 (1912))

Values at 18° C.						Values at 25° C.			
Cs	68.0	Ba	55.4	Br	67.7	Tl	76.0	I	76.5
Rb	67.5	Ca	51.9	I	66.6	K	74.8	Cl	75.8
Tl	65.9	Sr	51.9	Cl	65.5	Ag	63.4	NO_3	70.6
NH_4	64.7	Zn	47.0	NO_3	61.8	Na	51.2	BrO_3	54.8
K	64.5	Cd	46.4	SCN	56.7	H	350.0	OH	196.0*
Ag	54.0	Mg	45.9	ClO_3	55.1	Pb	71.0	SO_4	80.0
Na	43.4	Cu	45.9	BrO_3	47.6	Ba	65.2	C_2O_4	72.7
Li	33.3	La	61.0	IO_3	34.0	Ca	60.0	$C_2H_3O_2$	40.8*
H	314.5			F	46.7	Mg	55.0	$Fe(CN)_6$†	110.5
Pb	60.8			SO_4	68.5	La	72.0		
				C_2H_3O	35.*	NH_4	74.8*		
				C_2O_4	63.0				
				$Fe(CN)_6$†	95.0				
				OH	174.*				

* From Kohlrausch's values at 18°. These values for 25° are calculated from 18° values and the temperature coefficients given.

† Ferrocyanide ion.

CHAPTER XXVIII

ELECTROLYTIC DISSOCIATION

FROM the equivalent conductance of solutions compiled in Table L, it will be seen that the only substances listed are acids, salts, and bases. It has also been found that the only aqueous solutions that conduct the electric current are solutions of these three classes of substances, which are termed electrolytes. It has also been shown that it was these same three classes of substances which in aqueous solutions gave abnormal values for (1) the osmotic pressure, (2) the lowering of the vapor pressure, (3) the lowering of the freezing point, and (4) the rise of the boiling point. If 342 grams of cane sugar are dissolved in water and made up to one liter we have a molar solution. A molar solution of grape sugar will contain 180 grams. The osmotic pressures of these two solutions are the same, the vapor pressures are the same, the freezing points are the same, and the boiling points are the same. That is, one gram-molecule of any substance, such as these, will produce the same lowering of the vapor pressure of the solvent, whatever the difference in the formula weights may be. It is the *same number* of moles of the different solutes that causes the same change of the boiling points, the same lowering of the freezing points and of the vapor pressures, when dissolved in the same amounts of the same solvent. If we have the same number of moles of different solutes dissolved in the same quantity of solvent, the osmotic pressures of all the solutions will be the same.

Those properties such as the osmotic pressure, the lowering of the vapor pressure, the rise of the boiling point, etc., which depend upon the number of moles or parts in solution, are designated *Colligative Properties.* The relative magnitudes of the values are proportional to the number of moles of solute.

It was shown in the discussion of osmotic pressure measurements that a large number of substances gave abnormal values for the osmotic pressure and that van't Hoff proposed to introduce a correcting factor i in the formula to take care of these. The formula then took the form $p_0 V = iRT$, in which i is the number of times larger the osmotic pressure found is than it should be on the basis of the formula weight of the solute. The value of i is then the value of the ratio of the number of moles present to the number which corresponds to the formula weight; this is on the basis that the osmotic pressure is a colligative property.

Similarly we have seen that the vapor pressures of solutions of salts, acids, and bases are much lower than they should be. In Table XLVIII the last columns show that the rise of the boiling point of some solutions is two and in some cases three times what the changes should be. From these values we may obtain the ratio of the number of moles necessary to produce this pressure to the number of molecules represented by the formula weight, *i.e.* the value i of van't Hoff's formula, or as sometimes called, van't Hoff's coefficient. If g grams of the solute produces a lowering of Δ degrees when dissolved in 100 grams of the solvent, the formula weight, m, will produce a lowering of $\frac{m\Delta}{g}$ degrees, and as the gram-molecular lowering is 18.6°, it follows that $i = \frac{\frac{m\Delta}{g}}{18.6°}$.

Arrhenius recognized that the aqueous solutions of acids, bases, and salts also conduct the electric current. He formulated the Electrolytic Dissociation Theory in order to account for the extra number of moles present in these aqueous solutions which apparently produce these abnormal values of the osmotic pressure, the lowering of the vapor pressure, the lowering of the freezing point, and the elevation of the boiling point. We saw that Clausius in his explanation of the passage of electricity assumed that there were a few ions in solution resulting from the bombardment and collision of the polarized molecules. Arrhenius went considerably farther and assumed that a large part of the solute existed in the ionic form and that through the mere act of solution the solute is separated into its ions, that is, the solute is *dissociated.* Arrhenius assumed that the solute exists in solution in two ways, part of it as active and part inactive, the active part being the part dissociated, existing as ions, and the inactive part being the part remaining undissociated.

On dissolving sodium chloride in water we would then have

$$\begin{array}{c} NaCl \rightleftarrows Na^+ \cdot Cl^- \\ \text{inactive} \rightleftarrows \text{active} \end{array}$$

the inactive sodium chloride being in equilibrium with the active part, which is the part ionized and existing as Na and Cl ions. The relative quantities of the active and inactive parts of the molecule depend upon the dilution. As water is added, the amount of dissociation increases, while if the concentration of the salt is increased, the inactive part increases, and the dissociation decreases. To these dissociated or active parts in solution Arrhenius gave the term *ions*, retaining the term introduced by Faraday to represent *that which* conducted the electric current. He further showed that one gram-equivalent of the ions which migrated to the cathode carried 96,540 coulombs or one *faraday* of electricity, and the ions which migrated toward the anode carried a charge of 96,540 coulombs of electricity but of the opposite sign. It was recognized that the dissociated parts, the ions, are not like the metallic sodium and the elemental chlorine, but that they are decidely different, and this difference is due to the difference of their energy content, for when the ions reach the electrodes in the processes of electrolysis they give up their electrical charge and become the elemental substances. The ionic form differs from the elemental form in that the ions carry charges of electricity; the cations positive charges and the anions negative charges. The sodium ion is represented thus, Na^+, the symbol for sodium with a small plus sign indicating that the electrical charge is positive and that on each gram-equivalent of ions there is a positive charge of 96,540 coulombs. The chlorine ion is expressed Cl^-, the negative sign indicating a negative charge of 96,540 coulombs of electricity residing on one gram-equivalent of chlorine ions. The difference between the atomic and ionic form is then merely a difference in their energy content.

The dissociation of acids results in the formation of hydrogen ions and the ion of the acid part or radical thus: $H^+ \cdot Cl^-$; $H^+ \cdot H^+ \cdot SO_4^{--}$; $H^+ \cdot NO_3^-$; $CH_3COO^- \cdot H^+$. From the dissociation of bases we have the basic ion and the hydroxyl ions; thus, $Na^+ \cdot OH^-$; $NH_4^+ \cdot OH^-$; $Ba^{++} \cdot OH^- \cdot OH^-$; while in the case of salts we have the part that takes the place of the hydrogen in acids and the acid part of the compound; thus, $K^+ \cdot Cl^-$; $Sr^+ \cdot NO_3^- \cdot NO_3^-$; $Na^+ \cdot C_2H_3O_2^-$; etc. The dissociation into ions is the same as the separation which takes place in chemical reactions. In fact, some go so far as to state that all reactions are ionic, hence, the reacting parts and the parts which go from one compound to another are those which in aqueous solutions are recognized as the ions.

It was shown by Kohlrausch and confirmed subsequently that the conductance is the sum of the ionic conductances, and hence the maximum equivalent conductance must be attained when the electrolyte is completely dissociated. Ostwald showed that the conductance at any other dilution could be represented by $\Lambda = \alpha(\Lambda_c + \Lambda_a)$ or $\frac{\Lambda}{\Lambda_c + \Lambda_a} = \alpha$, or $\frac{\Lambda}{\Lambda_\infty} = \alpha$, which is the ratio of the conductance at the given dilution to the conductance at infinite dilution. α is called the *Degree of Dissociation*. We saw when we were studying the dissociation of gases that a relation between the degree of dissociation α and i was expressed as follows: $i = 1 + (f - 1)\alpha$ or $\alpha = \frac{i - 1}{f - 1}$. The factor i is the ratio of the total number of parts present after dissociation to the original number. The original number of parts is defined by $\frac{g}{m} = n$, in which g is the weight in grams, m is the formula weight, and n is the number of gram-molecules or moles. The value for α can be obtained from the electrical conductivity methods; van't Hoff showed that the value for i could be obtained from osmotic pressure data.

We have seen that the freezing point, boiling point, and vapor pressure methods all give abnormal values for the molecular weight of the solute, and from these the value of i can be calculated. Then from the above relation between i and α the value for i can be calculated, providing α is known and f, the number of parts into which the dissolved electrolyte is dissociated. Arrhenius did this, taking the best data available at that time (1887), and found that the values for i calculated by the two methods agreed fairly well. He concluded that the value for i could be ascertained from any of the five methods; viz. osmotic pressure, boiling point, freezing point, vapor pressure, and electrical conductivity. Hence it follows that all of them can be used for the determination of α, the degree of dissociation.

Table LIII — Degree of Dissociation

	Method	Liters per Gram Equivalent						
		200	100	50	20	10	5	2
KCl	F. P.	96.3	94.3	91.8	88.5	86.1	83.3	80.0
	Cond.	95.6	94.1	92.2	88.9	86.0	82.7	77.9
NH_4Cl	F. P.	94.7	92.8	90.7	87.8	85.6	83.2	
	Cond.		94.1	92.1				
NaCl	F. P.	95.3	93.8	92.2	89.2	87.5	85.0	82.4
	Cond.	95.3	93.6	91.6	88.2	85.2	81.8	77.3
CsCl	F. P.			93.0	89.2	86.3	82.9	77.8
	Cond.	95.4	93.7			84.7		
LiCl	F. P.	94.4	93.7	92.8	91.2	90.1		
	Cond.	94.9	93.2	89.0	87.8	84.6	81.2	76.6
KBr	F. P.			92.9	88.9	86.3	83.9	81.3
	Cond.	95.5	94.0	92.1	88.8	85.9	82.5	76.6
$NaNO_3$	F. P.		90.3	88.5	85.5	83.0	79.8	
	Cond.	95.0	93.2	91.0	87.1	83.2	78.8	71.9
KNO_3	F. P.		90.1	88.0	83.6	78.1	71.1	
	Cond.	95.3	93.5	91.1	86.7	82.4	77.2	68.8
$KClO_3$	F. P.		91.4	89.1	84.9	79.8		
	Cond.	95.2	93.3	91.0	86.6	79.9	78.0	70.3
$KBrO_3$	F. P.		91.4	89.1	84.9	79.8		
	Cond.	95.4	93.4	91.0	86.8			
KIO_3	F. P.	94.1	91.3	88.2	82.8	76.5		
	Cond.	94.6	92.8	90.3	86.0	81.9	77.5	
$NaIO_3$	F. P.	93.9	91.6	89.0	84.2	77.3		
	Cond.	93.9	91.7	89.0	84.2	80.1	75.2	
$KMnO_4$	F. P.	93.8	92.1	91.3				
	Cond.	96.8	95.1	93.0				
HCl	F. P.	99.1	97.5	95.7	93.3	91.7		
	Cond.	98.1	97.2	96.2	94.4			
HNO_3	F. P.	97.4	96.0	94.2	91.2	90.0	87.9	
	Cond.		97.0		94.0			
$BaCl_2$	F. P.	89.9	87.8	85.5	81.9	78.8	75.8	
	Cond.		88.3	85.0	79.8	75.9	72.0	67.2
$CaCl_2$	F. P.			87.6	83.7	81.5	80.4	
	Cond.	91.0	88.3	85.1	80.3	76.4	72.7	68.8
$MgCl_2$	F. P.			88.5	85.4	83.9	83.3	
	Cond.	91.0	88.3	85.1	80.3	76.5	72.8	68.7
$CdCl_2$	F. P.		79.1	76.8	69.0	60.5	53.9	
	Cond.	80.3	73.5	66.4	55.9	45.3	37.5	28.9
$CdBr_2$	F. P.		78.0	70.4	58.9	48.2	36.7	
	Cond.	74.9	66.1	57.3				
CdI_2	F. P.		59.3	54.0	40.0	22.5	10.0	
	Cond.	67.5	57.3	46.9				
$Cd(NO_3)_2$	F. P.	94.8	92.1	90.1	88.7	88.4		
	Cond.	91.7	87.1	84.8	79.2	73.1	68.4	62.8
$Ba(NO_3)_2$	F. P.	91.7	88.8	85.5				
	Cond.	89.8	86.1	81.8	74.4	67.9	60.9	50.4
$Pb(NO_3)_2$	F. P.	89.0	85.0	80.4	72.4	64.9	56.8	42.7
	Cond.	88.6	84.5	79.3	70.8	63.5	55.9	45.4
K_2SO_4	F. P.	92.9	89.9	85.7	78.5	73.0	66.7	56.8
	Cond.	90.5	87.2	83.2	77.1	72.2	67.3	61.8
Na_2SO_4	F. P.			86.7	79.5	73.6	67.2	56.7
	Cond.	89.3	85.7		75.6	70.4	65.2	
$MgSO_4$	F. P.	69.4	61.8	53.6	42.0	32.4	22.3	8.4
	Cond.	74.0	66.9	59.6	50.6	44.9	40.3	
$CuSO_4$	F. P.	61.6	54.5	45.5	31.8			
	Cond.	70.9	62.9	55.0	45.5	39.6	35.1	
$ZnSO_4$	F. P.	66.5	58.2	48.9				
	Cond.	71.0	63.3	55.6	46.4	40.5	36.0	
$CdSO_4$	F. P.	65.8	56.9	47.7	34.3			
	Cond.	69.4	61.4	53.4	43.7	37.7	33.2	29.0
$K_3Fe(CN)_6$	F. P.	89.4	86.8	77.8				
	Cond.	86.9	82.7					
$K_4Fe(CN)_6$	F. P.				63.4	58.1	52.0	42.5
	Cond.				59.1	53.8	49.8	

In Table LIII are given data compiled by Noyes and Falk which are supposed to be the best available, and from these it is apparent that Arrhenius was justified in his conclusion that the degree of dissociation is practically the same when determined from the lowering of the freezing point and from the electrical conductance of the solution, although the former is determined at 0° C. and the latter at 18° C. From the data available Arrhenius pointed out many discrepancies and called special attention to the sulphates. For the sulphates of the alkalies the values for the degree of dissociation vary several per cent, while in the case of $CuSO_4$, $ZnSO_4$, $CdSO_4$, etc., the variation according to the data in this table is very marked, amounting in some cases to 10 or 12 per cent. In the case of $MgSO_4$, at the dilution of 5 liters, according to the freezing point method, the value of α is 22.3, while by the electrical conductance 40.3 was found.

The value for the degree of dissociation of K_2SO_4 is 89.9 in solutions in which one gram-equivalent is contained in 100 liters. Taking this value as 90 per cent, what will be the value of i? The electrolyte dissociates according to this equilibrium equation, $K_2SO_4 \rightleftarrows K^+ \cdot K^+ \cdot SO_4^{--}$, *i.e.* it dissociates into three parts, and f then $= 3$. The relation is $i = 1 + (f - 1)\alpha$. Substituting these values for f and α, we have $i = 1 + (3 - 1)0.9$. Solving, $i = 2.80$, that is, there are 2.8 times as many parts in the solution after it is 90 per cent dissociated as before dissociation. In case of complete dissociation α is one, or the degree of dissociation 100 per cent. Then substituting in the formula, we have $i = 1 + (3 - 1)1$, and $i = 3$, the number of times the total number of parts is of the original number of molecules. This is apparent from an inspection of the equilibrium equation; if we have one mole of K_2SO_4, and it dissociates into 2 K^+ and one SO_4^{--}, there are three times as many parts (ions in this case) as there were of the original number of molecules.

An examination of the values of the equivalent conductances given in Table XLVIII shows that the values for the acids HCl, HNO_3, and H_2SO_4 are very high as compared with the values of the other electrolytes; the values for the bases, KOH and NaOH, are next in size; while the values for the salts of the alkalies are next in magnitude. Since the speeds of the H and OH ions are the most rapid, we expect solutions containing them to be the best conductors. Such is the case, and in general acids are the best conductors, bases next, and salts of the alkalies are all good conductors. It will be observed, however, in the case of acetic acid, that the value of the equivalent conductance is only about one tenth that of the other acids, yet each solution contains the same gram-equivalent of hydrogen. Similarly, solutions of NH_4OH are very poor conductors, the value of Λ_{100} being 7.1 as against 203 for NaOH and 228 for KOH, yet there is the same quantity of OH by weight in the solutions. How, then, is the difference in the conductance accounted for? Since the current is carried by the ions, we assume that there is not the quantity of H ions in a solution of acetic acid that there is in the HCl solution, nor are there the OH ions in the solution of NH_4OH that there are in the NaOH solution. Since these ions come from the dissociation of the electrolytes, we conclude they are very slightly dissociated. In different ways the strength of the different acids can be determined, and they all give values showing that acetic acid is a weak acid as compared to HCl. It is concluded that those acids that are highly dissociated and yield a large number of hydrogen ions are strong acids and the slightly dissociated acids are weak acids. The same holds true for bases; NH_4OH is therefore a weak base. Upon the basis of this we may formulate the following definitions: An acid is a substance which in an aqueous solution yields hydrogen ions. A base is a substance which in an aqueous solution yields hydroxyl ions. Electrolytes in general may be classified into strong electrolytes or those which in aqueous solutions are highly dissociated, and weak electrolytes or those which are but slightly dissociated. The salts of the alkalies and of the alkaline earths are more than 80 per cent dissociated in dilutions greater than 100 liters and the sulphates of the heavy metals are only about 50 to 60 per cent dissociated, and the weak electrolytes, such as the weak acids and bases, are less than 25 per cent dissociated.

The question arises, how can the equivalent conductance be obtained in the case of weak electrolytes? Suppose the equivalent conductance at infinite dilution, Λ_∞, of acetic acid, CH_3COOH, is to be obtained. Acetic acid is so slightly dissociated that the value at infinite dilution cannot be determined experimentally. The value for H^+ can be obtained from the completely dissociated HCl providing the equivalent ionic conductance of Cl^+ is known. Then in a similar way by taking a solution of an alkali acetate such as CH_3COONa, the maximum value, Λ_∞, can be obtained experimentally since it is a strong electrolyte. From Kohlrausch's Law we have $\Lambda_\infty = \Lambda_c + \Lambda_a$. From Table L we find the value of the equivalent ionic conductance of Cl^- at 18° C. is 65.5, and if Λ_∞ for HCl is 377, then we have $377 - 65.5 = 311.5$ as the value of the equivalent ionic conductance of H^+. Similarly for CH_3COONa we have $\Lambda_\infty = 76.8$, and the equivalent ionic conductance of Na^+ is 43.4; then the value for the acetate-ion is $76.8 - 43.4 = 33.4$. The value of Λ_∞ for acetic acid is then $311.5 + 33.4 = 344.9$, but the value at the dilution 100 liter is $\Lambda_{100} = 14.3$, and the degree of dissociation is $\frac{\Lambda_{100}}{\Lambda_\infty} = \frac{14.3}{344.9} = 4.1$ per cent.

There are a number of interesting properties of solutions which are attributed to the properties of the ions, and many of these have been put forth as confirmatory evidence in favor of the theory of electrolytic dissociation. The theory has been applied to explain many phenomena and particularly in qualitative analysis. We shall present a few of the more general and commonly accepted applications of the electrolytic dissociation theory in order to emphasize the method of using it to explain the properties of solutions and chemical reactions.

1. *Effect of temperature* on the conductance is shown in Table L, in which is given the equivalent ionic conductances of the separate ions. For example, the value for K at 18° is 64.5, while at 25° it is 74.8 mhos, thus showing a marked increase in the ionic conductances with the temperature. The equivalent conductances of the electrolytes then increase with the increase in the temperature, and tables have been compiled showing the temperature coefficient of the conductance of a large number of electrolytes. The transport numbers also vary with the temperature, as is shown in Table XLIX. As the conductance is proportional to the speed of the ions, the equivalent conductance is proportional to the number of these which are transporting the current. It follows then that in order to determine the effect of temperature upon the degree of dissociation a number of factors will have to be taken into consideration. In addition to the number resulting from the dissociation their speed will be influenced by the viscosity of the solution, that is, to the friction which the ions encounter in their passage through the solution, which varies with the temperature. The thermal change accompanying the ionization is termed the heat of ionization, and Arrhenius calculated this from the rate of change of conductance with the temperature. The heat of ionization, while it may be either positive or negative, is usually positive, which means that the ionization is accompanied with evolution of heat, and according to Le Chatelier's theorem the ionization should decrease with a rise in temperature. The heat of ionization may be determined from the constant of the heat of neutralization and from the law of thermal neutrality, reference to which will be made subsequently, but it

would lead us too far to develop the thermodynamic formula for calculating the influence of temperature on the degree of ionization.

2. *Basicity of organic acids* has been shown by Ostwald to bear a definite relation to the equivalent conductance of the sodium salts of the acid at 32 and 1024 liters dilution. For monobasic acids this difference is 10 units, and as the basicity increases the differences are found to be multiples of 10. That is, $\frac{\Lambda_{1024} - \Lambda_{32}}{10}$ = the basicity of the organic acid. In Table LIV from data according to Ostwald is given the difference in the equivalent conductance of the sodium salts of a number of organic acids, and in the last column the basicity as calculated from the above formula.

TABLE LIV

Sodium Salt	($\Lambda_{1024}-\Lambda_{32}$)		Difference	Basicity
Sodium nicotinate	78.8	68.4	10.4	1
Sodium quinolinate	90.0	69.2	20.8	2
Sodium pyridinetricarbonate . .	113.1	82.1	31.0	3
Sodium pyridinetetracarbonate .	121.2	80.8	40.4	4
Sodium pyridinepentacarbonate .	127.8	77.7	50.1	5

3. *Additive Properties.* We have seen that some properties of substances were attributed to permanent characteristics of the elements, and that the sum of these gave the properties of the substances, such as the atomic volume, atomic heat, index of refraction, magnetic rotatory power, etc. These, however, we saw were only approximations at best, but in solutions of electrolytes these additive relations appear to be much more exact. Very extended data have been presented by MacGregor, Groshaus, Ostwald, Gladstone, and numerous other authors, in which they emphasize the additive properties of solutions of electrolytes, and even

before the formulation of the electrolytic theory many observers attributed the properties of the solution to the independent characteristic properties of the constituents of the solute.

Whetham calls attention to the following relations which emphasize the additive properties of solutions of electrolytes. When ionization is complete, the properties of the solution should be the additive result of the individual properties of the ions and of the solvent, and when dissociation is not complete, there should appear an additive factor due to the undissociated solute. The specific gravities of salt solutions were calculated by Valson from experimentally determined moduli of the elements. By the specific volume relations Groshaus showed that the molecular volume of the solute is, in dilute solutions, the sum of two constant factors, one for the acid and the other for the base. That the densities and thermal expansions of solutions are also additive has been confirmed by Bender. The volume change accompanying the neutralization of acids by bases also illustrates the additive properties as shown by Ostwald and by Nicol.

The additive character of colored solutions is readily seen from an examination of the absorption spectra of a series of such solutions containing a common ion, the absorption spectra due to this ion being unaffected by the other parts of the solute in solution. In aqueous solutions anhydrous cobalt chloride forms solutions red in color while the pure salt itself is blue. The color of the cobalt ion is then red. In alcoholic solutions, in which the dissociation as obtained from the conductance is practically negligible, the color of the solution is blue—the color of the undissociated compound. Upon addition of water to this solution the red color gradually appears. Copper ions are blue, hence all aqueous solutions of copper salts should be blue. If, however, we add KCN to an ammoniacal copper sulphate solution, we have the solution completely decolorized with the formation of

$K_3Cu(CN)_4$ and the complete disappearance of copper ions. K_2CrO_4 dissociates into $2\ K^+ \cdot CrO_4^{--}$ and forms yellow aqueous solutions; hence the CrO_4 ion is yellow; as solutions of salts of the alkalies are colorless, their ions are colorless. If the chromate is reduced by H_2S, we obtain a greenish solution with the formation in the presence of H_2SO_4 of $Cr_2(SO_4)_3$, which dissociates as follows: $2\ Cr^{+++} \cdot 3\ SO_4^{--}$. Since the SO_4 ions are colorless, the green color of the solution is attributed to the green color of the Cr ions.

Similarly manganese, when it functions as a base with the formation of manganous salts, $MnCl_2$, $MnSO_4$, etc., produces very pale pink or nearly colorless solutions, while $KMnO_4$ solutions are highly colored, due to the presence of the MnO_4 ions. In its salts manganese has a valency of two, while in the permanganate compounds its valency is seven, and it is fulfilling the function of an acid. Hence, the change from a cation to an anion consists in increasing the valency of the manganese from two to seven. The same is true for chromium as illustrated above; as in the cation it has the valency of three, and in the anion its valency is six. In both cases we have the change from cation to anion accompanied by an increase in valency, which process we call *oxidation* and the reverse process *reduction*.

So, too, for iron in ferrous chloride we have $FeCl_2 \rightleftarrows Fe^{++} \cdot 2\ Cl^-$. The solution is practically colorless, but when this is oxidized we have a yellow solution, $FeCl_3 \rightleftarrows Fe^{+++} \cdot 3\ Cl^-$, the difference being that in one case the colorless ion of iron carries two charges, and the colored iron ion carries three charges of electricity. Hence, the process of oxidation is due to the increase in the valency of the iron obtained by adding an additional *faraday* of electricity to the gram-equivalent of the iron ions. It is evident that our processes of oxidation and reduction may be explained upon this basis.

That the rise in temperature decreases the degree of dissociation may be illustrated in the case of colored solutions.

Copper chloride solutions are blue, and anhydrous copper chloride is yellow. When this latter is added to aqueous solutions of copper chloride to produce concentrated solutions, we have the combination of the blue and yellow producing a solution with a decided green color. If water is now added, the solution becomes blue, and on heating the green color can be restored, thus showing the reduction in dissociation on heating the same as on increasing the concentration of the solution.

Other properties of solutions, such as viscosity, surface tension, optical rotatory power, etc., illustrate the additive properties of the solutions which are attributed to the additive properties of the dissociated parts.

4. *Substitution.* We have seen the effect of the substitution of a group such as CH_3 upon the various properties of the compound, such as boiling point, refraction, etc. The effect of the first substitution is greatest and diminishes with the successive substitutions. In the case of the electrical conductance of aqueous solutions of these substitution products we likewise find a marked effect resulting from these substitutions. This will be considered more in detail under the discussion of the dissociation constant, page 340.

5. The mutual reaction of two electrolytes resulting in the so-called process of double decomposition is explained upon the basis of the electrolytic dissociation theory. In the equilibrium equation $Ag^+ \cdot NO_3^- + H^+ \cdot Cl^- \rightleftarrows AgCl + H^+ \cdot NO_3^-$ expressed as an ionic reaction, we see that there has been a disappearance of the Ag and Cl ions, resulting in the formation of AgCl, which we recall is insoluble and is precipitated. We say that the chlorine and silver ions cannot exist in solution at the same time and are consequently precipitated. In the reaction representing the neutralization of a base by an acid, we have $Na^+ \cdot OH^- + H^+ \cdot Cl^- \rightleftarrows Na^+ \cdot Cl^- + H_2O$. Here we have the disappearance of the H^+ and OH with the formation of H_2O, which is soluble, while the Na^+ and Cl^- re-

main in solution as before the reaction, but we say we have a salt formed, and this is dissociated, thus giving us practically the Na and Cl ions as they originally existed. We have the undissociated water produced by this process of neutralization, and for all cases we have approximately the same amount of heat evolved for each gram-molecule of water produced. In other words, neutralization consists in the formation of water from the union of the H^+ and OH^-. In like manner, the chemical reactions representing double decompositions may be explained. The application of the theory to Qualitative Analysis is evident and serves as a basis for the presentation of this subject. Some authors state that all chemical reactions are ionic, and that it is only between the ions that reactions occur, whether these be in aqueous or non-aqueous solutions and even in cases where no solvent medium is employed. These relations will be considered somewhat more in detail in a few specific cases subsequently.

CHAPTER XXIX

EQUILIBRIUM BETWEEN THE DISSOCIATED AND UNDISSOCIATED PARTS OF AN ELECTROLYTE IN SOLUTION

ARRHENIUS assumed that the electrolyte exists in solution as the active and the inactive parts, and that the active part consists of the ions or constitutes the parts into which the electrolyte is dissociated. As we have just seen, it is to these parts, the ions, that the chemical reactions are all attributed. Since there is an equilibrium always existing between these two parts, Ostwald, as well as van't Hoff, showed that the Mass Law is applicable to this equilibrium between the undissociated part of the electrolyte and the ions into which it is dissociated. Applying the Mass Action Law to the equation

$$\mathrm{NaCl} \rightleftarrows \mathrm{Na^+} \cdot \mathrm{Cl^-}$$

we have

$$\frac{k[\mathrm{NaCl}]}{V} = \frac{[\mathrm{Na^+}]}{V} \cdot \frac{[\mathrm{Cl^-}]}{V}$$

but the concentration of the sodium and chlorine ions is the same, as there are the same number of positive ions produced as there are negative ions when the NaCl is dissociated, hence $[\mathrm{Na^+}] = [\mathrm{Cl^-}]$ and the equation may be written

$$\frac{k[\mathrm{NaCl}]}{V} = \left(\frac{[\mathrm{Na^+}]}{V}\right)^2.$$

Since we represent the degree of dissociation by α, then

α = the part or concentration of the dissociated parts

and $1 - \alpha$ = the part or concentration of the undissociated part.

Substituting these respectively for $[\mathrm{Na^+}]$ and $[\mathrm{NaCl}]$ the equation becomes

$$k\frac{1-\alpha}{V} = \left(\frac{\alpha}{V}\right)^2$$

which becomes

$$k(1 - \alpha)V = \alpha^2.$$

This is known as *Ostwald's Dilution Law*, and may be written

$$k = \frac{\alpha^2}{V(1-\alpha)}.$$

The degree of dissociation is usually obtained by the electrical conductance method, *i.e.* $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, and substituting this value for α we have

$$k = \frac{\left(\frac{\Lambda_v}{\Lambda_\infty}\right)^2}{V\left(1 - \frac{\Lambda_v}{\Lambda_\infty}\right)} \text{ or } \frac{\Lambda_v^2}{V(\Lambda \quad - \Lambda_v)\Lambda_\infty}$$

from which the value of k, *the dissociation constant*, can be readily determined by measuring the electrical conductance, Λ_v, at the volume, V, and knowing Λ_∞. This Law of Dilution has been verified in the case of over two hundred forty organic acids, and Ostwald's data given in Table LV illustrate the satisfactory agreement for the values of k over a wide range of concentration.

TABLE LV

V	Acetic Acid			Propionic Acid			Succinic Acid		
	Λ	$100\,\alpha$	k	Λ	$100\,\alpha$	k	Λ	$100\,\alpha$	k
8	4.34	1.193	1.80×10^{-5}	3.65	1.016	1.30×10^{-5}	11.40	3.20	6.62×10^{-5}
16	6.10	1.673	1.79	5.21	1.452	1.34	16.03	4.50	6.62
32	8.65	2.38	1.82	7.36	2.050	1.34	22.47	6.32	6.67
64	12.09	3.33	1.79	10.39	2.895	1.35	31.28	8.80	6.64
128	16.99	4.68	1.79	14.50	4.04	1.33	43.50	12.24	6.68
256	23.82	6.56	1.80	20.38	5.68	1.33	59.51	16.75	6.59
512	32.20	9.14	1.80	28.21	7.86	1.31	81.64	22.95	6.68
1024	46.00	12.66	1.77	38.73	10.79	1.28	109.5	30.82	6.71
	$\Lambda_\infty = 364$			309			355		
	Mean value		$k = 1.80 \times 10^{-5}$			$k = 1.34 \times 10^{-5}$			$k = 6.65 \times 10^{-5}$

In Table LV V is the volume in liters of solution in which one gram-equivalent of the acid is contained; Λ the equivalent conductance for the given volume at 25° C.; the third column, 100 times α, the per cent dissociation, and in the last column, k, the dissociation constant.

Bredig found upon investigation 50 bases conforming fairly well to the Dilution Law of Ostwald as the data in Table LVI illustrate. The molecular conductance μ is expressed in reciprocal Siemens units. One ohm equals 1.063 Siemens units.

TABLE LVI

	Ammonium Hydroxide			Ethylamine			Methylamine		
V	μ	$100\,\alpha$	k	μ	$100\,\alpha$	k	μ	$100\,\alpha$	k
8	3.20	1.35	2.3×10^{-5}	13.8	6.45	5.6×10^{-4}	14.1	6.27	5.2×10^{-4}
16	4.45	1.88	2.3	19.6	9.16	5.8	19.6	8.71	5.2
32	6.28	2.65	2.3	27.0	12.6	5.7	27.0	12.0	5.1
64	8.90	3.76	2.3	36.6	17.1	5.5	36.7	16.3	5.0
128	12.63	5.33	2.3	49.4	23.1	5.4	49.5	22.0	4.9
256	17.88	7.54	2.4	65.6	30.7	5.3	65.4	29.1	4.7
	$\mu_\infty = 237$ Mean $k = 2.3 \times 10^{-5}$			$\mu_\infty = 214$ Mean $k = 5.6 \times 10^{-4}$			$\mu_\infty = 225$ Mean $k = 5.0 \times 10^{-4}$		

The degree of dissociation of these organic acids is very slight, and the same is true of the bases all of which come under the classification of *weak* electrolytes. For this class of electrolytes the law was found to hold very well. In the case of highly dissociated substances, the strong electrolytes, no such uniform values for the constant were obtained, and no explanation has yet been given to account for this fact. Many efforts have been made to modify the equation so that it would give a value for k which was more nearly a constant. Rudolphi proposed that the square root of the volume be substituted for V. The equation takes the form

$$k = \frac{\alpha^2}{(1 - \alpha)\sqrt{V}}.$$

Ostwald's equation may be written $\frac{[i]^2}{[u]} = k$, in which $[i]$ is the concentration of each of the ions and $[u]$ is the concentration of the un-ionized part. Van't Hoff proposed the empirical equation

$$k = \frac{\alpha^3}{(1 - \alpha)^2 V} \text{ or } k = \frac{\alpha^{1.5}}{(1 - \alpha)\sqrt{V}}$$

which then becomes $k = \frac{[i]^{1.5}}{[u]}$, which gives us a simple relation between the concentration of the ionized parts and the undissociated part. For Ostwald's formula the exponential value is 2, that of van't Hoff 1.5, and Bancroft proposed that the general character n be employed, which gives the equation $k = \frac{[i]^n}{[u]}$. He found that for strong electrolytes this value ranges from 1.43 to 1.56, while for the weak electrolytes it is practically two. In Table LVII are given the values of k for NH_4Cl at 18° C. as determined by all three of these equations.

TABLE LVII

V	Λ	α	$(1-\alpha)$	$\frac{\alpha^2}{(1-\alpha)V} = k$ Ostwald	$\frac{\alpha^2}{(1-\alpha)\sqrt{V}} = k$ Rudolphi	$\frac{\alpha^{1.5}}{(1-\alpha)\sqrt{V}} = k$ van't Hoff
1	97.0	.749	.251	2.23	2.24	2.58
2	101.4	.783	.217	1.41	2.00	2.26
5	106.5	.823	.177	.764	1.71	1.89
10	110.7	.855	.145	.504	1.59	1.72
20	115.2	.890	.110	.360	1.61	1.71
50	119.6	.924	.076	.178	1.59	1.64
100	122.1	.942	.058	.122	1.53	1.58
200	124.2	.959	.041	.112	1.59	1.62
500	126.2	.975	.025	.076	1.70	1.72
1000	127.3	.983	.017	.057	1.80	1.81
5000	128.8	.995	.005	.039	2.80	2.80
10000	129.2	.998	.002	.005	4.98	4.99
Λ_∞	129.5					

Both the Rudolphi and van't Hoff equations give equally constant values for k, particularly for the more dilute solutions (from $V = 10$ to $V = 1000$ liters), while the Ostwald equation gives values for k which decrease regularly and rapidly.

Several attempts have been made to obtain a physical significance for van't Hoff's equation, such as the equations of Kohlrausch, of Kendall, and of Partington particularly, whose equation gives a constant that passes through a maximum and holds only fairly well for strong electrolytes. It is, however, still a question whether the Law of Mass Action can be applied to the electrolytic dissociation of strong electrolytes.

Dissociation or Ionization Constant. — The strong electrolytes, which include practically all of the ordinary inorganic acids, bases, and salts, with a few exceptions, are highly dissociated, and the values of the dissociation constant, as we saw in the case of NH_4Cl, are not of the same magnitude for the different dilutions. But in the case of the weak electrolytes, which include a few inorganic acids, bases, and salts, and most of the organic acids and bases, we have a class of substances slightly dissociated to which the Law of Mass Action appears to be applicable or sufficiently so that the degree of dissociation can be calculated and also the dissociation constant. It is to be remembered that the value of α, which as we have seen can be ascertained in a variety of ways, is usually very small. Then too the value of the conductance at infinite dilution, Λ_∞, is not easy to determine, and slight variations in this value may affect the value of α greatly, since $\frac{\Lambda_v}{\Lambda_\infty} = \alpha$, and then the value of the dissociation constant becomes somewhat uncertain.

There have been compiled in Landolt-Börnstein's *Tabellen* the dissociation constants of a large number of acids and bases, both inorganic and organic, and in Table LVIII we have selected a few of these in order to show the order of the constant at 25° C.

TABLE LVIII

SUBSTANCE	FORMULA	VOLUME IN LITERS	DISSOCIATION CONSTANT
Acids			
1. Acetic acid	CH_3CHOO	8 − 1024	1.80×10^{-5}
2. Boric acid	BO_3H_3	46 − 185	6.6×10^{-10}
3. Benzoic acid	C_6H_5COOH	64 − 1024	6.0×10^{-5}
4. Carbonic acid . . .	H_2CO_3		1.3×10^{-11}
5. Monochlor acetic acid	$CH_2ClCOOH$	16 − 1024	1.55×10^{-3}
6. Dichlor acetic acid .	$CHCl_2COOH$	32 − 1024	5.1×10^{-2}
7. Trichlor acetic acid .	CCl_3COOH	8 − 1011 (18° C.)	3.0×10^{-1}
8. Cyan acetic acid . .	$CH_2(CN)COOH$	16 − 1024	3.7×10^{-3}
9. *m*-chlor benzoic acid	$mC_6H_4ClCOOH$	256 − 1024	1.55×10^{-4}
10. Formic acid	$HCOOH$	8 − 1024	2.14×10^{-4}
11. Hydrocyanic acid . .	HCN	20	7.2×10^{-10}
12. Hydrogen sulphide .	H_2S	25 − 125 (18° C.)	5.7×10^{-8}
13. Lactic acid	$CH_3CHOHCOOH$	8 − 1024	1.38×10^{-4}
14. Malonic acid . . .	$COOHCH_2COOH$	16 − 2048	1.58×10^{-3}
15. Nitrous acid	HNO_2	512 − 1536	4.5×10^{-4}
16. Oxalic acid	$(COOH)_2$	32 − 4096	3.8×10^{-2}
17. Phenol	C_6H_5OH	50 − 100	1.09×10^{-10}
18. Trichlor phenol . . .	$C_6H_2OHCl_3$	256 − 1024	1.0×10^{-6}
19. Propionic acid . . .	CH_3CH_2COOH	16 − 1024	1.3×10^{-5}
20. Salicylic acid . . .	$C_6H_4OH(COOH)$	64 − 1024	1.06×10^{-3}
21. Succinic acid . . .	$C_2H_4(COOH)_2$		1.3×10^{-2}
22. Sulphuric acid . . .	H_2SO_4	10 − 40	3.0×10^{-2}
23. Tartaric acid . . .	CH(OH)−COOH | CH(OH)−COOH	16 − 2048	9.7×10^{-4}
Bases			
1. Acetamid	CH_3CONH_2	100	3.1×10^{-15}
2. Acetanilid	$CH_3CONHC_6H_5$	10 (40° C.)	4.1×10^{-14}
3. Ammonia	NH_3 (NH_4OH)	2 − 100	1.8×10^{-5}
4. Aniline	$C_6H_5NH_2$		4.6×10^{-10}
5. Cocain			4.7×10^{-7}
6. Ethylamine	$C_2H_5NH_2$	8 − 256	5.6×10^{-4}
7. Diethylamine . . .	$NH(C_2H_5)_2$	8 − 256	1.26×10^{-3}
8. Triethylamine . . .	$N(C_2H_5)_3$	8 − 256	6.4×10^{-4}
9. Hydrazine	N_2H_5OH	8 − 256	3.0×10^{-6}
14. Pyridine	C_5H_5N	50 − 599	2.3×10^{-9}
10. Methylamine . . .	CH_3NH_2	8 − 256	5.0×10^{-4}
11. Dimethylamine . .	$NH(CH_3)_2$	8 − 256	7.4×10^{-4}
12. Trimethylamine . .	$N(CH_3)_3$	8 − 256	7.4×10^{-5}
13. Butyro nitrile . . .	C_3H_7CN	100	1.8×10^{-1}
15. Urea	$CO(NH_2)_2$	4 − 5	1.5×10^{-1}
16. Strychnine	$C_{21}H_{22}N_2O_4$	20	1.43×10^{-7}

The degree of dissociation of weak acids is comparatively small, and α is therefore very small as compared to unity. Hence in the equation $k = \frac{\alpha^2}{(1 - \alpha)V}$ the expression $(1 - \alpha)$ is not materially different from unity (1), and the equation then becomes $k = \frac{\alpha^2}{V}$ or $\alpha^2 = kV$, and $\alpha = \sqrt{kV}$. The degree of dissociation of two acids can then be readily compared by expressing the ratio of these two factors or the square root of the value of the dissociation constant, thus $\frac{\alpha_1}{\alpha_2} = \frac{\sqrt{k_1 V}}{\sqrt{k_2 V}}$, and for the same volume we have $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{k_1}{k_2}}$. Since the strength of acids is proportional to their degree of dissociation, we can readily ascertain from the dissociation constants the relative strength of the acids (and the bases as well) since the dissociation constant is also a measure of the concentration of the hydrogen ions. For example, from Table LVI we find the dissociation constant for acetic acid is 1.8×10^{-5}, and for the trichlor acetic acid is 3.0×10^{-1}; we then have

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{1.8 \times 10^{-5}}{3.0 \times 10^{-1}}} = \sqrt{\frac{0.000018}{0.3}} = \sqrt{\frac{1}{16666.66}} = \frac{1}{129.1}.$$

The substitution of chlorine for the hydrogen of the methyl group increases the strength of the acid enormously. The same is true in the case of the bases ammonia and diethylamine. The dissociation constants are respectively 1.8×10^{-5} and 1.26×10^{-3}. The ratio becomes

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{0.000018}{0.00126}} = \sqrt{\frac{1}{70}} = \frac{1}{8.37}$$

which shows that the strength of the base is increased several times by substituting two ethyl groups in place of the hydrogen of ammonia.

Isohydric Solutions. — Arrhenius showed that two acids which have the same concentration of hydrogen ions can be mixed in any proportions without changing their degrees of dissociation. He termed these solutions which have the same concentration of hydrogen ions, *isohydric solutions*, and went further and stated, "what has just been said about isohydric solutions of acids can be applied without change to other isohydric solutions which have a common ion." Arrhenius based this upon the assumption that all electrolytes follow the dilution law, but this statement is too sweeping and must be revised if what we have seen above is true. He found that in the cases of mixtures of hydrochloric acid and of acetic acid the specific conductance of the mixture was practically the same as the sum of the specific conductances of the two solutions and complied with the mixture law which may be expressed as follows:

$$\kappa_m = \kappa_a \frac{V_a}{V_a + V_b} + \kappa_b \frac{V_b}{V_a + V_b}.$$

In this equation κ_m is the specific conductance of the mixture, κ_a is the specific conductance of one solution at volume V_a, and κ_b is the specific conductance of the other solution at volume V_b. It is further assumed that the two solutions are sufficiently dilute so that the final volume is the sum of the original volumes, that is, $V_a + V_b$. This is the case in concentrations of above 10,000 liters. The degree of dissociation of weak electrolytes at these dilutions is very small, while that of the strong electrolytes is over 80 per cent.

The following presentation follows Bancroft very closely:

In the case of mixtures of solutions of acetic acid and of potassium acetate we have

$$CH_3COOH \rightleftarrows CH_3COO^- \cdot H^+$$

and

$$CH_3COOK \rightleftarrows CH_3COO^- \cdot K^+$$

Assuming the Law of Mass Action to hold if one formula weight of acetic acid is used, then there will be formed x formula weights of CH_3COO^- and we have

$$k_1\frac{1 - x}{V} = \frac{x}{V} \cdot \frac{x}{V}.$$

We have a different dissociation constant k_2 for potassium acetate than for acetic acid, as they are very differently dissociated, and we cannot therefore start with equivalent quantities in equal volumes in order to obtain the same concentration of the common anion of acetic acid, CH_3COO^-, but with some concentration such as C formula weights. The Mass Law Equation for potassium acetate then takes the form $k_2\frac{C - x}{V} = \frac{x}{V} \cdot \frac{x}{V}$. Substituting for the right-hand member of this equation its equal in the above equation, for acetic acid we have $k_2\frac{C - x}{V} = k_1\frac{(1 - x)}{V}$.

Solving for C, we have

$$C = \frac{k_1 + (k_2 - k_1)x}{k_2}.$$

Now let us add the volume nV of the potassium acetate solution to the acetic acid solution. We have for the acetic acid

$$k_1\frac{1 - x}{(n + 1)V} = \frac{(n + 1)x}{(n + 1)V} \cdot \frac{x}{(n + 1)V}$$

and for the potassium acetate

$$k_2\frac{n(C - x)}{(n + 1)V} = \frac{(n + 1)x}{(n + 1)V} \cdot \frac{nx}{(n + 1)V}$$

as when the volume nV of potassium acetate is added the total volume becomes $V + nV$ or $(n + 1)V$, and the mass of the anion of acetic acid becomes $(n + 1)x$, and that of the hydrogen ion remains the same, while the mass of the K^+ is nx. By canceling $(n + 1)$ and n, the equations simplify to

$$k_1 \frac{1 - x}{V} = \frac{x}{V} \cdot \frac{x}{V} \text{ and } k_2 \frac{C - x}{V} = \frac{x}{V} \cdot \frac{x}{V}$$

which are the original equations of equilibrium, thus showing that the degree of dissociation of each of the electrolytes remains unchanged.

For solutions of acetic acid and of zinc acetate we have $CH_3COOH \rightleftarrows CH_3COO^- \cdot H^+$ and $(CH_3COO)_2Zn \rightleftarrows 2\ CH_3COO^- \cdot Zn^{++}$, from which we have respectively

$$k_1 \frac{1 - x}{V} = \frac{x}{V} \cdot \frac{x}{V} \text{ and } k_2 \frac{C - 1/2\,x}{V} = \left(\frac{x}{V}\right)^2 \cdot \frac{1/2\,x}{V}.$$

From this the value of C becomes

$$C = \frac{(k_1 + k_2 V)x - k_1 x^2}{2\,k_2 x}.$$

Now add volume, nV, of zinc acetate solution to the acetic acid solution. We obtain for the acetic acid

$$k_1 \frac{1 - x}{(n + 1)V} = \frac{(n + 1)x}{(n + 1)V} \cdot \frac{x}{(n + 1)V}$$

and for the zinc acetate

$$k_2 \frac{n(C - 1/2\,x)}{(n + 1)V} = \left(\frac{(n + 1)x}{(n + 1)V}\right)^2 \cdot \frac{1/2\,nx}{(n + 1)V}.$$

By canceling $(n + 1)$ and n the two equations reduce to the original equilibrium equations, thus showing no change in the degree of dissociation when the isohydric solutions are mixed in any volume.

For solutions of zinc acetate and of zinc sulphate we have

$$(CH_3COO)_2Zn \rightleftarrows 2\ CH_3COO^- \cdot Zn^{++}$$

and

$$ZnSO_4 \rightleftarrows Zn^{++} \cdot SO_4^{--}$$

for which we have, assuming x formula weights of zinc ions, the Mass Law Equations

$$k_1 \frac{1 - x}{V} = \left(\frac{2\,x}{V}\right)^2 \cdot \frac{x}{V} \text{ and } k_2 \frac{C - x}{V} = \frac{x}{V} \cdot \frac{x}{V}.$$

Now add the volume, nV, of the zinc acetate solution, when we obtain for the zinc acetate

$$k_1 \frac{n(1 - x)}{(n + 1)V} = \left(\frac{n2x}{(n+1)V}\right)^2 \cdot \frac{(n + 1)x}{(n + 1)V}$$

and for the zinc sulphate

$$k_2 \frac{(C - x)}{(n + 1)V} = \frac{(n + 1)x}{(n + 1)V} \cdot \frac{x}{(n + 1)V}.$$

Simplifying, we have

$$k_1 \frac{(1 - x)}{V} = \frac{n}{n + 1}\left(\frac{2x}{V}\right)^2 \cdot \frac{x}{V}$$

and
$$k_2 \frac{C - x}{V} = \frac{x}{V} \cdot \frac{x}{V}$$

from which it appears that for the zinc sulphate we have the same equilibrium equation as before mixing, but in the case of the zinc acetate the factor $\frac{n}{n + 1}$ does not cancel out. There will therefore be increased dissociation of zinc acetate, and as a secondary phenomenon a decrease in the dissociation of zinc sulphate.

These are, however, not binary electrolytes which Arrhenius was considering in his generalizations. Sodium sulphate and zinc sulphate are similar to zinc acetate and zinc sulphate, and sodium sulphate and sodium oxalate are analogous to zinc acetate and zinc chloride. In the case of sodium sulphate and sodium oxalate there would, however, be no change in dissociation, but for sodium sulphate and potassium sulphate or zinc chloride and zinc acetate both salts tend to dissociate and a general expression has been worked out for all of these cases.

Bancroft further applies van't Hoff's equation to the case of isohydric solutions, and for hydrochloric acid and potassium chloride shows that the degree of dissociation of each of the electrolytes should be decreased. The recent experimental work on the mixtures of salt solutions, including acids, shows a decided change in the degree of dissociation of these, and since solutions are considered isohydric on the basis of their conductance, it emphasizes Arrhenius' definition of isohydric solutions that *the ion concentration is independent of the concentration of the undissociated substances*. The concentration of the undissociated part is very great relatively to the concentration of the ions in the case of the weak electrolytes. We know that in many cases the concentration of the ions does not remain constant, and particularly is this true when salt solutions containing a common ion are mixed, such as potassium cyanide and silver cyanide. Even when the solutions containing different ions are mixed we have marked change in the conductance, demonstrating the increased dissociation of many acids caused by the presence of other electrolytes, producing ions not common to the acid.

Mutual Effect of Ions. — The effect of mixing solutions of electrolytes may be illustrated in the case of the addition of two acids. Let HA_1 and HA_2 be the two acids, and their dissociation constants k_1 and k_2 respectively. Let these acids be mixed when c_1 and c_2 represents the concentration of the two acids in the mixture, and α_1 and α_2 their degree of dissociation respectively. Then in the mixture we have

the concentration of the H^+ ions $= \alpha_1 c_1 + \alpha_2 c_2$,
the concentration of the A_1^- ions $= \alpha_1 c_1$,
the concentration of the A_2^- ions $= \alpha_2 c_2$.

According to Ostwald's Dilution Law we have for each acid

$$k_1(1 - \alpha_1)c_1 = \alpha_1 c_1(\alpha_1 c_1 + \alpha_2 c_2)$$
$$k_2(1 - \alpha_2)c_2 = \alpha_2 c_2(\alpha_1 c_1 + \alpha_2 c_2).$$

This gives the relation

$$\frac{k_1(1 - \alpha_1)c_1}{k_2(1 - \alpha_2)c_2} = \frac{\alpha_1 c_1}{\alpha_2 c_2}$$

which becomes

$$\frac{k_1(1 - \alpha_1)}{k_2(1 - \alpha_2)} = \frac{\alpha_1}{\alpha_2}.$$

Now since, in the case of weak electrolytes, the degrees of dissociation are very small, it follows that $\frac{(1 - \alpha_1)}{(1 - \alpha_2)}$ is approximately unity, and the expression becomes $\frac{k_1}{k_2} = \frac{\alpha_1}{\alpha_2}$.

The ratio of the dissociation constants is equal to the ratio of the degrees of dissociation, and we have seen that the acids with the greater dissociation constants are the more highly dissociated acids and therefore the stronger.

Let us consider the case of a weak acid, such as acetic, and a strong acid, such as hydrochloric.

For acetic acid we have in the mixture of the two

$$k_1(1 - \alpha_1)c_1 = \alpha_1 c_1(\alpha_1 c_1 + \alpha_2 c_2)$$

and for hydrochloric acid

$$k_2(1 - \alpha_2)c_2 = \alpha_2 c_2(\alpha_1 c_1 + \alpha_2 c_2).$$

These may then be written in the following form:

$$k_1 = \frac{\alpha_1}{1 - \alpha_1}(\alpha_1 c_1 + \alpha_2 c_2)$$

and

$$k_2 = \frac{\alpha_2}{1 - \alpha_2}(\alpha_1 c_1 + \alpha_2 c_2).$$

But in the case of acetic acid the degree of dissociation is so slight that the value of $(1 - \alpha_1)$ is so nearly unity (1) that no great error will be made by this substitution and our equation then takes the form

$$k_1 = \alpha_1(\alpha_1 c_1 + \alpha_2 c_2).$$

In the case of dilute solutions of hydrochloric acid the dissociation is practically complete, hence $\alpha_2 = 1$. We then have $k_1 = \alpha_1^2 c_1 + \alpha_1 c_2$. As α_1 is very small, much less than unity, the value of the first term may be neglected in comparison to the second, and we then have $k_1 = \alpha_1 c_2$, from which we have $\alpha_1 = \frac{k_1}{c_2}$. That is, the degree of dissociation of the weak acid in the mixture is inversely proportional to the concentration of the strong acid. Hence by adding large quantities of hydrochloric acid to an acetic acid solution, the dissociation of the acetic acid will be forced back and may become practically undissociated.

The forcing back of the dissociation is of great importance in analytical chemistry, as may be illustrated in a large number of cases. When NH_4OH is added to a solution of $MgCl_2$, a precipitate of $Mg(OH)_2$ is produced according to the ionic reaction,

$$Mg^{++} \cdot 2\,Cl^- + 2\,NH_4^+ \cdot OH^- \rightleftarrows Mg(OH)_2 + 2\,NH_4^+ \cdot Cl^-.$$

Now NH_4OH is a weak base and therefore produces few OH ions, according to the ionic equilibrium equation $NH_4OH \rightleftarrows NH_4^+ \cdot OH^-$, for which we would have the Mass Law Equation

$$k_1 \frac{[NH_4OH]}{V} = \frac{[NH_4^+]}{V} \cdot \frac{[OH^-]}{V}.$$

Now when mixed with a strong electrolyte containing the common NH_4 ion, such as any ammonium salt, the concentration of the ions furnished by this would be very much in excess of that furnished by the NH_4OH. According to the equilibrium equation above we readily see that with the increase of the concentration of the NH_4Cl the value for the degree of dissociation of the NH_4OH becomes very small and can be decreased to such an extent that the number required for the formation of $Mg(OH)_2$ is not sufficient to produce enough of the $Mg(OH)_2$ to precipitate; *i.e.* it will all remain in solution. So in the preparation of the so-called magnesium mixture enough ammonium salts are added to prevent the ionization of the NH_4OH to the extent necessary to produce enough $Mg(OH)_2$ so that it will exceed its solubility. Since the hydroxides of Fe, Al, and Zn are but slightly soluble, it is more difficult to prevent their precipitation in this manner.

Ionic Product. — If the dissociation of the precipitating reagent can be forced back to such an extent that the ions it produces are practically negligible, then to precipitate a substance and prevent it from going into solution again would require the presence of a large number of either of the ions resulting from the solution of that substance. For example, if to a solution of $BaCl_2$ a concentrated solution of HCl be added, the concentration of the chlorine ion can be increased to such an extent that the $BaCl_2$ will be precipitated. For this reason it is recommended that an excess of the precipitating reagent be added.

In order to prevent the precipitate from redissolving, the precipitating reagent containing an ion in common with the saturated solution is present in excess, but as the precipitate is washed and thus separated from the excess of the common ion, the pure water will dissolve the precipitate. It is therefore necessary to wash the precipitate with wash water which contains an ion common with that produced in saturated solutions of the precipitate. Magnesium ammonium phosphate is washed with ammonia water, ammonium phosphomolybdate with a solution of NH_4NO_3, $PbSO_4$ with wash water containing H_2SO_4, etc. Electrolytes chosen for this purpose should be readily volatile if the precipitate is to be weighed.

In saturated solutions the concentration of the undissociated solute in solution is in equilibrium with the solid solute, and this concentration is a constant quantity. The solute in solution is dissociated and there exists, as we have seen, a condition which is represented by the equilibrium relation

$$\underset{\text{solid}}{AgCl} \rightleftarrows \underset{\substack{\text{undis-}\\\text{sociated}}}{AgCl} \rightleftarrows Ag^+ \cdot Cl^-$$

and for a saturated solution the concentration of the undissociated solute is a *constant*. It is evident that the silver ion and the chlorine ion are found in equivalent quantities and in definite concentrations, and according to the Law of Mass Action we have the products of the concentration of the ions proportional to the concentration of the undissociated part, and as this latter is constant we then have $[Ag^+] \cdot [Cl^-] =$ a *constant*, which is usually designated by L_0 and is called the *Solubility Product* or the *Ionic Product*. This equation is then

$$L_0 = [Ag^+] \cdot [Cl^-].$$

Lewis says, " Again, as already pointed out, the saturated solution of a body such as AgCl is very dilute, and since it is a salt, the small quantity which is dissolved suffers almost complete dissociation in solution. Hence the concentration of the undissociated molecules must be small compared even with the ions. That is, C_0 is negligible compared to the concentration $[Ag^+]$ or $[Cl^-]$. Hence in such a case, say when AgCl is dissolved in water alone, the concentration of Ag^+ or Cl^- in gram ions per liter gives a number identical with the solubility of the entire salt. But $[Ag^+] \cdot [Cl^-] = L_0$. Hence the solubility is identical with the $\sqrt{\text{solubility product}}$. Now take the case of AgCl in presence of some KCl. The solubility simply becomes identical with the concentration of the least represented ion, *i.e.* the Ag^+ ion. An estimation of the Ag^+ ion in solution is therefore the experimental way of arriving at the solubility of AgCl in aqueous KCl solution. We can evidently calculate this quantity if we know what value L_0 has (say by estimating the Ag^+ or Cl^- in *absence* of KCl) and remembering that L_0 is constant whether KCl is present or not. By the addition of KCl in a given amount we know the quantity of Cl^- present (the Cl^- originally present from the AgCl itself being usually negligible compared to the quantity added), and the ' solubility ' of the AgCl in presence of KCl, or the Ag^+ concentration is simply

$$[Ag^+] = \frac{L_0}{[Cl^-]}."$$

The numerical value of the ionic product may be calculated if the solubility of the salt and its degree of dissociation are known. At 25° the solubility of $BaSO_4$ is 0.0023 gram per liter, or practically 0.0_41 mole. The $BaSO_4$ is assumed to be completely dissociated, then $L_0 = [Ba^{++}] \cdot [SO_4^{--}] = 0.0_41 \times 0.0_41 = 0.0_91$, which is the ionic product of $BaSO_4$, and as determined by Hulett is 0.94×10^{-10}. The amount of $BaSO_4$ remaining in solution would be very small, 23 mg. per liter. In the determination of sulphur in sulphates by the $BaCl_2$ method the SO_4 ions left would be reduced by a slight excess of $BaCl_2$ so that there would be but a small fraction of a milligram per liter remaining. We have again emphasized the necessity for adding a small excess of the precipitating reagent.

The ionic product of AgI is much smaller than that of AgCl, so that on the addition of a solution of KI to a saturated solution of AgCl in equilibrium with an excess of the solid AgCl the concentration of the Ag^+ would be decreased. This will result in a final state of equilibrium according to the following equation:

$$\underset{\text{solid}}{\mathrm{AgCl}} \rightleftarrows \underbrace{\underset{\substack{\text{undissociated}\\ \text{(negligible)}}}{\mathrm{AgCl}} \rightleftarrows Ag^+ + Cl^- + K^+ + I^- \rightleftarrows \underset{\substack{\text{undissociated}\\ \text{(negligible)}}}{\mathrm{AgI}}}_{\text{solution}} \rightleftarrows \underset{\text{solid}}{\mathrm{AgI}}$$

When equilibrium is established, the concentration of the ions must be such that their products are the ionic products (solubility products) of the silver chloride and of the silver iodide, that is,

$$[Ag^+] \cdot [Cl^-] = L_{AgCl}$$
$$[Ag^+] \cdot [I^-] = L_{AgI}.$$

But the concentration of the Ag^+ is the same in both cases, therefore by division we have

$$\frac{[Cl^-]}{[I^-]} = \frac{L_{AgCl}}{L_{AgI}}.$$

This means that at equilibrium the concentration of the Cl^- must be greater than the concentration of the I^- in the ratio of their ionic products. The ionic product of AgCl is 1.56×10^{-10} and of AgI is 0.94×10^{-16}, then

$$\frac{[Cl^-]}{[I^-]} = \frac{1.56 \times 10^{-10}}{0.94 \times 10^{-16}} = 1.6 \times 10^6$$

which means that the concentration of the I^- must become about one millionth of that of the chlorine ions, hence virtually all of the AgCl can be transformed into AgI and practically all of the silver precipitated from the solution.

In Table LIX there are compiled the values of the Ionic Product or Solubility Product of a few of the more common compounds.

TABLE LIX — IONIC PRODUCT

SUBSTANCE	TEMP.	IONIC PRODUCT	K_S
Silver chloride	25°	$[Ag^+] \cdot [Cl^-]$	1.56×10^{-10}
Silver chromate	25	$[Ag^+]^2 \cdot [CrO_4^{--}]$	9×10^{-12}
Silver bromide	25	$[Ag^+] \cdot [Br^-]$	4.4×10^{-13}
Silver oxalate	25	$[Ag^+]^2 \cdot [C_2O_4^{--}]$	1.03×10^{-11}
Silver iodide	25	$[Ag^+] \cdot [I^-]$	1.1×10^{-16}
Silver iodate	25	$[Ag^+] \cdot [IO_3^{--}]$	3.49×10^{-8}
Barium sulphate	25	$[Ba^{++}] \cdot [SO_4^{--}]$	0.94×10^{-10}
Calcium oxalate + H_2O .	25	$[Ca^{++}] \cdot [C_2O_4^{--}]$	2.57×10^{-9}
Calcium sulphate . . .	18	$[Ca^{++}] \cdot [SO_4^{--}]$	6.1×10^{-5}
Magnesium hydroxide . .	18	$[Mg^{++}] \cdot [OH^-]^2$	1.2×10^{-11}
Manganese sulphide . . .	18	$[Mn^{++}] \cdot [S^-]$	1.4×10^{-15}
Lead oxalate	25	$[Pb^{++}] \cdot [C_2O_4^{--}]$	3.5×10^{-11}
Lead chromate	18	$[Pb^{++}] \cdot [CrO_4^{--}]$	1.77×10^{-14}
Lead sulphate	18	$[Pb^{++}] \cdot [SO_4^{--}]$	0.61×10^{-8}
Thallium chloride . . .	25	$[Tl^+] \cdot [Cl^-]$	2.21×10^{-4}
Water	25	$[H^+] \cdot [OH^-]$	1.04×10^{-14}

RELATIVE STRENGTH OF ACIDS AND BASES

The relative strength of acids and bases depends upon the conditions under which they react, or in other words, upon whether the conditions under which they react are such that both are under the most favorable conditions. If many acids or salts of these acids are treated with H_2SO_4 and heated, sulphuric acid will take their place, according to the reaction $H_2SO_4 + 2\ NaCl = Na_2SO_4 + 2\ HCl$, which is the usual method for the preparation of HCl. From such reactions one would say that H_2SO_4 is the stronger acid. If a number of acids or their salts are heated, they would pass off in the order of their volatility, and phosphoric acid would be among the ones to remain, therefore phosphoric acid would be considered stronger than HCl or HNO_3. In the glazing of pottery NaCl is introduced on to the hot pottery, which is covered with SiO_2, where we have a replacement of the chlorine with the formation of sodium silicate. By analogous reasoning we should conclude that silicic acid is stronger than hydrochloric acid. The difficulty with methods of this kind is that under the conditions the two acids have not equal chances to compete for the base, as one of the acids is volatile and is readily removed from the scene of action.

Many terms have been applied to what we call strength of acids, such as *affinity*, *activity*, and *avidity*. Many methods have been devised for determining the strength or avidity of acids, such as the method of "turning out" one by the other, but we have seen that this is not a really satisfactory method.

Since the degree of dissociation determines the number of hydrogen ions, and this is readily ascertained from the electrical conductivity method, we then have a satisfactory and convenient method for ascertaining the relative strength of acids from their conductance. From the values of the dissociation constants given in Table LVIII the relative strength of these weak acids can be readily obtained.

Suppose we have two weak acids, HA_1 and HA_2, which form salts with the strong base BOH. Let us assume that we have one mole each of the two acids and of the base. Then there will not be enough of the base to supply the requirements of the two acids, and so it will be distributed between the acids in proportion to their dissociation. Let x be the fraction of a mole which reacts with the acid HA_1, then $(1 - x)$ moles of the base react with the acid HA_2. Accordingly we shall then have the equilibrium equation

$$BA_1 + HA_2 \rightleftarrows BA_2 + HA_1.$$

From which the concentrations are

x moles of the salt BA_1 and $(1 - x)$ moles of HA_1
$(1 - x)$ moles of the salt BA_2 and x moles of HA_2.

Now assuming that Ostwald's Dilution Law holds, we have for the two acids

$$k_1 = \frac{[H^+] \cdot [A_1^-]}{[HA_1]} = \frac{[H^+] \cdot [x]}{[1 - x]}$$

and
$$k_2 = \frac{[H^+] \cdot [A_2^-]}{[HA_2]} = \frac{[H^+] \cdot [1 - x]}{[x]}.$$

The above equations then become, dividing the one by the other,

$$\frac{k_1}{k_2} = \frac{[H^+] \cdot [x] \cdot [x]}{[1 - x] \cdot [H^+] \cdot [1 - x]} = \frac{[x]^2}{[1 - x]^2}.$$

But since the distribution of the base between the two acids is in the ratio of their degrees of dissociation, and when one mole of the base meets with one mole each of the two acids we have

$$\frac{k_1}{k_2} = \frac{[x]^2}{[1 - x]^2} \text{ or } \frac{[x]}{[1 - x]} = \sqrt{\frac{k_1}{k_2}}.$$

Hence, the distribution ratio is obtained by determining the dissociation constant of each acid and the ratio of the strength of the acids is equal to the square root of the ratio of the dissociation constants.

Thomsen's Thermochemical method for the determination of the relative strength of acids, of their *avidity*, as he termed it, consisted in treating a salt of an acid, Na_2SO_4, with HCl, and determining the heat effect. Having determined the heat of neutralization of NaOH by H_2SO_4 and by HCl, and the actual heat absorbed when Na_2SO_4 reacts with HCl, it would be an easy matter to calculate the proportion of the sodium sulphate converted into sodium chloride. From this the relative amounts of the sodium distributed between the two acids can be readily ascertained.

By employing this method Thomsen determined the relative strengths of a number of acids upon the basis of HCl as 100 and his values are given in Table LX under the heading Avidity.

TABLE LX — RELATIVE STRENGTH OF ACIDS AS DETERMINED BY A NUMBER OF THE COMMON METHODS, ASSUMING HCL = 100

(After Walker)

Acid	Avidity	Electrical Conductance	Velocity Constants	
			Sugar Inversion	Catalysis of Acetate
Hydrochloric . . .	100	100	100	100
Nitric	100	99.6	100	91.5
Sulphuric	49	65.1	53	54.7
Oxalic	24	19.7	18.6	17.4
Ortho phosphoric .	13	7.3	6.2	—
Monochloracetic .	9	4.9	4.8	4.3
Tartaric	5	2.3	—	2.3
Acetic	3	0.4	0.4	0.35

A number of other methods for ascertaining the relative strength of acids and bases have been employed, such as the volume method of Ostwald, which consists in measuring the change in volume produced by the reaction of various salts of the acids with the different acids. From these volume changes Ostwald calculated the relative strength of some of the more common acids and found the same general order to prevail as by the other methods. The values as determined by the rate of inversion of cane sugar and by the catalysis of an acetate are in agreement with the other methods. These two methods will be referred to subsequently.

The order is the same by all methods.

Practically the same methods may be employed for determining the relative strength of bases. The values in Table LXI illustrate about the average relative strength of the common bases and their order, assuming lithium hydroxide as 100.

TABLE LXI

(After Walker)

BASES	AVIDITY
Lithium hydroxide	100
Sodium hydroxide	98
Potassium hydroxide	98
Thallium hydroxide	89
Tetraethylammonium hydroxide	75
Triethylammonium hydroxide	14
Diethylammonium hydroxide	16
Ethylammonium hydroxide	12
Ammonium hydroxide	2

The hydroxides of the alkalies are practically completely dissociated and are the strong bases, the hydroxides of the alkaline earths are also strong bases, while ammonium hydroxide is a very weak base.

CHAPTER XXX

CONCENTRATED SOLUTIONS

In the presentation of the relations of the vapor pressure to osmotic pressure it was emphasized that The Gas Law could be applied to solutions, but that these solutions had to be of the type known as *ideal* or *perfect solutions*, and this is analogous to the statement that The Gas Law holds only for Perfect Gases. We saw that certain modifications of The Gas Law were made in attempting to use it in connection with most gases under the usual conditions; so, too, in the application of The Gas Law to solutions other than the *perfect solutions* certain modifications must be made in order to take into consideration the numerous assumptions postulated in connection with the applications of The Gas Law.

In the formulation of his Modern Theory of Solutions van't Hoff fully realized the limitations of his conceptions of solutions and showed the necessity of limiting its application, and in his presentation stipulated the explicit assumptions made in applying the Laws of Gases to solutions; and these may be summarized as follows:

1. There is no reaction between the solvent and the solute.

2. The solvent and the solute are neither associated nor dissociated.

3. The compressibility of the solution is negligible.

4. The Heat of Dilution of the solution is zero.

We know from experience, in many solutions at least, that there is a marked reaction between the solvent and solute and that the heat of dilution is zero in but few cases. Further, we have just been considering a number of methods by means of which the dissociation of the solute can be determined, and we have also presented methods for determining the association constant of liquids. It will therefore be necessary for us to take up a more detailed consideration of these assumptions and see in what ways van't Hoff's formula will be affected by dropping each and all of these assumptions.

Weight Normality. — As van der Waals' equation was one of the modifications of the Gas Law Equation to account for the variations from the law that occurred in concentrated gases, there are likewise numerous equations which attempt to represent the quantitative relations between the osmotic pressure and the concentration of the solution by correcting for the mutual attraction of the solute molecules and also for the attraction between the solvent and solute. The main idea is to get an expression which would incorporate the volume of the solvent and not the volume of the solution that contained the molar concentration of the solute. It was through the work of Earl of Berkeley and E. G. J. Hartley and of Morse that the best agreement between theory and experimental data was obtained by expressing the concentration in terms of *weight normality* instead of *volume normality*, as was done by van't Hoff, and is usually employed in practically all lines of experimental work.

What difference these methods of expressing the concentration makes will become more apparent by a specific example. Suppose we have a 40 per cent cane sugar solution. What is the normal volume concentration of this solution and what is the normal weight concentration? The specific gravity of a 40 per cent sugar solution at 20° C. is 1.17648; then one liter of this solution would weigh 1176.48 grams, and it would contain 470.59 grams or 1.376 moles of sugar and 705.89 grams of water. That is, there are 1.376 moles of sugar contained in one liter of a 40 per cent sugar solution. Now by weight normal we mean the number of moles contained in 1000 grams of water. Since there are 470.59 grams of sugar contained in 705.89 grams of water, then we have 470.59 : 705.89 :: x : 1000 grams. Solving for x, we have 666.7, therefore there are 666.7 grams, or 1.9493 moles, of sugar in 1000 grams of water. From this then we see that a 40 per cent sugar solution expressed as a normal volume solution would have a concentration of 1.376 moles dissolved in one liter of the solution, and expressed as a normal weight concentration of 1.949 moles dissolved in one liter of solvent. So it is apparent that there is a very decided difference whether our concentration is expressed as a normal volume or as a normal weight concentration. As stated above, Morse found better agreement between the experimental results and theoretical values by employing normal weight, that is, a volume of 1000 grams of the solvent.

Thermodynamic Equations for Concentrated Solutions. — For solutions a complete thermodynamic equation would be very complicated, as it would have to take into consideration a large number of assumptions concerning the two components, the solvent and the solute. The expression would have to include among other assumptions the molecular state of the solvent and of the solute, their volume change when mixed, the heat of dilution, compressibility, etc. By simplifying the conditions there has been obtained a general equation for ideal or perfect solutions by assuming that these two components do not interact with each other, that there is no heat of dilution, that the resulting volume on dilution is the sum of the original volume plus that of the solvent, and that the properties are intermediate between the properties of the pure components.

Previously we saw that $\log_e p/p_1 = \frac{M}{\rho}\frac{p_O}{RT}$ and since $\frac{M}{\rho} =$ the molecular volume V_m we have $\log_e p/p_1 = \frac{Vp_O}{RT}$, from which we get $p_O = \frac{RT}{V_m} \log_e p/p_1$. From Raoult's Law we have

$$\frac{p - p_1}{p} = \frac{n}{N}$$

which gives us

$$1 - \frac{p_1}{p} = \frac{n}{N}$$

and if we define the ratio of the number of molecules of the solute to the total number of molecules by x, then $x = \frac{n}{N}$. Substituting and transposing we obtain $\frac{p_1}{p} = 1 - x$. Substituting this value of $\frac{p_1}{p}$ in the equation $p_0 = \frac{RT}{V_m}\left(\log_e \frac{p}{p_1}\right)$ we have $p_0 = \frac{RT}{V_m}[-\log_e (1 - x)]$, which on expanding log $(1 - x)$ into a series, the equation then takes the form

$$p_0 = \frac{RT}{V_m}(x + \frac{x^2}{2} + \frac{x^3}{3} + \cdots) \text{ or}$$

$$p_0 = \frac{RT}{V_m}x(1 + \frac{x}{2} + \frac{x^2}{3} + \cdots).$$

This equation, into which a factor for the compressibility of the solutions has been introduced, is the one given by Findlay and takes the following form:

$$p_0 = \frac{RT}{V_m}x(1 + \frac{x}{2} + \frac{x^2}{3} + \cdots) - \frac{a}{2}$$

in which p_0 is the osmotic pressure and defined as the additional pressure that must be put upon the solution to prevent the inflow of the solvent through a perfectly semipermeable membrane, V_m is the molecular volume of the solvent under standard pressure, x is the ratio of the number of moles of the solute to the number of moles of the solvent, and a is the coefficient of compressibility. But since the compressibility of solutions is very slight except for enormous pressures, it is assumed for moderate pressures that the compressibility factor is negligible, and no appreciable error is introduced by omitting this factor entirely.

So employing the equation without the compressibility factor we have

$$p_O = \frac{RT}{V_m} x\left(1 + \frac{x}{2} + \frac{x^2}{3} + \cdots\right).$$

For concentrated solutions Raoult used $N + n$ as the total number of molecules in the system and then x would be $\frac{n}{N+n}$, and substituting in the above equation this value, we have

$$p_O = \frac{RT}{V_m} \frac{n}{N+n}\left(1 + \frac{n}{2(N+n)} + \cdots\right).$$

In the case of infinitely dilute solutions, however, $\frac{n}{N+n}$ becomes $\frac{n}{N}$, and the value of this fraction becomes very small and the terms involving the higher powers of the fraction are negligible. The equation then simplifies to

$$p_O = \frac{RT}{V_m} \frac{n}{N}.$$

Now since $V_m N$ represents the volume, V, of the solution itself we have $p_O = \frac{nRT}{V}$, or $p_O V = nRT$, which is the usual form of van't Hoff's equation or the Gas Law Equation.

Another Form of the Equation. — By employing a method of expansion [1] for the term $\log \frac{p}{p_1}$ in the equation $p_O = \frac{RT}{V_m} \log \frac{p}{p_1}$, different from the one employed above, we obtain the following:

$$p_O = \frac{RT}{V_m} \cdot 2\left[\frac{p - p_1}{p + p_1} + \frac{1}{3}\left(\frac{p - p_1}{p + p_1}\right)^3 + \frac{1}{5}\left(\frac{p - p_1}{p + p_1}\right)^5 + \cdots\right].$$

From Raoult's formula $\frac{p - p_1}{p} = \frac{n}{N + n}$ the following relation may be obtained: $\frac{p - p_1}{p + p_1} = \frac{n}{2N + n}$. Substituting this value in the above equation we have

[1] See Wells' *College Algebra*.

$$p_O = \frac{RT}{V_m} \cdot 2\left[\frac{n}{2\,N+n}1 + \frac{1}{3}\left(\frac{n}{2\,N+n}\right)^3 + \frac{1}{5}\left(\frac{n}{2\,N+n}\right)^5 + \cdots\right]$$

$$\text{or } p_O = \frac{RT}{V_m} \cdot \frac{n}{N+\frac{n}{2}}\left[1 + \frac{1}{3}\left(\frac{n}{2\,N+n}\right)^2 + \frac{1}{5}\left(\frac{n}{2\,N+n}\right)^4 + \cdots\right].$$

This equation may preferably be employed for the calculation of the osmotic pressure from the experimental data. Exact values are obtained by employing the first term of this expression, while with the other formula two and sometimes three terms are required for the same degree of exactness.

It will be recalled that Morse employed normal weight concentrations in expressing his osmotic pressure results. So in the equation

$$p_O = \frac{RT}{V_m}\frac{n}{N+n}\left[1 + \frac{n}{2(N+n)} + \frac{1}{3}\left(\frac{n}{N+n}\right)^2 + \cdots\right]$$

the values for a solution containing *n* moles of sugar dissolved in 1000 grams of water at 20° C. would be: $T = 273° + 20° = 293°$; V being the volume of 1000 grams of water at 20°, which is 1001.8 cc.; N, the number of moles of water, is $1000 \div 18 = 55.5$; the molecular volume V_m is 1001.8 divided by 55.5; $x = \frac{n}{55.5 + n}$; $R = 81.6$ cc. atmos., as employed by Morse on the basis that $H = 1$ instead of the usual value 82.04 cc. atmospheres.

Substituting these values, we have

$$p_O = \frac{81.6 \times 293 \times 55.5}{1001.8} \cdot \frac{n}{55.5+n}\left(1 + \frac{n}{2(55.5+n)} + \cdots\right)$$

from which the osmotic pressure may be calculated. This gives us the osmotic pressure of solutions by means of which Morse's observed values are checked fairly closely, as shown in the third column of Table LX.

Now let us assume that the solvent *is* associated, then the equation takes the form

$$p_0 = \frac{RT}{V_m}\frac{n}{\frac{N}{a}+n}\left[1 + \frac{n}{2\left(\frac{N}{a}+n\right)} + \frac{1}{3}\left(\frac{n}{\frac{N}{a}+n}\right)^2 \cdots\right]$$

where a is the association factor for the solvent. The number of moles of the solvent then is $\frac{N}{a}$.

According to van Laar the association factor, a, for water at 20° C. is 1.65, and the number of associated molecules in 1000 grams of water is $\frac{55.5}{1.65} = 33.7$, and the molecular volume of the associated molecule is $\frac{1001.8}{33.7}$, which is V_m of the formula. Substituting these values in the equation above and calculating for the osmotic pressure, we obtain 23.5 atmospheres as against the value 23.64 without correction for the association of the solvent. These values are practically the same, showing that up to this concentration the association of the solvent can be neglected.

Even making the calculations upon the basis of normal weight relations instead of normal volume relations, and correcting for the association of the solvent, there still remains some considerable discrepancy between the experimental values of the osmotic pressure and the values calculated in the manner just indicated. Now let us make the additional assumption that the solvent and the solute do react with the formation of hydrates of the solute. In the process of hydration there is then removed from the solvent that amount of the solvent which is in combination with the solute molecules, and this quantity will disappear in so far as its action as a solvent is concerned. Hence the number of molecules of solvent will be decreased by this amount. Then the equation becomes

$$p_0 = \frac{RT}{V_m}\frac{n}{N - \beta n + n}\left[1 + \frac{n}{2(N - \beta n + n)} + \cdots\right]$$

in which we have introduced the correction β for the number of molecules of the solvent combining with each molecule of the solute, and βn is then the number of moles of solvent that have disappeared from the scene of action as solvent. The molecular volume of the solvent then should be the volume of $(1000 - 18\ \beta n)$ grams of water at the specified temperature, divided by $(N - \beta n)$, the number of molecules of solvent actually serving as solvent. The values as calculated according to this assumption with $\beta = 5$ are given in the fifth column of Table LXII.

TABLE LXII

(Findlay's *Osmotic Pressure*, page 41)

Weight Normal	Osmotic Pressure Observed	Osmotic Pressure Calculated by above Equations				
		Assuming no Hydration of Solute and no Association of Solvent	Assuming no Hydration of Solute but Association of Solvent	Assuming Hydration		
				$\beta = 5\ H_2O$		$\beta = 6\ H_2O$
				Solvent not Associated	Solvent Associated	
0.1	2.59	2.38	2.38	2.41	2.42	2.42
0.2	5.06	4.76	4.76	4.85	4.90*	4.90
0.3	7.61	7.14	7.13	7.33	7.45	7.40
0.4	10.14	9.51	9.49	9.87	10.07*	9.94
0.5	12.75	11.87	11.84	12.43	12.78	12.59
0.6	15.39	14.24	14.19	15.05	15.54*	15.28
0.7	18.13	16.59	16.53	17.71	18.40	17.97
0.8	20.91	18.94	18.85	20.42	21.32*	20.76
0.9	23.72	21.29	21.19	23.15	24.37	23.55
1.0	26.64	23.64	23.50	25.96	27.50	26.45

Now if we retain the idea of the association of the solvent, then the equation becomes

$$p_0 = \frac{RT}{V_m} \frac{n}{\frac{N - \beta n}{a} + n}\left[1 + \frac{n}{2\left(\frac{N - \beta n}{a} + n\right)} + \cdots\right].$$

* Calculated by author and the last column added.

In this case the value of V_m, the molecular volume, would be the volume $(1000 - 18\,\beta n)$ grams of water divided by $\frac{N - \beta n}{a}$ moles. Upon the basis of these two formulæ and on the assumption that sugar forms a pentahydrate, values for the osmotic pressure have been calculated from Morse's data and are incorporated in Table LXII, the columns being fully explained by their headings.

In the last column there are added the calculated values on the assumption of association of the solvent, that the molecule of sugar has six molecules of water of hydration, and the usual value (82.04) of R is employed. With these assumptions the calculated values approximate very closely to the observed experimental values of Morse.

From these values it is seen that by introducing into the equation for *ideal* solutions factors for the association of the solvent and the hydration of the sugar, we obtain values for the osmotic pressure nearer those actually obtained experimentally than the values given in the third column, where these assumptions were not made. Further, the hydration correction is much more pronounced in the more concentrated solutions than the association factor correction. The same is noticed if the data of Earl of Berkeley and Hartley are employed and a hexahydrate of sugar be assumed.

Heat of Dilution. — More than ten years ago Bancroft called attention to the relation of the Heat of Dilution and its bearing on the van't Hoff-Raoult Formula, and referred to Ewan's discussion (1894) of this problem and the formula he worked out showing the relation of the heat of dilution to the osmotic pressure, which had been practically neglected. Bancroft formulates a relation and proceeds to show how the osmotic pressure varies with the heat of dilution, that the abnormal molecular weights for sodium in mercury, sulphuric acid in water, resorcinol in alcohol, cupric chloride in water, and alcohol in benzene are due wholly or in part to the heat of dilution, but the abnormal weights for sodium chloride in water are not due to the heat of dilution. In the case of sodium in mercury the apparent molecular weight was found to be 16.5, and, correcting for the heat of dilution, 22.7 was obtained. The apparent molecular weight of sulphuric acid varies from 57.7 in a 5.6 per cent solution to 11.7 in a 68.5 per cent solution, and when the correction for the heat of dilution is applied we get molecular weights that are approximately constant but somewhat in excess (115) of the true molecular weight (98), and increasing at first and then remaining practically constant with the increase of concentration. In the case of sodium chloride the apparent molecular weight is about 29, or one half of the formula weight at infinite dilutions, while the change of the heat of dilution with the concentration is zero, hence these abnormal values for sodium chloride are real and are not to be explained on the basis of the heat of dilution.

CHAPTER XXXI

HYDRATION

We have seen that by assuming the hydration of the solute and thus removing a part of the solvent from the sphere of action as solvent, the solution becomes more concentrated, and the osmotic pressure calculated on this basis conforms more nearly to the values determined experimentally. Jones and his students ascribed the deviation in the freezing point determinations to the formation of hydrates and assumed that they existed only in concentrated solutions. In the case of many of the other properties of solutions which are colligative, there is a marked difference in the values determined experimentally and calculated upon the basis of the Arrhenius Electrolytic Dissociation Theory. There is now a tendency to explain these abnormal results upon the assumption of the union of the solvent and the solute, *i.e.* on the assumption of the existence of hydrates in solution. This is bringing us back to the fundamental conceptions of the old Hydrate Theory of Solutions which was strongly advocated by Mendeléeff (1886) and by Pickering (1890). In the foundation of the old Hydrate Theory, the points of discontinuity in the plotted observed data wherein the graphic method was employed were taken as evidence of the existence of hydrates. Pickering justified this method and fully appreciated the difficulties in its application, as is shown from the following quotation:

"The application of the graphic method requires a great amount of care and a close attention to experimental and other conditions, and it is to be feared that hurried use of it by those who have not taken the trouble to master the necessary details, or to acquire the requisite amount of skill, may bring it into undeserved disrepute. From the study of any one, or any few, particular breaks I concluded nothing; from a study of a whole series of density results I only concluded that it was advisable to make other series at other temperatures; from a study of the series at four different temperatures I concluded only that I had 'strong presumptive evidence' of the existence of changes, but that confirmatory evidence from the study of independent properties was necessary before such changes could be regarded as established, and it was only after obtaining such evidence from the study of three or four properties that I ventured to call the evidence proof, and then only with oft-repeated caution, 'that many of these changes were admittedly of a very doubtful nature.'"

The points of discontinuity were observed in the case of density curves, the determination of capillarity, viscosity, etc. This group of physical properties of solutions conforms to the so-called Law of Mixtures and is additive with respect to the constituents. Where there is a variation from the law it is customary to assume that the molecular property of the solvent remains unchanged and to ascribe all deviations to changes in the physical property of the solute, which in many cases has led to absurd conclusions. To get around these, complexes between the solvent and solute have been assumed, and the literature contains references to a large number of such cases which have been determined from the discontinuity in property-curves of the following physical properties of solutions: heat capacity, density, viscosity, refractivity, conductivity, compressibility, surface tension, coefficient of expansion, and heat of solution. It would, however, lead us too far to consider in detail the evidence presented by these experimental methods, but many experimenters attribute the irregularities in the property curves to the presence of hydrates and use these properties for proving the presence of hydrates in solution.

In Fig. 55 we have from the so-called solubility curve for SO_3 in H_2O, a confirmation of the "breaks" of Mendeléeff and of Pickering. We now recognize definite hydrates among which it is possible to account for all "breaks" between 10 and 90 per cent H_2SO_4 by assuming three known hydrates and one unknown hydrate instead of the three known and six unknown hydrates of Pickering. We have the following well-defined hydrates:

1. $SO_3 \cdot 1/2\ H_2O$ is very stable but does not reveal itself by any abrupt change in the density curve, but the capillarity and the viscosity curves both reveal it. This is known as *pyro-sulphuric acid* and is not usually considered as a hydrate.

2. $SO_3 \cdot H_2O$, a monohydrate, is familiarly known as *sulphuric acid* and contains 100 per cent H_2SO_4.

3. $H_2SO_4 \cdot H_2O$, the dihydrate of SO_3, is scarcely a matter of controversy.

4. $H_2SO_4 \cdot 2\ H_2O$ has been obtained in the crystalline form.

5. $H_2SO_4 \cdot 4\ H_2O$, the pentahydrate, may be responsible for breaks at 59 per cent.

The electrical conductance of solutions of sulphuric acid gives a curve that indicates most clearly the presence of three hydrates. Water and the trioxide of sulphur are both excellent insulators, but a mixture of two parts of SO_3 to four parts of H_2O is one of the best conductors known, the specific resistance being 0.7388 ohm at 18° C. The curve is smoothly rounded, and according to Kohlrausch's rule that mixtures give higher conductance than the pure substances, there is no reason for attributing this maximum to the formation of hydrates — it would agree fairly well with the formula $SO_3 \cdot 18\ H_2O$. The mixture, on changing the ratio, decreases in conductance until at the concentration 81.44 per cent SO_3 the value is 0.0080 ohm, which is about one per cent of the maximum value. This minimum is very clearly defined, as the conductance increases 100 per cent when the solution is mixed with 0.17 per cent of H_2O or with 0.23 per cent of H_2O. Kohlrausch has shown that this minimum is reached when the SO_3 and H_2O are in the ratio of 0.9975 : 1, which is virtually 1 : 1, and therefore this minimum can be attributed to the hydrate $SO_3 \cdot H_2O$, which is a chemical compound and is an insulator. The hemi-hydrate $2\ SO_3 \cdot H_2O$ has even a lower conductance (0.0008) than the monohydrate, and solutions of SO_3 in this give zero conductance. The minimum value at 69 per cent SO_3 corresponds to the dihydrate $SO_3 \cdot 2\ H_2O$, the conductance at 18° being 0.098 ohm, and this minimum is 300 times less sensitive than in the case of the monohydrate.

It will be recalled that the Arrhenius Theory of Electrolytic Dissociation was advanced to account for the abnormal values that are obtained by the lowering of the freezing point, the elevation of the boiling point, the osmotic pressure, and the lowering of the vapor pressure. The degree of electrolytic dissociation could be determined with equal accuracy by these various methods and also by the electrical conductivity. These properties of solutions are *Colligative*, that is, they depend upon the number of parts in the solution, and, the solutes are said to be ionized in order to account for these additional parts in solution.

What is the cause of this ionization? One of the questions that has been asked frequently is, Why is it that these substances which liberate so much heat when they are formed become dissociated so easily when they are dissolved? In other words, what is the *motive* of the electrolytic dissociation? In the formation of KCl from its elements there is a liberation of 105,600 calories, which means an absorption of this same amount of heat when the compound is again decomposed, but the heat of electrolytic dissociation is given as 250 calories. Bonsfield says:

"This extraordinary discrepancy between the two values appears to indicate that the process of ionization cannot consist merely of the separation of the molecule into its constituent atoms even though they may be endowed with electrical charges, and we are driven to assume that the essentially endothermic process of dissociation must be balanced by some powerful exothermic action, associative rather than dissociative."

Fitzgerald in his classic Helmholtz Memorial Lecture delivered in 1892 says:

"Why is there then so little heat absorbed when ions are dissociated by going into solution? It has been proposed to explain this by various suggestions which do little more than re-state the facts in some other form and call for new properties of ions especially invented to suit the circumstances. The suggestion mentioned is that the presence of a body of high specific inductive capacity, like water, very much diminishes the force of the attraction between the electrons by providing, what comes to the same thing, induced electrons in the water molecules to help in drawing those in the salt apart. This is an excellent suggestion; but is it not really the same thing, under another guise, as stating that it is by chemical combination with water that the salt has conferred upon it the property of exchanging partners? What are these electric charges supposed to be induced on water but electrons thereon? and what is the attraction of the electrons among the molecules but another name for chemical combination? All of this hangs together, but it lends no support at all to the dynamically impossible theory that the ions are *free*. What it suggests is that this so-called freedom is due to there being complete bondage with the solvent."

At the time Arrhenius published the relative values of i and α calculated from the electrical conductance, the freezing point, and the boiling point determinations, he recognized great discrepancies in the cases of the sulphates in general, which he sought to explain by assuming polymerization of the undissociated molecules. Since the data employed by Arrhenius were obtained, more accurate data have been collected, showing that these abnormal values are real. The freezing point determinations by Loomis, Abegg, Jones, Roth, Raoult, Ewan, Kahlenberg, Biltz, as well as boiling point determinations by the same experimenters, and particularly the data by Smits, show that these methods give values for the degree of electrolytic dissociation which are in many cases entirely different from the values obtained by the conductivity method. A few specific cases will suffice to illustrate the general trend of these irregularities. The data given in Table LXIII are taken from that compiled in Landolt and Börnstein's *Tabellen* with the exception of that for KBr and some of the data for NaCl by the boiling point method, which were obtained from the original source. The degree of dissociation from the electrical conductance method are taken partially from Jones' work, and the other values were calculated from data given in Landolt and Börnstein's *Tabellen.*

TABLE LXIII

FREEZING POINT OF SOLUTIONS

Gram Anhydrous Salt in 100 gr. H_2O	Freezing Point Lowering	Molecular Weight	Degree of Dissociation	
			From Freezing Point	From Electrical Conductance
NaCl, Molecular Weight 58.5				
0.01047	0.006403°	30.4	92.4	94
0.03738	0.02339	29.0	101.7	91
0.1250	0.07584	30.6	91.2	85
0.4887	0.2897	31.4	86.3	79
1.479	0.8615	31.9	83.3	68
5.770	3.293	32.6	79.6	
$MgSO_4$, Molecular Weight 120.4				
0.00141	0.000433	60.6	98.7	
0.00813	0.002221	68.1	76.8	
0.1520	0.03430	82.4	46.1	
2.534	0.469	100.5	19.8	75 } Jones
5.994	1.006	110.8	8.7	55 } Jones
9.768	1.629	111.5	8	44 } Jones
18.343	3.471	98.3	22.5	32 } Jones
$ZnSO_4$, Molecular Weight 161.5				
0.00644	0.001387	109	48.2	
0.08333	0.01499	103.4	56.2	
0.2246	0.03701	113	42.9	
2.063	0.285	134	20.5	44 } Jones
5.026	0.625	149.5	8.0	33 } Jones
16.169	1.87	166		26 } Jones

From the data obtained by the freezing point method the molecular weight of NaCl is practically constant for all concentrations, showing, however, a slight decrease in the degree of dissociation with the increased concentration up to about molar concentrations. At the lower dilutions the degree of dissociation as calculated from the conductance agrees very well with that obtained from the freezing point data, but at the higher concentrations there begins to appear a marked divergence. For $MgSO_4$ the degree of dissociation decreases very rapidly with the concentration and becomes only a few per cent at approximately normal concentration. The conductance gives at these higher concentrations a degree of dissociation of about 40 per cent. Practically the same holds for $ZnSO_4$, at molar concentration the degree of dissociation is practically zero according to the freezing point determinations and 26 per cent by the electrical conductivity method.

TABLE LXIV

BOILING POINT DETERMINATIONS

Gram Anhydrous Salt in 100 gr. H_2O	Rise of Boiling Point	Molecular Weight	Degree of Dissociation	
			From Boiling Point	From Electrical Conductance
NaCl, Molecular Weight 58.5				
0.4388	0.074°	30.91	89.3	86
0.747	0.119	32.7	78.9	84
2.158	0.351	32.0	82.8	77
4.386	0.717	31.8	84	71
7.27	1.235	29.9	95.7	66
12.17	2.182	29.0	101.7	59
18.53	4.032	26.7	119	48.5
31.242	6.82	24.1	142.7	38
KBr, Molecular Weight 119.1				
2.614	0.206	66.0	80.5	82.2
5.504	0.433	66.1	80.2	79.5
9.593	0.763	65.4	82.1	77
23.393	1.968	61.8	92.7	72.4
33.278	2.899	59.7	99.5	69.0
43.418	3.932	57.4	107.5	65.8
51.204	4.778	55.7	113.7	63.2

TABLE LXIV — *Cont.*

MgCl₂, Molecular Weight 95.3

3.371	0.416°	42.1	61.1	60
6.199	0.850	37.9	75.7	53 Jones
13.87	2.380	30.3	107.2	43 Jones
22.06	4.720	24.3	146.1	31 Jones

$BaCl_2$, Molecular Weight 208.3

3.397	0.208	84.9	72.8	72
8.777	0.525	86.6	70.2	64.8
18.619	1.174	82.5	76.2	58.5
35.036	2.517	72.4	86.9	52
54.519	4.157	68.2	102.9	45

$CuSO_4$, Molecular Weight 159.7

3.356	0.091	191.8
7.811	0.189	214.9
15.952	0.374	221.8
32.36	0.874	192.5
39.57	1.192	172.6
56.95	2.283	129.7
73.77	3.768	101.8

Cane Sugar, Molecular Weight 342

2.447	0.035	363.5
4.316	0.064	350.7
7.25	0.103	366
11.02	0.164	349.4
14.82	0.240	321
21.66	0.363	310.0
36.15	0.55	342
65.97	1.13	304
100.95	1.853	283
175.1	3.84	237
276.2	6.71	214

Boiling point data are given in Table LXIV for NaCl, KBr, $MgCl_2$, $BaCl_2$, $CuSO_4$, and sugar. The molecular weight for NaCl decreases with the increased concentration, giving a dissociation increasing with the increased concentration. For concentrations of about three to five molar, the degree of dissociation calculated from the boiling point data gives over 140 per cent, while according to the conductivity method the dissociation is from 48 to 38 per cent respectively. For

KBr the same is true, for concentrations 2.8 to 4.3 molar the degree of dissociation ranges from 99.5 per cent to 114.9, while according to the conductivity method the values for the same concentrations are 69 and 63.2 per cent respectively. For $MgCl_2$ the molecular weight decreases with increased concentration, giving a dissociation increasing with concentration, being at approximately 2 molar concentration 146 per cent as against about 31 per cent as determined by Jones. For $BaCl_2$ the molecular weight decreases as the concentration is increased, showing a dissociation ranging from 53 per cent for approximately 0.15 molar solution to 103 per cent, while for the same concentrations the degree of dissociation by the electrical conductivity method is 72 per cent and 45 per cent respectively. For $CuSO_4$ the molecular weights are all above that represented by the formula weight except at the very highest concentration which is nearly 5 molar. There would be no dissociation at the lower concentration, but at the higher concentrations the molecular weight found is lower than the theoretical value. The same is also found for the non-electrolyte sugar, the molecular weight decreases with increased concentration. In the dilute solutions the molecular weight is about normal, while at about 8 molar concentration the value is 214.

By the vapor pressure measurements at 0° Dieterici found that the molecular lowering for $CaCl_2$ diminished rapidly with the increase of dilution, and at about 0.1 N concentration increased with the dilution. The freezing point determinations of Loomis and of Ponsot show a minimum for the molecular lowering of the freezing point at nearly the same concentration. Jones and Chambers' results confirm this. For H_3PO_4, H_2SO_4, NaCl, $CaCl_2$, cane sugar, dextrose, and urea in concentrations 0.1 to 1.0 N, Dieterici found that the molecular lowering of the vapor pressure diminishes as the dilution increases, which is opposite to that required by the electrolytic dissociation theory as stated. Dieterici therefore refrains from even attempting to make any further comparison between the degree of dissociation as calculated from the vapor pressure measurements on the one hand and the conductivity on the other. From vapor pressure determinations Lincoln and Klein found practically the same values for the molecular weight of KNO_3 as that found by other workers by the freezing point and boiling point methods. For $NaNO_3$, however, the value for the molecular weight was practically the same, 48.13–48.91, over the whole range of concentration. This is approximately one half the theoretical value, 85.1, and the degree of dissociation would be the same for the whole range of concentration. For the most concentrated solutions of $LiNO_3$ the molecular weight was found to be 17.58, and for the most dilute, 36.09, as compared to the formula weight, 69.07. In the most dilute solutions the molecular weight, 34.5, is practically one half the theoretical value, giving a degree of dissociation virtually of 100 per cent, while for the most concentrated solutions employed the value 17.35 found is about one fourth the molecular weight and would correspond to a dissociation of about 200 per cent. By the freezing point method Biltz found the same general results, *i.e.*, in the more highly concentrated solutions the $LiNO_3$ is the more highly dissociated.

Various explanations have been put forth to account for these numerous irregularities such as illustrated above, and there is one marked similarity in them. They all aim to explain these anomalous results upon the assumption of some combination between the solvent and the dissolved substance.

Arrhenius was among the first to suggest that ionization depends not on the physical properties of the solvent but upon the *chemical* equilibrium between the solute and the solvent. As early as 1872 Coppet, from his freezing point measurements, ascribed his results to the formation of hydrates, and calculated the composition of many of them. Jones ascribes the deviation in the freezing point determinations to the formation of hydrates, but assumes that they exist only in concentrated solutions. He assumes that the degree of hydration can be calculated upon the normal volume plan, notwithstanding that this method involves the acceptance of the Ionic Hypothesis and the application throughout of the factor 18.6 in calculating the lowering of the freezing point. Jones also leaves out of account the effect of hydration on the ionic mobility, the polymerization effects, and practically all others, and concentrates the whole variation to the formation of hydrates resulting in the removal of part of the water from its function as a solvent. " The fact that a part of the water is combined with the dissolved substance and is not acting as solvent, must be taken into account in dealing with all solutions and especially concentrated ones. This accounts in large part for the abnormal behavior of concentrated solutions." " We conclude that both molecules and ions have the power to combine with water in aqueous solutions and form hydrates." In many cases the solvent " combined " amounts to a large percentage of the water present and in a few cases to between 100 per cent and 114 per cent.

Biltz, although he pointed out that Nernst had shown that the formation of hydrates is directly contrary to the Law of Mass Action, and consequently untenable, recognizes that their formation may be the cause of the abnormal properties of strong electrolytes. He argued that $CsNO_3$ to be slightly hydrated, if at all, lowers the freezing point in accordance with the Ostwald Dilution Law and is to be regarded as behaving normally. The electrical conductance of such solutions is not that to be expected from the freezing point determinations, and it therefore follows that conductivity cannot be taken as a true measure of the state of dissociation even in the case of salts that are not hydrated. Taking the cases of NaCl and KCl, which do not conform to the dilution law as regards freezing point, and assuming that they are dissociated to about the same extent as $CsNO_3$, Biltz calculated that NaCl can be associated with 19 to 20 molecules of water and KCl with 15 to 24 molecules, according to the concentration. Biltz, as well as Jones, finds indications that the complexity of the hydrates decreases with rise of temperature. The abnormal boiling point values are explained upon the basis of the formation of hydrates.

Smits determined the vapor pressure at 0° of NaCl, H_2SO_4, KNO_3, and sugar. For sugar he finds an average molecular hydration of 5.7 as compared to 6.0 obtained by the freezing point method, hence we would conclude that sugar exists in solution as a hexahydrate. Compare this with the assumed hydration, page 365.

Abegg has stated very clearly the application of the hydrate theory to the equilibrium between the solvent and solute, and his researches show that what is ordinarily termed normal or simple ionization may be to a very large extent a complex ionization in which the solvent molecules play an essential part. He assumes that the molecules possess a power of spontaneous ionization which is independent of the association of the ions with the solvent.

Armstrong says that apart from the fact that the Electrolytic Dissociation Theory is irrational and inapplicable to compounds in general, there are experimental facts obtained by several different lines that militate against it. Sucrose and esters are hydrolyzed in the presence of acids and also of enzymes, and in both cases the degree of acidity varies with the acid or with the enzyme. Since the selective action of the enzymes can be explained on the basis of combination with the hydrolyte, there is no reason why this explanation should not be extended to the acids. Further, it is found that the acidity of an acid as a hydrolyzing agent is frequently increased by the addition of its neutral salts, and as non-electrolytes also sometimes act in the same way there is no reason to account for the activity of the electrolytes by an explanation which is inapplicable to non-electrolytes. Since alcohol, equally with hydrochloric acid, causes the precipitation of chlorides from solution, the explanation which can be applied to alcohol, — namely, hydration formation, — should also be applicable to hydrochloric acid.

In 1886 Armstrong attributed the increased molecular conductivity of dilute solutions to the gradual resolution of the more or less polymerized molecules of the salt into simpler molecules or monads which, when combined with the solvent, constituted a "composite electrolyte." Recently he adds that "the electrolytically effective monads must be thought of as hydrated in some particular manner, perhaps as hydroxylated and that the association of the solvent with the negative radical of the solute was the determining factor in electrolysis." He considers that the positive radical of the solute has no tendency to associate with the solvent and that the power of ionization does not involve the resolution of the molecules into separate ions.

Werner in his *New Ideas on Inorganic Chemistry* presents a résumé of his work on the ammonia substitution products and the reactions in the formation of analogous compounds, which he develops into his theory of Bases and Acids and the Theory of Hydrolysis, etc. In this he presents, in opposition to the above idea, the suggestion that the ionization is due to the association of molecules of water or ammonia with the metal, the negative radicals being regarded as inert. Many metallic salts form hydrates with six molecules of water such as the following: $[Ni(OH_2)_6]Cl_2$, $[Co(OH_2)_6]Cl_2$, $[Zn(OH_2)_6](NO_3)_2$, $[Mg(OH_2)_6]Br_2$, $[Ca(OH_2)_6]Cl_2$, $[Sr(OH_2)_6]Br_2$, $[Fe(OH_2)_6]Cl_3$. Many of these hydrates contain the maximum number of water molecules known to the salt, and their constitution is analogous to the hexamine metallic salts which have been extensively studied. Werner assumes, therefore, that the hexahydrates are salt-like compounds in which the positive radical consists of complexes containing the metal and six molecules of water, which are linked directly to the metallic atom and in a separate sphere from the acid residues. The greenish blue hexahydrate $CrCl_3 \cdot 6\ H_2O$ dissolves, giving a blue-violet solution, and all three of the chlorine atoms are present as ions, as is shown by the electrical conductivity and freezing point determinations and by treatment with silver nitrate. It is therefore represented by the formula $[Cr(OH_2)_6]Cl_3$. On losing two molecules of water this is transformed into a green hydrate, $CrCl_3 \cdot 4\ H_2O$. This hydrate in solution shows that only part of its chlorine is in the ionogen condition as only two thirds of the chlorine can be precipitated by $AgNO_3$. The formula would then be $\left[Cr \begin{matrix} Cl \\ (OH_2)_5 \end{matrix}\right]Cl_2 \cdot H_2O$. There is still another hexahydrate which contains only one chlorine with ionogen properties, and the formula assigned to it is $\left[Cr \begin{matrix} Cl_2 \\ (OH_2)_4 \end{matrix}\right]Cl\ \ 2\ H_2O$. These extra molecules of water are not linked to the dissociated chlorine ions, and from evidence presented he concludes that they belong in some way to the chromium complex, and the following expression illustrates the relations between these three isomeric hexahydrates:

$[Cr(OH_2)_6]Cl_3$	$\left[Cr \begin{matrix} Cl \cdot H_2O \\ (OH_2)_5 \end{matrix}\right]Cl_2$	$\left[\begin{matrix} Cl \cdot H_2O \\ Cr\ Cl \cdot H_2O \\ (OH_2)_4 \end{matrix}\right]Cl$
Blue hydrate of chromium chloride	**Bjerrum's chloride**	**Green hydrate of chromium chloride**

Werner further shows that acids as well as bases are formed through the combination of the solvent and solute, so in general he expresses the view that the ionization is preceded by a combination with the solvent. It is primarily the metallic or positive part of the solute that is hydrated.

It would lead us too far to consider the experimental data that led Tammann to consider that salt solutions resemble the pure solvent under increased external pressure; Traube to state that each ion is in combination with a single molecule of water; Vaillant from density determinations to conclude most ions to be anhydrous, but OH^-, F^-, S^{--}, and CO_3^{--} to be monohydrated; Philip to deduce from solubility of hydrogen and oxygen in salt solutions the agreement of the degree of hydration with the values obtained by the acceleration of the inversion of cane sugar by acids as influenced by salts as measured by Caldwell and from the freezing point determinations by Bonsfield and Lowry; and to show how the Phase Rule could be applied to the determination of hydrates in solution.

Kohlrausch's observation led him to consider the ions water coated and that the combined water altered the size of the ions, and he concluded that the effect of the change of velocity and of size of the ions might adequately account for the change in the migration velocity observed with the change in the dilution, *i.e.* that there is a change in the degree of hydration of the ion with the change in the concentration of the solution. From Table XLIX of Transference numbers it appears that the heavier atoms yield the more mobile ions, and for this reason it is concluded that the ions are hydrated. Lithium ion is the most highly hydrated and the cæsium ion the least hydrated of the metals of the alkalies.

When a current is passed through the solution of an electrolyte the transfer of the current should be accompanied by the transfer of water if the ions are hydrated, and it should be an easy matter to detect this. Various attempts have been made to determine this transfer of water by electrolyzing a solution containing a small quantity of a non-electrolyte that could be used as a reference substance. This reference substance not being affected by the current will remain distributed, after the electrolysis, just as before, and any change resulting from the transference of the water from the anode chamber will be recognized by an increase in the concentration of the non-electrolyte at the anode and a corresponding decrease at the cathode. As no change takes place when the electrolyte is absent, it is assumed that the water is transported by the migrating ions and that this is the amount of water that is in combination with the respective ions. Nernst and his pupils have tried this method with indifferent success. Washburn found that the cations are hydrated as follows: $H(H_2O)_{0.3}$, $K(H_2O)_{1.3}$, $Na(H_2O)_{2.0}$, $Li(H_2O)_{4.7}$. Ganard and Oppermann have found by assuming the hydrogen ion to be anhydrous the following values of hydration for some of the anions: $SO_4(H_2O)_9$, $Cl(H_2O)_5$, $Br(H_2O)_4$, $NO_3(H_2O)_{2.5}$. Newberry[1] states: "Previous determinations of the hydration of ions by observations of the change of concentration of the non-electrolyte present have given incorrect values due the transport of the non-electrolyte by the ion present and also by the action of electric endosmosis." He concludes from a study of metal over voltage that H, OH, Fe, Ni, and Co ions are hydrated in aqueous solution while Cu, Ag, Zn, Cd, Hg^+, Tl, Pb, Sn, NH_4, Na, K, Cl, NO_3, SO_4 ions are not hydrated.

Constitution of Water. — We have seen on several occasions that water was considered a highly associated liquid, and the exact composition of the associated molecules has been the subject of extensive research. As early as 1891, Röntgen put forth the idea that water is a binary mixture of "water molecules" and of "ice molecules" of greater complexity but smaller density, so that when the liquid is heated these complexes are decomposed, and a contraction is produced which is sufficient between 0° and 4° to counteract the ordinary thermal expansion of the liquid. Tammann made use of the composite character of liquid water to account for the abnormal character of his data obtained on the compressibility of the liquid, and also regarded water as a binary mixture. Sutherland, within the last few years, from his extensive researches, concludes that water vapor in the condi-

[1] *Jour. Chem. Soc.* *111*, 470 (1917).

tion of a nearly perfect gas is hydrol (H_2O), ice is trihydrol $(H_2O)_3$, and liquid water is a mixture of the trihydrol and dihydrol $(H_2O)_2$ in proportions which vary with the temperature, pressure, and the presence of solutes. It is to this complex character of water that many of the exceptional properties of water and of aqueous solutions are attributed.

Bonsfield and Lowry, from a study of the density of aqueous solutions of caustic soda, sugar, chloral, acetic acid, silver nitrate, sodium chloride, potassium chloride, lithium chloride, and calcium chloride, conclude that water is really a ternary mixture consisting of the trihydrol, dihydrol, and monohydrol. On cooling liquid water there is a formation of the more polymerized ice molecules, and heating causes their dissociation, yielding the monohydrol or steam molecules. Each of these changes is accompanied by an increase of volume superimposed upon the expansion or contraction resulting from the mere temperature change. Hence the density of solutions is presented as evidence of the formation of hydrates. It is argued that the influence of the solute cannot be accounted for unless some abnormal value is assigned to the density of water in combination with the solute. Hydrate formation is stated to be always accompanied by a contraction of volume, hence, the density of this water must be greater than that of the water in the ordinary state. In 1875 F. W. Clark attributed to water of crystallization a molecular volume of 14 cc., and this is practically the same as that deduced by Thorp and Watts from the metallic sulphates, which was 14.5 cc. These values give a density of approximately 1.24 for the water of crystallization. Sutherland gives 1.089 as the density of dihydrol, and Bonsfield calculates the density of water of hydration of KCl as 1.1, which value gives a degree of hydration of this salt practically the same as the value found by Philip from the solubility of hydrogen gas in KCl solutions and that of Caldwell from the influence of KCl in accelerating the inversion of cane sugar by acids. Hence they conclude that the density of combined water approximates that of the denser constituent of liquid water.

Guye, from his extensive experimentation on vapor pressure, surface tension, molecular weight determinations, and association coefficients, concludes that the data obtained appear to form new evidence in favor of the chemical conception of the phenomenon of association or polymerization in the liquid phase of water or other associated liquids. And further, the coefficient of association of Dutoit and Majoin is in agreement with the results according to which liquid water at 0° is mostly trihydrol, $(H_2O)_3$, and at the boiling point dihydrol, $(H_2O)_2$.

Walden from his researches on the anomalous behavior of water when dissolved in solvents of high dielectric constants concludes that a *chemical* interpretation of these results must be attempted and that there is formed, owing to the chemical nature of the solvent and solute, a molecular combination of a *salt character* which is then the conductor of the electric current and an electrolyte.

From the foregoing we see that there is a tendency for the modern workers to get back to the earlier conception of a reaction between the solvent and the solute, and that the formulation of any theory of solutions should take this into consideration.

CHAPTER XXXII

HYDROLYSIS

We are familiar with the fact that a solution of Na_2CO_3 is alkaline in reaction; but Na_2CO_3 is defined as a normal salt, *i.e.* one in which all of the hydrogen of the acid had been replaced by sodium. We further define a substance which in aqueous solutions yields hydroxyl ions a base, and conversely, since there are hydroxyl ions in a solution of Na_2CO_3, it is therefore a base. As there is no OH in Na_2CO_3, the necessary hydroxyl ions must come from the water in which the carbonate is dissolved. So the reaction between the solvent, water, and the Na_2CO_3, the solute, is represented thus: $2\,Na^+ \cdot CO_3^{--} + 2\,(H^+ \cdot OH^-) \rightleftarrows 2\,(Na^+ \cdot OH^-) + H_2CO_3$. As NaOH is highly dissociated, this then is the source of the hydroxyl ions. A solution of ferric chloride is acid in reaction, and similarly this is accounted for by the following reaction: $Fe^{+++} \cdot 3\,Cl^- + 3\,(H^+ \cdot OH^-) \rightleftarrows Fe(OH)_3 + 3\,(H^+ \cdot Cl^-)$. The HCl is highly dissociated as it is a strong acid and yields hydrogen ions. It is to the presence of these that the acid character is attributed.

Dissociation of Water. — We have seen that pure water is one of the best of insulators; consequently, its electrical conductance is very slight. This conductance must be due to the presence of hydrogen and hydroxyl ions, but since their ionic conductances are the greatest of any ions there must be but a few of them to account for the slight conductance of pure water. Kohlrausch found, for the purest water that he could prepare, a conductance at 18° of 0.040×10^{-6}.

The conductance at 25° C. is 0.054×10^{-6}. From the conductance the concentrations of the hydrogen and of the hydroxyl ions have been calculated, and it is found to be about 1.0×10^{-7} normal. Or applying the Mass Law to the dissociation of water we have

$$H_2O \rightleftarrows H^+ \cdot OH$$
$$k[H_2O] = [H^+] \cdot [OH^-].$$

Solving for k, the dissociation constant, we have

$$k = \frac{[H^+] \cdot [OH^-]}{[H^2O]}.$$

but since the concentration of the undissociated water, $[H_2O]$, is very large as compared to the dissociated part, it may be considered as practically constant and the equation written $K_w = [H^+] \cdot [OH^-]$. Substituting the above value of the concentrations of H^+ and OH^-, we have

$$K_w = [1.0 \times 10^{-7}] \cdot [1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

as the Ionic Product or so-called Dissociation Constant of water. In Table LVIII we have compiled the Dissociation Constant of a few acids and bases, and the value for water is very small as compared with most of these.

There are a number of other methods by which the dissociation of water has been determined, and among these may be mentioned the Catalysis of Esters, Catalytic Muta-Rotation of Glucose, Hydrolysis of Salts, and the Electromotive Force Method. These methods, some of which will be considered subsequently, give results that compare very favorably with the above.

The change in temperature affects the degree of dissociation to a marked extent, as the data in Table LXV obtained by Heydweiller shows:

Table LXV

Dissociation Constant for Water

t° C.	0°	10°	18°	25°	50°	100°	150°	218°
$K_w \times 10^{14}$	0.116	0.281	0.59	1.04	5.66	58.2	269	630.1

When a salt is dissolved in water with the concomitant formation of free hydrogen or hydroxyl ions through the reaction of the salt with the water, we may have several cases, depending upon the ease with which the resulting products of the reaction are ionized. If the dissociation constant of the acid produced is greater than that of water, the solution will have an acid reaction; while if the dissociation constant of the base is greater than that of the water, the solution manifests an alkaline reaction. But should the base and acid be practically un-ionized, the solution will be neutral, and we have the case of the formation of a weak acid and a weak base or the reverse, while in the former case we have either one of the two constituents a strong electrolyte.

As an example of the case when one of the two products of hydrolysis is a strong electrolyte, we may select acetanilid hydrochloride, $C_6H_5NH_2C_2H_3OCl$. The ionic reaction is represented thus:

$$C_6H_5NH_2C_2H_3O^+ \cdot Cl^- + HOH \rightleftarrows C_6H_5NH_2C_2H_3OOH + H^+ \cdot Cl^-.$$

Applying the Mass Law we then have

$$k[C_6H_5NH_2C_2H_3O^+] \cdot [Cl^-] \cdot [HOH] = [C_6H_5NH_2C_2H_3OOH] \cdot [H^+] \cdot [Cl^-].$$

Since this is a dilute solution, the concentration of the water is constant and the concentration of the chlorine ions obtained from the completely dissociated salt is the same as that from the completely dissociated HCl, hence our equation may be written

$$K_h = k[HOH] = \frac{[C_6H_5NH_2C_2H_3OOH] \cdot [H^+]}{[C_6H_5NH_2C_2H_3O^+]}$$

in which K_h is termed the *Hydrolytic Constant.*

The dissociation constant of water is $K_w = [H^+] \cdot [OH^-]$, from which the concentration of the hydrogen ions is

$$[H^+] = \frac{K_w}{[OH^-]}.$$

The dissociation constant for the base is

$$K_b = \frac{[C_6H_5NH_2C_2H_3O^+] \cdot [OH^-]}{[C_6H_5NH_2C_2H_3OOH]}.$$

Substituting the value of the hydrogen ion, $[H^+]$, in the above equation we have

$$K_h = \frac{[C_6H_5NH_2C_2H_3OOH]K_w}{[C_6H_5NH_2C_2H_3O^+] \cdot [OH^-]}$$

but the terms in brackets are $\frac{1}{K_b}$. Therefore, substituting, we have $K_h = \frac{K_w}{K_b}$, in which K_h is the *Hydrolytic Constant* of the salt. K_w is the Ionic Product of the water; K_b is the Dissociation Constant of the base.

Similarly by selecting a salt such as KCN, which on hydrolysis gives an alkaline reaction, it may be readily shown that the hydrolytic constant $K_h = \frac{K_w}{K_a}$.

If we have the two products of hydrolysis both weak electrolytes, as in the case of aniline acetate, $C_6H_5NH_3CH_3COO$, the hydrolytic constant may be worked out in a similar manner.

The ionic reaction is as follows:

$$C_6H_5NH_3^+ \cdot CH_3COO^- + HOH \rightleftarrows C_6H_5NH_3 \cdot OH + CH_3COOH.$$

Applying the Mass Law Equation we have

$$k[C_6H_5NH_3^+] \cdot [CH_3COO^-] \cdot [HOH] = [C_6H_5NH_3OH] \cdot [CH_3COOH]$$

and since this is a dilute solution the concentration of the water [HOH] is constant and the products of the hydrolytic dissociation are assumed to be un-ionized, the equation becomes

$$K_h = \frac{[C_6H_5NH_3OH] \cdot [CH_3COOH]}{[C_6H_5NH^+{}_3] \cdot [CH_3COO^-]}.$$

The dissociation constant for the acid is

$$K_a = \frac{[CH_3COO^-] \cdot [H^+]}{[CH_3COOH]}$$

therefore,

$$\frac{[H^+]}{K_a} = \frac{[CH_3COOH]}{[CH_3COO^-]}$$

and similarly from the dissociation constant of the base we have

$$\frac{[OH^-]}{K_b} = \frac{[C_6H_5NH_3OH]}{[C_6H_5NH_3^+]}.$$

Now substituting these values in the equation above we have

$$K_h = \frac{[H^+] \cdot [OH^-]}{K_a \cdot K_b},$$

but the numerator is the dissociation constant of water, K_w, hence substituting we have

$$K_h = \frac{K_w}{K_a \cdot K_b},$$

which is the *hydrolytic constant* for the cases where both products of the hydrolysis are weak electrolytes.

Degree of Hydrolysis. — The Mass Law Equation for acetanilid hydrochloride gives us the hydrolytic dissociation constant according to the equation

$$K_h = \frac{[C_6H_5NH_2C_2H_3OOH] \cdot [H^+]}{[C_6H_5NH_2C_2H_3O^+]}$$

Now if x is the degree of hydrolysis, then as we have previously seen in the case of electrolytic dissociation, the concentrations of the ions when there is one mole of the salt dissolved in v liters of water are

$\frac{1 - x}{v}$ mole of $C_6H_5NH_2C_2H_3O^-$ ions unhydrolyzed

$\frac{x}{v}$ mole of H^+ ions

$\frac{x}{v}$ mole of $C_6H_5NH_2C_2H_3OOH$ undissociated base.

Substituting these values in the equation, we have

$$K_h = \frac{\frac{x}{v} \cdot \frac{x}{v}}{\frac{1 - x}{v}} \text{ which gives } K_h = \frac{x^2}{(1 - x)v}.$$

Similarly in the case of aniline acetate we have from

$$K_h = \frac{[C_6H_5NH_3OH] \cdot [CH_3COOH]}{[C_6H_5NH_3^+] \cdot [CH_3COO^-]}$$

the expression for the hydrolytic dissociation the equation

$$K_h = \frac{\frac{x}{v} \cdot \frac{x}{v}}{\left(\frac{1 - x}{v}\right)\left(\frac{1 - x}{v}\right)}$$

which becomes
$$K_h = \frac{x^2}{(1 - x)^2}$$

as the *hydrolytic constant* for the cases where the two products of hydrolysis are weak electrolytes. It is evident, since the term for the volume of the solution does not appear in this equation, that in cases of this type the hydrolytic dissociation is independent of the volume.

The value of x, the degree of hydrolysis, can be obtained experimentally from the speed of inversion of cane sugar or the hydrolysis of esters, which will be discussed subsequently. Then from this value the hydrolytic constant can be calculated from the equations given above.

The value of x is determined from the electrical conductance of the solutions on the assumption that the conductivity is an additive property, and hence the conductance of the solution is the sum of the individual conductances of the ions present. For example, in the case of acetaniline hydrochloride we have
$$\Lambda = (1 - x)\Lambda_v + x\Lambda_{HCl},$$

in which the total conductance, Λ, is the sum of the conductances of the un-hydrolyzed salt plus the conductance of the hydrochloric acid. Solving for x, we have

$$x = \frac{\Lambda - \Lambda_v}{\Lambda_{HCl} - \Lambda_v}.$$

As the HCl is completely dissociated, the value of Λ_{HCL} becomes its value Λ_∞, and the value Λ_v is the value of the conductance of the salt at the specified volume, assuming no hydrolysis. This value is obtained by forcing back the hydrolysis by the addition of a large excess of the salt, when Λ_v becomes the conductance of the solution Λ.

In Table LXVI will be found the values for the degree of hydrolysis and the Hydrolytic Constant K_h of a number of compounds.

Table LXVI

Substance	Temp. C.	Concentration Liters per 1 gm. Equiv.	Method	Per Cent Hydrolysis	Hydrolysis Constant
Acetanilid hydrochloride	25°	32	Catalysis	99.8	19
Acetanilid hydrochloride	40.2	10	Catalysis	88.9	
Acetanilid hydrochloride		20		93.8	
Acetamid hydrochloride	25	10	Catalysis	98	
Acetoxime hydrochloride	25	10	Catalysis	36	
Aluminium chloride	78	32	Inversion	4.72	
Aluminium chloride		64		6.90	
Aluminium chloride		128		8.49	
Aluminium chloride		256		14.4	
Aniline acetate	25	39.32	Cond.	51.3	
Aniline acetate	40	39.32		59.0	
Ammonium acetate	100	40.13	Cond.	4.61	
Ammonium bicarbonate	25				2.4×10^{-4}
Ammonium chloride	25	2–32		0.011	3.1×10^{-10}
Ammonium chloride	18	100	Indirect	0.02	
Ammonium chloride	218	100		1.6	
Ammonium chloride	306	100		4.1	
Ammonium citrate	100	5		3.86	
Ammonium succinate	100	5	Partial Press.	1.34	
		10	Partial Press.	24.4	
Bismuth chloride	25	0–4			4.0
	50	0.18–3.7			3.1
$Br_2 + HOH \quad H^+Br^- + HBrO$	25		Cond.		5.2×10^{-9}
Carbonic acid	25	10	Catalysis	3.17	
Cerium chloride	100	10		0.3	
$Cl_2 + H_2O \quad H^+Cl^- + HClO$	0				1.56×10^{-4}
$Cl_2 + H_2O$	15				3.16×10^{-4}
$Cl_2 + H_2O$	25				4.48×10^{-4}
$Cl_2 + H_2O$	39.1				6.86×10^{-4}
$Cl_2 + H_2O$	53.6				9.01×10^{-4}
$Cl_2 + H_2O$	67.6				10.36×10^{-4}
$Cl_2 + H_2O$	83.4				10.93×10^{-4}
Sodium Salt of Chlorphenol	25	10	Catalysis	1.62	
2 · 4 Dichlorphenol	25	10	Catalysis	0.29	
2 · 4 · 6 Trichlorphenol	25	10	Catalysis	0.21	
p. Cyanphenol	25	10	Catalysis	0.29	
Ferric chloride	25	6.67	Cond.	2	
Ferric chloride		33.34		37	
Ferric chloride		333.4		84	
Ferric chloride		666.7		91	
Glycocoll hydrochloride	25	10	Catalysis	19	
Glycocoll hydrochloride	25	10	Inversion	18	
Sodium cyanate	25	10	Catalysis	1.12	
Lanthanum chloride	100	10	Inversion	0.3	
Nickel chloride	25	44–35.2	Inversion	0.30	0.3×10^{-5}
Nickel sulphate	25	4–64	Inversion	32-.044	1.1×10^{-13}
Potassium cyanide	10.3	9.63	Inversion	1.48	
Potassium cyanide	25.05	9.63	Inversion	1.73	
Potassium cyanide	41.8	9.63		1.98	
Potassium cyanide	42.5	9.63		2.11	
Propionitrile hydrochloride	25	10	Catalysis	99	
Propionitrile hydrochloride	25	10	Inversion	92	
Sodium bicarbonate	18	1–1000			1.5×10^{-6}
Sodium bicarbonate	25	1–1000			2.5×10^{-6}
Sodium carbonate	25	5		1.3	1.9×10^{-4}
Sodium carbonate	25	10		2.9	
Sodium carbonate	25	20		4.5	

TABLE LXVI — *Cont.*

Substance	Temp. C.	Concentration Liters per 1 gm. Equiv.	Method	Per Cent Hydrolysis	Hydrolysis Constant
Sodium carbonate	25	100		11.3	
Sodium carbonate	25	200		16.0	
Sodium carbonate	25	1000		34.0	
Urea hydrochloride	25	10	Catalysis	90	
Urea hydrochloride	25	10	Inversion	81	
Thiourea hydrochloride . . .	25	10	Catalysis	99	
Thiourea hydrochloride . .			Inversion	92	
o-Toluidine hydrochloride . .	25	10	Inversion	3.2	
o-Toluidine hydrochloride . .	25	10	Conductivity	1.8	
p-Toluidine hydrochloride . .	25	10	Inversion	1.7	
p-Toluidine hydrochloride . .	25	10	Conductivity	0.9	

CHAPTER XXXIII

NONAQUEOUS SOLUTIONS

In our study of solutions we have been considering primarily aqueous solutions, and the numerous theories we have been studying have been developed from these. The question arises, Are these theories applicable to solutions wherein any substance may be taken as the solvent, or are they only applicable to the solutions in which water is the solvent? We have just considered in detail the Electrolytic Theory of Dissociation as developed to explain certain abnormal values obtained in aqueous solutions wherein the solute was assumed to be independent of the solvent and was dissociated by it. Then we saw that many facts have been collected that are now being explained upon the basis of a combination of the solvent and the solute as well as a combination of the dissociated parts of the solute with the solvent. Particularly in concentrated solutions have these assumptions of hydration been made to account for the abnormal values presented by the data collected and interpreted in the light of the theory of dilute solutions.

The question arises, Can we employ these methods to the determination of the various properties of nonaqueous solutions, and can the data collected by them be interpreted in a similar manner? For example, do nonaqueous solvents yield solutions that conduct the electric current, and does the conductance represent the degree of dissociation of the solute? Is an electrolyte dissociated to the same extent by all solvents; do the ions have the same ionic conductance in different solvents, — if they do not, why not, — or in other words, to what is the ionization of the solute due? We know that some solvents yield conducting solutions, while others do not. Then is the degree of dissociation as determined by the conductivity comparable to that determined by the other methods that are employed in aqueous solutions, such as freezing point, boiling point, osmotic pressure, and vapor pressure? It is therefore evident that the detailed consideration of nonaqueous solutions requires an extensive study of the methods and theories we have been considering, as applied to solutions of solvents other than water. During the last few years many investigators have collected an enormous amount of data and have attempted to correlate these in the light of the theories developed on the basis of aqueous solutions.

One of the principal questions that has been discussed is, To what is the ionizing power of a solvent due? Various explanations have been presented, and we shall take up a consideration of these in our presentation. Among these may be mentioned the relation between the ionization power of the solvent and its dielectric constant, its association factor, the electrical conductance of its solutions, the viscosity, the combination of the solvent and solute, as well as the lowering of the freezing point, the rise of the boiling point, and the osmotic pressure of the solutions.

Electrical Conductance. — Determinations of the electrical conductances of solutions of many solvents, both organic and inorganic, have been made. These show that, as in the case of water, the conductance of the pure solvent is very small, while the solutions have a very appreciable conductance. In most cases the conductance is less than in aqueous solutions, but in a few cases they conduct much better. Such inorganic solvents as NH_3, SO_2, and HCN yield solutions that conduct very well, in many cases as well as water solutions, while the solutions of various solutes in PCl_3, $AsCl_3$, etc., have a relatively small conductance. A consideration of the various groups of organic solvents shows, in a general way, that liquid hydrocarbon solutions, as well as their halogen substitution products, are nonconductors. The alcohols yield solutions that conduct very well, but the conductance decreases with the increase of the carbon content as well as with the complexity of the alcohol. The aldehydes yield conducting solutions, and many of the solutions of ketones are excellent conductors, while the esters yield conducting solutions which are however not very good conductors. Many of the organic compounds containing nitrogen, such as the organic bases, amines, and nitriles, yield solutions that conduct; the nitriles in particular yield solutions that are excellent conductors.

The conductance of alcoholic solutions, particularly methyl and ethyl alcohols, has been studied extensively, and in general limiting values of the conductance have been found. From these values, then, as in the case of aqueous solutions, the degree of dissociation of the solute has been calculated. In Table LXVII are given Carrara's values for Λ_∞ for a number of solutes in methyl alcohol solutions. Some of these may be readily compared with the values in aqueous solution Table L. These values of Λ_∞ are expressed in the reciprocal Siemens unit.

TABLE LXVII

Λ_∞ IN METHYL ALCOHOL

	Cl	Br	I	OH
H	133.80	——	134.5	——
Li	77.3	——	——	——
Na	86.80	87.58	89.77	71.83
K	95.57	96.52	97.63	75.75
NH_4	96.24	99.93	105.25	(82.00)
$N(CH_3)_4$	——	——	115.30	——
$N(C_2H_5)_4$	96.76	96.62	113.76	91.13
$S(CH_3)_3$	100.09	102.5	116.38	97.34

Since the value of Λ_∞ depends on the ionic conductances, Carrara has calculated these values for a number of the ions, and these are given in Table LXVIII. To compare these values with the values given for aqueous solutions in Table LII, they will have to be converted to mhos.

TABLE LXVIII

EQUIVALENT IONIC CONDUCTANCE IN METHYL ALCOHOL

	Cl	Br	I
Li	27.8	—	—
Na	37.3	37.3	37.3
K	46.1	46.3	45.2
NH_4	46.8	49.5	53.8
$N(CH_3)_4$	—	—	63.1
$N(C_2H_5)_4$	46.3	46.4	61.3
$S(CH_3)_2$	51.4	49.9	64.0
H	85.5	—	82.5
OH	32.0		
Cl	49.5		
Br	50.2		
I	52.4		
CH_3COO	33.0		
CCl_3COO	36.0		

With few other solvents has the work been so extensive as with the alcohols, but it is found that in most cases the limiting values of the equivalent conductance, Λ_∞, cannot be obtained experimentally, and neither have the ionic conductances been ascertained. We have therefore too meager data in most cases for the calculation of the degree of dissociation of the solute from the conductances of the solutions. The marked conductance of certain solutions of nonaqueous solvents is accounted for on the basis that although the degree of dissociation is less than in aqueous solutions the speed of migration of the ions is much greater than in water, and consequently the conductance is greater. In such solvents as hydrocyanic acid, ammonia, pyridine, and some nitriles, the conductance of solutions of certain electrolytes is much greater than their aqueous solutions. The equivalent conductance increases with the dilution, but there are a few marked exceptions. In pyridine and benzaldehyde solutions the equivalent conductance of ferric chloride decreases with the dilution. This was also found to be the case in solutions of HCl in ether and also in isoamyl alcohol, as well as in solutions of sulphuric acid; and in acetic acid the molecular conductance decreased with the increased dilution. Dutoit and Friderich found the conductance of CdI_2 to be practically constant with the change of dilution in acetophenone solutions, and in methly propyl ketone and methyl ethyl ketone the equivalent conductance decreases with the dilution. This is also true of stannous chloride in acetone. Euler found the molecular conductance of both NaI and NaBr in benzonitrile to decrease with the dilution and this is also true of solutions of silver nitrate in piperidine.

Dielectric Constant. — It will be recalled that the electrostatic action of two electrically charged bodies varies with the nature of the medium in which they are placed. A substance which is a very poor conductor, or is, as we say, an insulator, is also called a dielectric. Upon ionization of a solute in a nonconducting solvent, the charged ions will be separated by this medium, and Faraday emphasized that its nature must be taken into consideration. This is always constant for a given medium and is termed the specific inductive capacity and is familiarly known as the *Dielectric Constant*. Thomson, and subsequently Nernst, emphasized the relation between the dissociative or ionizing power of a solvent and its dielectric constant. They showed that the greater the dielectric constant the greater the ionizing power of the solvent, and this is known as the Thomson-Nernst Rule.

Table LXIX

Solvent	Coefficient of Association	Temp. C. t	Dielectric Constant Air=1	Temp. C. t	Viscosity η	Solute	V	Λ
Hexane		17	1.88	20	0.0033			
Amylene	0.96	15.8	2.20					
Benzene	1.01	18	2.3	20	0.0064			
Toluene	—	19	2.3	25	0.0054			
Chloroform	0.94	17	4.95	20	0.0057			
Ethylene chloride	—	20	10.4	20	0.0084			
Acetyl chloride	1.06	20	15.5					
Methyl alcohol	3.43	18	31.0	20	0.0060	KI	∞	97.6
						$N(C_2H_5)_4I$	∞	124
Ethyl alcohol	2.74	20	25.8	20	0.0119	KI	5000	47.8
						$N(C_2H_5)_4I$	∞	60
Allyl alcohol	1.88	21	20.6	20	0.0136	NaI	813.4	33.1
						NaCl	1066.6	33.1
Propyl alcohol	2.25		22.2	20	0.0225	SrI_2	128	10.2
Benzyl alcohol	—	21	10.6	20	0.0558	$FeCl_3$	895.2	6.3
Epichlorhydrine	—	20	23.0			$N(C_2H_5)_4I$	∞	66.8
Phenol	1.42	48	9.68	45	0.040			
Ethyl ether	0.99	18	4.35	20	0.00226			
Acetic aldehyde	—	20	14.8	19.2	0.00233			
Paraldehyde	0.85	20	11.8			$FeCl_3$	183.1	16.5
Benzaldehyde	0.97	20	18.0			$FeCl_3$	237.1	10.5
						$N(C_2H_5)_4I$	∞	43
Acetone	1.26	20	21.5	19	0.0033	$AgNO_3$	576	16.5
						$N(C_2H_5)_4I$	∞	225
Methyl propyl ketone	1.11	17	15.1	20	0.005	$FeCl_3$	1074	59.5
Methyl ethyl ketone	1.15	17	17.8	20	0.0044	$CHS \cdot NH_4$	94.8	19.7
Acetophenone	1.10	20	18.1			$FeCl_3$	293	13.1
Ethyl acetate	0.99	20	5.85	20	0.00451	$FeCl_3$	67.6	1.3
Ethyl cyan acetate	—	20	27.7			$FeCl_3$	185.2	11.6
Ethyl acetoacetate	0.96	22	15.7	20	0.0191	$FeCl_3$	503.5	23.4
Ethyl benzoate	—	19	6.04	20	0.0067	$FeCl_3$	517.2	1.91
Nitrobenzene	1.13	18	36.45	25	0.0183	$FeCl_3$	2904	20.5
						$N(C_2H_5)_4I$	∞	40.0
Aniline	1.05	18	7.32	20	0.0447			
Pyridine	0.93	21	12.4	25	0.0089	$AgNO_3$	140.7	36.2
						NH_4I	2528.6	41.0
Piperidine	1.08	20	5.8			$AgNO_3$	4.24	0.37
Quinoline	0.81	21	8.8			$AgNO_3$	129.9	3.62
Phenyl hydrazine	—	23	7.15					
Acetonitrile	1.67	20	38.8		0.0033	$AgNO_3$	128	118.3
						$N(C_2H_5)_4I$	∞	200
Propionitrile	1.77	20	27.7		0.0040	$AgNO_3$	256	38.9
						$N(C_2H_5)_4I$	∞	165
Butyronitrile	1.22	21	20.3		0.0056	$AgNO^3$	150	32.1
Benzonitrile	1.00	20	26.5			$AgNO_3$	803	21.6
						$N(C_2H_5)_4I$	∞	56.5
Inorganic Solvents								
NH_3		−50°	22.7			$AgNO_3$	251.4	195.2
						Orthonitrophenol	2000	10.3
SO_2		20°	14.0			KI	2048	126.0
						$N(C_2H_5)_4I$	1024	154.7
HCN		21°	95			KI	1024	308
						Orthonitrophenol	2299	148.3
$AsCl_3$		17°	3.6					
PCl_3	1.02	22°	4.7					
H_2O		18°	81.1	20	0.01006	$AgNO_3$	∞	115.8
						KI	∞	131.1

In Table LXIX will be found the dielectric constants for a large number of types of solvents. It has been found that in general the Thomson-Nernst rule does hold, and those solvents with the highest dielectric constants yield the best conducting solutions. The conductance of the solution is, however, not commensurate with the dielectric constant, as is shown by an examination of the columns containing the data of the conductances of a number of solutes in various solvents. Some of the most conspicuous exceptions to the rule are given in the Table. In addition to these it may be mentioned that the value for LiCl in water of Λ_∞ at 18° is 95, and that at dilution of 3000 liters in propyl alcohol is 128.9; in fact, most of the values for propyl alcohol solutions (D.C. 21.6) are greater than those for solutions in water (D.C. 81). The values of Λ for acetonitrile (D.C. 38.8) solutions approximate closely those of many of the solutes in water. The value of Λ for NaI, NH_4I, $N(C_2H_5)_4I$ and of $S(C_2H_5)I$ in acetone (D.C. 21.5), according to Carrara, is greater in dilute solutions than the assigned values of Λ_∞ in aqueous solutions. In the case of hydrocyanic acid solutions the dielectric constant (95) indicates that we should have excellent conducting solutions, but as a matter of fact they are comparatively poor conductors as compared with aqueous solutions. Orthonitrophenol forms solutions that conduct poorly as compared with solutions of the same solute in ammonia. In general, however, ammonia solutions are better conducting solutions than the corresponding aqueous solutions. Nitrobenzene (D.C. 36.5) yields poor conducting solutions, the conductivity of which is not at all commensurate with the magnitude of its dielectric constant.

The increase in the conductance with the increased temperature holds generally, as in the case of aqueous solutions, but there are a few marked exceptions. The conductance of CdI_2 in acetonitrile is practically the same over the range of temperature from 0.2° to 37.2° C., and in acetone the temperature coefficient is virtually zero.

Association Constant. — Dutoit and Friderich from the result of their extensive researches on nonaqueous solutions concluded that only in associated liquids are the electrolytes dissociated, and the more highly the solvent is associated the greater is its ionizing power and consequently the better do its solutions conduct the electric current. In Table LXIX are given the association constants of a number of solvents, and while in general the solvents that yield the best conducting solutions are polymerized, the reverse is not true, for many solvents that are not supposed to consist of associated molecules do yield solutions that conduct the electric current. For example, water, the alcohols, the nitriles, and the ketones are the most highly associated liquids, and they are the solvents that yield the best conducting solutions. The aldehydes, nitrobenzene, benzonitrile, and the esters are not polymerized liquids, but they yield solutions that conduct the electric current, and many of them are fairly good conductors. Crompton emphasized the connection between the specific inductive capacity and the degree of association of the solvents, and Abegg also pointed out this parallelism, but he also observes that nitrobenzene, ethyl nitrite, and benzonitrile all have rather high dielectric constants; yet their association factors are unity. Crompton states: "It is almost impossible to doubt that association plays an all-important part in determining the value of the specific inductive capacity of a liquid and that if there is any connection between the specific inductive capacity and the power of forming electrolytes, it may be looked for rather in the fact that electrolytes are solutions of approximately monomolecular salts in an associated solvent rather than in there being any peculiar 'dissociative power' attached to the solvent."

Colligative Properties. — Numerous freezing point and boiling point determinations of nonaqueous solutions have been recorded, but the data on vapor pressure and osmotic pressure measurements are rather meager.

The degree of dissociation as calculated from boiling point determinations shows closer agreement with the values by the conductivity method in methyl alcohol solutions than in the case of other alcoholic solutions. In Table LXX are given the comparative values of the degree of dissociation as calculated from the boiling point determinations of Woelfer and the conductivity measurements of Vollmer.

TABLE LXX

Solute	Methyl Alcohol			Ethyl Alcohol		
	Per Cent of Solute	α by the Boiling Pt.	α by the Conductivity	Per Cent of Solute	α by the Boiling Pt.	α by the Conductivity
LiCl . .	0.45	0.63	0.57	0.9	0.35	0.32
KI . .	0.36	0.61	0.79	0.78	0.29	0.49
NaI . .	0.44	0.87	0.74	2.14	0.27	0.45
NaI . .				0.68	0.51	0.56
$AgNO_3$.				0.533	0.65	0.38
CH_3COOK	0.48	0.48	0.63	1.07	0.18	0.22
CH_3COONa	0.40	0.49	0.63	0.97	0.01	0.24

It must be remembered that these sets of values are calculated from data at different temperatures. At the temperature of the conductivity measurements, 18°, the viscosity factor for ethyl alcohol is about 0.01211, while at the boiling point it has decreased to approximately 0.00521, yet there is no regularity of results.

In acetone solutions Dutoit and Friderich found normal values for the molecular weight by the boiling point method, yet these solutes yield solutions that conduct. LiCl and CdI_2 yield solutions that conduct fairly well, which would indicate that they are quite highly dissociated, but the boiling point determinations indicate that they are not dissociated.

In benzonitrile Werner found normal molecular weights for $AgNO_3$, while the solutions conduct well, showing marked dissociation. He also found normal molecular weights for salts of the heavy metals in pyridine. The average of the values for $AgNO_3$ is 165.4, theory, 169.55; for $Hg(CN)_2$, 216.68, theory, 251.76; for HgI_2, 308.0, theory, 452.88; and for $Pb(NO_3)_2$, 352.07, theory requires 330.35. In most cases he found values slightly under the theoretical.

From these data it is apparent that there is not that agreement between the degree of dissociation as calculated from the boiling point or the cryoscopic determinations and from the conductivity measurements in nonaqueous solutions as has been found to hold in aqueous solutions, and this has been confirmed by numerous investigators.

Ostwald's Dilution Law. — We have already seen how well this Dilution Law of Ostwald holds in the case of aqueous solutions, and many attempts have been made to apply it to nonaqueous solutions. Most investigators, including Vollmer, Woelfer, Cattaneo, and others, have found that Ostwald's Dilution Law does not hold for methyl and ethyl alcoholic solutions. Cohen, who has considered this subject at considerable length, comes to the same conclusion. The data given in Table LXXI show that the formulæ of Rudolphi and of Ostwald do not hold when applied to alcoholic solutions. The following data for a solution of potassium acetate are taken from Cohen's results.

Table LXXI

V	Λ	$100\ K_R$	$100\ K_O$
11.4	8.28	0.82	0.242
113.0	17.18	0.59	0.055
1120.0	27.00	0.49	0.014
3520.0	29.20	0.36	0.006

The value of the constant obtained by Rudolphi's formula, K_R, does not vary nearly so much as that obtained from Ostwald's formula, K_O. The value of Λ_∞ is necessary for the calculation of these constants, and we have seen that the data for this are very meager, and not sufficiently exact, in most cases, to justify its use in this connection, and particularly is this true in those cases where the conductance decreases with the dilution.

Mixtures of Solvents. — Within recent years the problem of the conductance of electrolytes in mixtures of two different solvents has been the subject of numerous investigations. It is beyond our purpose to discuss this work in detail, but a few illustrations of the data collected will indicate some of the peculiarities of these solutions.

In Table LXXII are given the molecular conductances of certain salts in aqueous solutions, *A*; in methyl alcoholic solutions, *B*; and in 50 per cent solutions of methyl alcohol and water, *C*. These values are taken from the work of Zelinsky and Kraprivin, and expressed in the reciprocal Siemens unit.

TABLE LXXII

V	Δ FOR KBr			Λ FOR NH_4Br		
	A	*B*	*C*	*A*	*B*	*C*
16	123.1		59.82	127.2	65.43	61.16
32	127.5	69.02	62.46	131.8	72.73	63.81
64	130.5	76.70	65.36	135.3	79.56	66.04
128	132.9	83.60	67.11	138.6	85.80	67.45
256	136.4	88.96	69.26	141.2	90.88	68.32
512	140.2	93.26	70.53	143.5	94.99	69.10
1024	143.4	97.25		145.6	98.24	70.11

It will be noticed that the equivalent conductance of the methyl alcohol solutions, *B*, is less than that of the aqueous solutions, *A*, and that of the mixtures, *C*, is much below that of the methyl alcohol solutions. These *minimum* values have been emphasized by several workers, including Jones and his colaborers, Cohen, and others. In other cases marked *maximum* values are found in solutions of other salts in mixtures of solvents, as illustrated in the case of lithium nitrate in mixtures of acetone and methyl alcohol and of silver nitrate in mixtures of ethyl alcohol and acetone, particularly at the higher dilutions. There seems to be some parallelism between these maximum values and the minimum viscosity of the mixtures.

Carrara has shown that the electrolytic dissociation of water in methyl alcohol is greater than in aqueous solutions, while the reverse is the case in ethyl alcohol. It is also of interest to note that KOH and NaOH in methyl alcohol show the same conductance as CH_3OK and CH_3ONa.

Additional Theories. — From a consideration of the optical properties of solvents, Brühl comes to the conclusion that oxygen is generally tetravalent. He attributes the polymerization of the molecules of water and of other oxygenated liquids, their high specific inductive capacity, as well as the dissociative power exerted upon the dissolved substance, to their being unsaturated compounds. It is true that a great many oxygenated solvents do yield solutions that conduct electricity; but it has been pointed out by Dutoit and Friderich that the ethers and the ether salts are not polymerized solvents, and that they yield solutions that do not conduct, or the conductance of which is very slight, as in the case of ferric chloride solutions in phenyl-methyl ether. Ethyl carbonate does not yield solutions that conduct. The same is true for chloral solutions, and the esters of high carbon content yield solutions the conductance of which is very slight. In the case of the substitution of chlorine for the ethoxy group in ethyl carbonate, the number of spare valences is undoubtedly reduced, yet this product, ethyl chlorcarbonate, yields solutions that conduct well.

In compounds containing nitrogen, Brühl holds that the conductance of their solutions is due to the extra valences of the nitrogen. He predicts that hydrazine will prove to yield solutions that conduct, but phenylhydrazine does not yield solutions of the salts tested that conduct electricity; however, it still remains to be seen what hydrazine will do. He states that, in general, the dissociative power in the case of nitrogen compounds will vary with the nitrogen content, without being proportional to it, however; just as he claims that it varies with the oxygen content of oxygen compounds. He further predicts that the anhydrous hydrocyanic acid, diazo compounds, and even unsaturated compounds of the elements other than oxygen, namely, PCl_3, $AsCl_3$, mercaptans, and sulphur ethers, will possess dissociation power. Attention has been called to the fact that when the CN group is substituted for hydrogen in ethyl acetate, the equivalent conductance is materially increased. Hydrocyanic acid and nitriles do yield solutions that conduct very well. Contrary to Brühl's prediction, PCl_3 does not yield solutions that conduct; but in the case of $AsCl_3$ his prediction is confirmed. Werner found that solutions of cuprous chloride in methyl sulphide conduct very poorly. From the evidence we have at present it seems that the theory that the dissociative power of solvents is due to the unsaturated valences, that is, that the only solvents that yield solutions that conduct electricity are unsaturated compounds, is not substantiated by the facts in many cases. Therefore the theory as promulgated by Brühl is untenable.

It is quite noticeable that a large number of the investigators of the properties of nonaqueous solutions express the thought that there is manifested considerable influence between the dissolved substance and the solvent. This factor of the influence of the solvent upon the dissolved substance is one that is no doubt of very great importance; and in the development of the electrolytic dissociation theory (which is based upon the behavior of aqueous solutions) the action of the solvent upon the dissolved substance has been entirely neglected.

Fitzpatrick concludes from his investigation on the conductivity of alcoholic solutions that the action of the solvent upon the dissolved substance is a chemical one. He conceives the dissolved salt as decomposing and forming molecular groups in the solvent. Owing to the large excess of the solvent there will be a continual decomposition and recombination of these molecular groups. He cautions one against regarding the solvent as a medium in which the salt particles are suspended or as a dissociating agent. Wildermann, on the other hand, recognizes two kinds of dissociation — one the electrolytic dissociation of the dissolved substance, and the other, the dissociation of the larger molecular aggregates into smaller ones. For example, in a solution of KCl in water the following aggregates are assumed to exist: K_2Cl_2, KCl, $K_2{}^+Cl$, $KCl^-{}_2$, K^+, and Cl^-. He further maintains that solutions of all substances, whatever the solvent or concentration, undergo electrolytic dissociation.

Cattaneo was impressed with the fact that the molecular conductivity is greatly influenced by the nature of the solvent employed. He was not able, however, to point out any direct relation existing between the various properties of the solvents which yield solutions that conduct. Konovaloff, from his work on the amines, concludes that only those solvents that react chemically with the dissolved substance yield solutions that conduct. It is true that there are many solvents of this nature which do react with the dissolved substance, and yet which do not yield solutions that conduct electricity. Picric acid reacts with benzene, but the resulting solution does not conduct electricity. Hence chemical combination of the dissolved substance with the solvent may take place and yet the solutions need not necessarily conduct. Werner has isolated and analyzed a large number of products of pyridine and piperidine, among those of other organic solvents, with salts of the heavy metals. From the boiling point determinations, the molecular weights of these salts seem to be very slightly influenced by their union with the solvent. This is analogous to the fact that salts which crystallize from an aqueous solution with water of crystallization yield the same molecular weights whether dissolved in the anhydrous form or with their water of crystallization. Carrara thinks that the union of solvent and dissolved substance accounts for the slight conductivity in certain cases. The low values for Λ in the case of acetone solutions of HCl and LiCl he attributes to this fact.

It has been pointed out by Ciamician that the dissociative power of a solvent depends principally upon its chemical structure. That is, compounds of the same chemical type, for example, of the HOH type, yield solutions that conduct well. This is true in the case of alcoholic solutions, which are not the only class of compounds that possess dissociative power, as has already been pointed out. In general, however, if one member of a particular type of compounds (*e.g.* nitriles) yields solutions that conduct, it has been found that other members also possess this property; and if a member of some other type (*e.g.* hydrocarbons), is found not to yield solutions that conduct, other members do not possess dissociative power.

The data collected are as yet insufficient to show what the relation between solvent and dissolved substance must be in order to yield solutions that conduct electricity. Enough facts have been presented, however, to make it apparent that any theory that aims to explain the electrical conductivity of solutions in general must take into consideration the influence of the solvent upon the dissolved substance. This subject is replete with interest; for closely connected with it is the true cause of the solubility of substances.

CHAPTER XXXIV

THERMOCHEMISTRY

In the consideration of the various chemical reactions no account is usually taken of the energy changes accompanying them. But it is fully recognized now that the thermal change which results from the reaction may so modify the temperature of the system that the best results are not obtainable and consequently it is necessary to control the temperature very carefully, as it is only over a small range of temperature, relatively, that the particular reaction takes place best. In a few special industrial applications only is the energy manifest in the thermal changes considered of sufficient importance to be utilized. In the combustion of fuel, which is a chemical reaction consisting of the union of oxygen and the constituents of the fuel, the reaction is carried on for the sole purpose of obtaining the energy in the form of heat. The study of the heat energy changes associated with and accompanying chemical reactions and changes constitute what is termed *Thermochemistry.*

A large amount of thermochemical data has been obtained, but most of this was collected some time ago when the field of chemical reactions was confined to a comparatively small range of temperature — being only a few hundred degrees above ordinary room temperature. By the use of such appliances as the electric furnace the temperature range for chemical reactions has been so extended that entirely new conditions have been provided which have resulted in the production of entirely new types of chemical reactions. The thermal energy changes accompanying these reactions are entirely different from those of the analogous reactions under ordinary conditions, and the thermochemical data available for these are not applicable to the new conditions, nor are the data for these new reactions under the new conditions available. Richards[1] states that the available thermochemical data "enable us to figure out easily the energy of a chemical reaction beginning and ending at ordinary temperatures, when the heats of formation of all the substances concerned are contained in the tables. They give us no exact information at all about the energy of the chemical reaction at temperatures other than the ordinary room temperature. . . . A larger part of metallurgical reactions are carried on at temperatures above the ordinary, running up to 3000° C. in electric furnaces. But, for any temperature above the ordinary, the thermochemical data are not exact, and the energy involved in the reaction is different from what it is beginning and ending at room temperature."

Units of Thermochemistry. — The amount of heat is measured in a number of different units. Those employed in technical work differ from those used in scientific investigations. The unit most extensively used is the 15°-calorie, which is the amount of heat required to raise one gram of water 1° C., the mean temperature being 15° C. On page 91 we saw that the specific heat of water is different at different temperatures, and so the value of the calorie varies with the temperature taken.

The Bureau of Standards employs the 20°-calorie. Affirming that, "In view of the greater convenience of 20° as a working temperature, smaller rate of variation in the heat capacity of water at this temperature, and the fact that calorimetric observations are commonly made at temperatures near this, it appears desirable to follow what seems to be a growing tendency among experimenters and

[1] J. W. Richards, *J. I. E. C.*, *9*, 1056 (1916).

adopt the 20° as the basis for expressing the results of this investigation."

"Although the calorie has been adopted as the primary unit of heat, the extreme precision with which electrical measurements can be made has led to the use of the joule expressed in electrical units, as a calorimetric unit. Such use involves the acceptance of a specific value for the ratio *J* of the joule to the calorie, when results are to be expressed in calories. The adoption of such secondary units is hardly justifiable unless greater comparative accuracy can be obtained thereby. — Investigation seems to show that this is not true; . . . therefore, the calorie should be adopted for work of this kind . . . and the incidental value of *J* (one 20° cal = 4.181 joules) will serve as an excellent check on the other measurements. . . ."[1]

The following heat units are employed:

The Gram Calorie (cal.)

The 15° calorie is the heat required to raise one gram of water 1° at the mean temperature of 15° C. or 60° F.

The 20° calorie is the heat required to raise one gram of water one degree at the mean temperature of 20°.

The mean calorie is one one-hundredth of the heat required to raise one gram of water from 0° to 100° C. This is practically the same as the 15° calorie.

The Kilogram Calorie (Cal.) is 1000 times the gram calorie; *i.e.* the heat required to raise one kilogram of water one degree.

The Ostwald Calorie (*K*) is the heat required to raise one gram of water from 0° to 100° C. and is also termed the average calorie. This is practically 100 times the value of the 15° calorie.

The Pound Calorie (pound cal. or Calb.) is the heat required to raise the temperature of one pound of water 1° C.

The British Thermal Unit (b. t. u.) is the amount of heat required to raise the temperature of one pound of water 1° F., from 60 to 61° F.

The Evaporation Unit is the amount of heat required to convert one pound of water at 212° F. into steam at the same temperature, at normal atmospheric pressure.

[1] Bull. Vol. *11*, 220 (1915).

The relation between the various heat units may be expressed as follows:

1 b. t. u.	= 252 cal.
1 Evaporation Unit	= 967 b. t. u.
1 15° cal.	= 4.186 joules (or 4.2)
1 20° cal.	= 4.181 joules (Beau. Stan.)
1 watt hour	= 0.86 Cal.

Specific Heats. — The specific heat capacity, C, is defined as the amount of heat required to raise one gram of the substance one degree. This amount will of course depend upon the temperature of the substance as well as upon its physical state, for the capacity for heat of a body varies with these factors. Hence it is necessary to designate both.

The *atomic heat* of an element is the specific heat multiplied by the atomic weight. Dulong and Petit stated (1819) that this value is a constant quantity, *i.e.* the capacity of atoms for heat is practically the same for all solid elements. This is Dulong and Petit's Law. The value of the constant varies between 6 and 7 with an average of 6.4. It was chiefly upon the accurate determinations of Regnault of the specific heats of the metals at ranges of temperatures from 10 to 100° that this generalization was based and consequently there were many marked exceptions. The most pronounced exceptions are carbon, silicon, and boron. By using the specific heats of these elements at higher temperatures, the atomic heat approaches more nearly that of the constant 6.4.

The following values show the most marked variations:

Element	Al	B	Be	C	Si	P	S
Atomic heat	5.4	2.8	3.7	1.8	4.5	5.9	5.7

The variation from the constant becomes less marked if the specific heat at higher temperatures is employed. The values given in Table LXXIII illustrate the change of the specific heat with the temperature.

TABLE LXXIII

Aluminium			Boron		
Temp.	Sp. Heat	At. Heat	Temp.	Sp. Heat	At. Heat
0°	0.2089	5.66	26.6°	0.2382	2.62
100	0.2226	6.04	76.7	0.2737	3.01
625	0.3077	8.34	125.8	0.3069	3.37
			233.2	0.3663	4.04
Beryllium			**Silicon**		
Temp.	Sp. Heat	At. Heat	Temp.	Sp. Heat	At. Heat
23°	0.397	3.61	−135°	0.0861	2.44
73	0.448	4.08	+ 24	0.1712	4.85
157	0.519	4.73	128.7	0.1964	5.56
257	0.582	5.29	232.4	0.2029	5.74
Graphite			**Diamond**		
Temp.	Sp. Heat	At. Heat	Temp.	Sp. Heat	At. Heat
− 50.3	0.1138	1.36	− 50.5	0.0635	0.762
+ 10.8	0.1604	1.92	+ 10.7	0.1128	1.35
138.5	0.2542	3.05	85.5	0.1765	2.12
249.3	0.3250	3.90	206.1	0.2733	3.28
641.9	0.4450	5.34	606.7	0.4408	5.29
977.0	0.4670	5.60	985.0	0.4589	5.51
0° − 3000°	0.535	6.42			

The values for graphite and for diamond show that the specific heats of allotropic modifications of elements are different at low temperatures, but at high temperatures this difference becomes less marked.

The atomic heat constant, 6.4, may be employed as a means for determining the atomic weight of elements, since the atomic weight × specific heat = 6.4. Hence, knowing the specific heat of an element, its atomic weight may be calculated. In the formulation of this law Dulong and Petit changed the accepted value of the atomic weight of a number of the elements. For example, two thirds of the original value for bismuth was selected; twice the value of lead; one and one half times the value of cobalt; and one half the value of silver. These new values selected were all found subsequently to be the true ones.

There is a marked difference in the specific heat of a substance, depending upon the physical state in which it exists. This is illustrated in the case of water by the following data:

Phase	Temperature	Specific Heat	Observer
Ice	– 78° to 18°	0.463	Dewar
Liquid	20°	1.000	Callender
Vapor	100° to 200°	0.465	Holborn and Henning

Specific Heat of Compounds. — Neumann (1831) showed that the specific heat multiplied by the formula weight of a compound is a constant. That is, the molecular heat of compounds similarly constituted is nearly equal. Kopp (1864) showed that as the molecular weight of compounds is the sum of the atomic weights, so too is the molecular heat the sum of the atomic heats. This is, however, not universally true, and particularly is this the case of compounds containing the halogens, nitrogen, and oxygen. In homologous series, Ostwald has shown that there is an almost constant difference in the molecular heats of the compounds corresponding to the specific heat of the group CH_2. This varies, however, from series to series. Isomeric compounds should have the same molecular heat, and this is true for those compounds that are similar in constitution, but those that differ, such as alcohols and aldehydes, have different values.

In the case of alloys, the specific heat is almost exactly the sum of the specific heats of the constituents, and this applies to mixtures in general, as well as to compounds.

The specific heat of water varies with the temperature, and this is shown by the values given in Table X. For most liquids the specific heat increases with an increase in the temperature, but mercury is an exception. The specific heat of twenty-seven esters of the aliphatic series can be represented by a linear equation, but other series do not give as good an agreement. The specific heat of gases has been considered in Chapter IX.

Heats of Reactions. — The heat capacity of a substance varies with its state of aggregation; hence, it is necessary to designate the phase in which the material under discussion exists. So, in writing equations representing thermochemical reactions, different methods are employed to distinguish the different phases; the following is the usual form: solid $[H_2O]$, liquid, H_2O, and vapor or gas (H_2O). In ascertaining the thermal change accompanying a chemical reaction it is not only necessary to know the phase in which the reacting substances exist, but also whether there is a change from one phase to another, whether the substances reacting are in solution, and if so what the solvent is, and also the concentration of the solution.

The *Heat of Reaction* is defined as the number of calories of heat absorbed or evolved by the reaction of stoichiometrical quantities of the substances that are represented by the chemical equation. When the reaction represents the formation of a substance, it is termed the *heat of formation;* when the combustion of a substance is represented, it is termed the *heat of combustion;* when the process of neutralization is represented, it is termed the *heat of neutralization.* Similarly we have the *heat of solution, heat of dilution, heat of precipitation, heat of ionization;* and when there is a change of state involved, we have *heat of fusion* and *heat of vaporization.*

The reaction representing the formation of ferrous oxide is expressed by the equation

$$[Fe] + (O) = [FeO] + 65{,}700 \text{ cal.}$$

which shows that during the formation of one mole of ferrous oxide there are 65,700 calories of heat liberated. In the reaction representing the decomposition of ferrous oxide there would be absorbed this same quantity of heat in order to obtain the original conditions. This illustrates what is sometimes called the First Law of Thermochemistry, which was first stated by Lavoisier and Laplace in 1780. This may be expressed as follows: *The amount of heat required to decompose a compound into its elements is equal to the heat evolved when the elements combine to form the compound.*

It is well known that many compounds cannot be formed directly from the elements, and so the heat of formation cannot always be obtained by direct means. In 1840 Hess discovered the *Law of Constant Heat Summation*, which is the fundamental law upon which all thermochemical calculations are based. This law is stated as follows: *The total heat effect of a chemical change depends only on the initial and final stages of the system and is independent of the intermediate stages through which the system passes.* The heat of the reaction, then, should be the same in employing different methods, irrespective of the number of different processes or reactions involved in the production of the particular substance. This is illustrated in the formation of an aqueous solution of ammonium chloride.

$$\begin{array}{lr} & (NH_3) + (HCl) = [NH_4Cl] + 42{,}100 \text{ cal.} \\ & [NH_4Cl] + aq = NH_4Cl\,aq - 3{,}900 \text{ cal.} \\ \hline \text{Adding,} & (NH_3) + (HCl) + aq = NH_4Cl\,aq + 38{,}200 \text{ cal.} \\ \text{Or,} & (NH_3) + aq = NH_3aq \quad + 8{,}400 \text{ cal.} \\ & (HCl) + aq = HCl\,aq \quad + 17{,}300 \text{ cal.} \\ \text{Mixing,} & NH_3aq + HCl\,aq = NH_4Cl\,aq + 12{,}300 \text{ cal.} \\ \hline \text{Adding,} & (NH_3) + (HCl) + aq = NH_4Cl\,aq + 38{,}000 \text{ cal.} \end{array}$$

The small difference in the heat of formation of an aqueous solution of ammonium chloride by the two methods indicates that it is immaterial which method is employed, for the same heat value is obtained.

The term *aq* signifies that such a quantity of water has been employed that upon further addition of water the *heat of dilution* is practically zero. Hence HCl*aq* signifies a dilute aqueous solution of HCl such that the further addition or subtraction of water would produce no appreciable heat effect.

Heat of Formation. — The heat of formation of methane is represented by the following equation,

$$[C] + 2\ (H_2) = (CH_4) + 22{,}250 \text{ cal.}$$

for ethylene by

$$2\ [C] + 2\ (H_2) = (C_2H_4) - 11{,}250 \text{ cal.}$$

In the formation of methane there is an evolution of heat. Reactions of this type are designated *exothermic*, and the compound is termed an *exothermic compound*. There is a loss of heat from the system itself, that is, an evolution of heat, and this is the usual type of thermochemical reactions. In the formation of ethylene there is an absorption of heat and the reaction is termed *endothermic*, while the compound is designated an *endothermic compound*. The following are endothermic compounds: Acetylene absorbs 54,750 calories of heat in the formation of one mole; $[CaC_2]$ absorbs 6,259 cal.; (AsH_3) absorbs 44,200 cal.; CS_2 absorbs 25,400 cal. Endothermic compounds are comparatively unstable and readily decomposed, sometimes with violence.

Heats of Combustion. — Since the heats of combustion of carbon compounds are of great practical importance and the values are comparatively easily determined, the values are usually employed in calculating the heats of formation of compounds.

Depending upon the allotropic modification of carbon employed, different values are obtained for the heat of formation of carbon dioxide, as the following shows:

$[C]$ diamond $+ (O_2) = (CO_2) + 94,300$ cal.

$[C]$ graphite $+ (O_2) = (CO_2) + 94,800$ cal.

$[C]$ amorphous $+ (O_2) = (CO_2) + 97,200$ cal. (Richards)

$[C]$ amorphous $+ (O) = (CO) + 29,160$ cal.

The heat of formation of carbon monoxide from the combustion of carbon cannot be determined experimentally, but it can be obtained indirectly as follows:

$[C]$ amorphous $+ (O_2) = (CO_2) + 97,200$ cal.

$(CO) + (O) = (CO_2) + 68,040$ cal.

If x is the heat of formation of carbon monoxide, according to Hess' Law $x + 68,040 = 97,200$. Solving, we have $x = 29,160$, or subtracting the second thermochemical equation from the first, we have $C - (CO) + (O) = 29,160$ cal., or

$$[C] + (O) = (CO) + 29,160 \text{ cal.}$$

Many of the compounds containing carbon are of particular importance as fuels, and the heat obtained by burning them is utilized as a source of heat in many of the industries. Then, too, the calorific value of foods which are oxidized in the body in order to maintain its normal temperature is assuming more and more importance in dietary studies, not only for the human race, but particularly in providing balanced rations for animals.

Calorific Power of Fuels. — In the combustion of fuels water is one of the products, — and the temperature of the furnace is such that the water is usually uncondensed. So in the calculation of the calorific power of fuels, in order to obtain the correct heat balance sheet for the furnace, it is necessary to consider the water as vapor, for the condensation of the vapor would give a large increase in heat due to the latent heat of condensation, and this would result in a loss which would appear in the waste gases and thus unduly increase the apparent chimney loss.

In the calculation of the calorific power of fuels, as in the combustion of other substances, Dulong and Petit's method is employed. That is, the heat value is obtained by assuming the carbon all free to burn, the oxygen present combined with hydrogen in the ratio $2\ H_2 : O_2$, and the excess of hydrogen free to burn. The calorific value of fuel may be determined directly in a calorimeter or may be calculated from the analysis. The maximum temperature attainable depends upon many factors, among which are the conditions under which the fuel is burned, whether the fuel is cold or hot, and whether the air used is cold or has been preheated. It is not possible to preheat many gaseous fuels because they are decomposed and carbon is deposited. Another important factor is the heat radiation of the furnace, which introduces in this connection the construction of the various furnaces and particularly the heat conductance of materials; this is becoming one of the important departments of thermochemistry. Particularly is this true of electric furnaces, in which the external source of heat energy is supplied, not from a fuel, but from an electrical source, and also sometimes partially from the chemical reactions between the substances employed. But as this subject requires an extended discussion, reference is given to special presentations, such as *The Electric Furnace*, by Stansfield, Chapter III.

Methane burns according to the following thermochemical equation:

$$\begin{array}{lcl} (CH_4) + (2\ H_2) & = & (CO_2) + (2\ H_2O) \\ 22{,}250 + \quad 0 & & 97{,}200 + 2 \times 58{,}060 \end{array}$$

If the water is assumed to be in the form of vapor, its heat of formation is $2 \times 58{,}060$ cal., and the heat of formation of carbon dioxide from amorphous carbon is 97,200 cal., which would give as the total heat liberated in the formation of two formula weights of water and one formula weight of carbon dioxide, 213,320 calories. But a part of this will be required to decompose the methane, and this quantity will be equivalent to the heat of formation of methane, which has been found to be 22,250 cal. Then the difference, 191,070 cal., is the heat of combustion of methane, which may also be obtained by adding the numerical values in the above equation.

In the case of the combustion of ethylene we have in a similar manner the following equation:

$$\underset{(-\ 11{,}250)}{(C_2H_4)} + (O_2) = \underset{2 \times 97{,}200}{2\ (CO_2)} + \underset{2 \times 58{,}060}{2\ (H_2O)}$$

In the formation of ethylene, since it is an endothermic compound, the summation of these heats of formation would be

$$-(-\ 11{,}250) + 2 \times 97{,}200 + 2 \times 58{,}060 = 312{,}770 \text{ cal.}$$

as the heat of combustion of one formula weight of ethylene, assuming that both the products of combustion are gaseous. If, however, we assume the water vapor to condense, then its heat of formation would be 69,000 cal. and we have

$$-(-\ 11{,}250) + 2 \times 97{,}200 + 2 \times 69{,}000 = 343{,}650 \text{ cal.}$$

as the heat of combustion of ethylene when the products are gaseous carbon dioxide and liquid water.

For endothermic compounds as illustrated by ethylene, the heat of combustion is greater than the heat obtainable if the amounts of carbon and hydrogen in the compound were burned in the free state; while exothermic compounds give less heat than could be obtained by the direct combustion of free carbon and hydrogen equivalent to the formula weight.

The heats of formation as well as the heats of combustion of a few of the more common compounds are given in Table

LXXIV. The products of the reaction are assumed to be gases and the water formed to be uncondensed. Most of the data are from Richard's *Metallurgical Calculations*.

TABLE LXXIV

Substance		Molecular Heat in Calories (cal.)	
		of Formation	of Combustion
Water	H_2O	58,060	
Methane	CH_4	22,250	191,070
Ethane	C_2H_6	26,650	341,930
Ethylene	C_2H_4	− 11,250	321,770
Benzene	C_6H_6	− 7,950	765,330
Anthracene	$C_{14}H_{10}$	− 39,050	1,690,000
Acetylene	C_2H_2	− 54,750	307,210
Hydrogen			58,060
Hydrogen sulphide	H_2S	4,800	122,520
Carbon bisulphide	CS_2	− 25,400	
Calcium oxide	CaO	131,500	
Silica	SiO_2	180,000	
Ferrous oxide	FeO	65,700	
Ferric oxide	Fe_2O_3	195,600	
Sulphur dioxide	SO_2	69,260	
Sulphur trioxide	SO_3	91,900	

That the ordinary thermochemical data, or zero thermochemical data as sometimes called, cannot be utilized in the study of chemical equilibrium at high temperatures is illustrated in Preuner's work on the equilibrium reaction on the reduction of Fe_3O_4 by hydrogen. He obtained the equilibrium constant of the following reaction

$$Fe_3O_4 + 4\,(H_2) \rightleftarrows 3\,Fe + 4\,(H_2O)$$

at different temperatures, and showed that the heat value of the reduction at 960° is − 11,900 cal. Upon the basis of the ordinary heats of formation the value is − 270,800 + 4 × 58,060 = − 38,560 cal. From which Preuner concluded that van't Hoff's formula for calculating heats of reaction is not applicable to this class of reactions. But J. W. Richards shows from the following calculations that this conclusion is not justifiable.

The heat in the products at 960° is

$$3\,Fe = 3 \times 56 \times (0.218 \times 960 - 39) = 28{,}560 \text{ cal.}$$
$$4\,H_2O = 4(22.22\text{ l.}) \times (0.34 \times 960 + .00015 \times 960^2) = 41{,}300$$
$$69{,}860 \text{ cal.}$$

Heat in the reacting substances at 960° is

$$Fe_3O_4 = 232 \times (0.1447 \times 960 + 0.0001878 \times 960^2) = 72{,}384$$
$$4\,H_2 = 4(22.22\text{ l.}) \times (0.303 \times 960 + 0.000027 \times 960^2) = 28{,}075$$
$$100{,}459 \text{ cal.}$$

The heat of reaction at 960° is therefore the summation of the heats of the reactions beginning and ending at zero $-$ 38,560 cal. and these heats of the compounds at 960°, which gives

$$-38{,}650 - 69{,}860 + 100{,}459 = -7{,}761 \text{ calories, which}$$

is in better agreement with the value obtained by Preuner.

The following example illustrates the general methods employed in certain types of thermochemical calculations. A natural gas was found by analysis to have the following percentage composition by volume: CH_4, 94.16; H_2, 1.42; C_2H_4, 0.30; CO, 0.55; CO_2, 0.27; O_2, 0.32; N_2, 2.80; H_2S, 0.18. The following solutions are desired: What would be the maximum flame temperature, (1) if burned cold with the theoretical amount of cold air; (2) if burned cold, employing air preheated to 1000°?

First find the heat of combustion of one cubic meter of the gas. If the molecular weights of the constituents are expressed in kilograms, then the volume will be 22.4 cubic meters, and the molecular heat of combustion the values expressed in Table LXXIV in kilogram calories (Cal.). The heat of combustion of one cubic meter will be this value divided by 22.4. The values employed are for 22.22 as used by Richards and have not been recalculated. We then have the following for the heats of combustion:

	Cubic Meters				
CH_4	0.9416	×	8,598	=	8,095.2 Cal.
H_2	0.0142	×	2,613	=	37.1 Cal.
C_2H_4	0.0030	×	14,480	=	43.4 Cal.
CO	0.0055	×	3,062	=	16.8 Cal.
H_2S	0.0018	×	5,513	=	9.9 Cal.
					8,203.1 Cal.

The oxygen needed for the combustion of these respective quantities of the gases can be readily calculated and also the air necessary to supply it. These values are given in the second column of the following table:

Table LXXV

	1 Cu. Meter of Gas Contains	Oxygen Required Cubic Meters	Products of Combustion			
			CO_2	H_2O	SO_2	N_2
CH_4 . .	0.9416	1.8832	0.9416	1.8832	—	—
C_2H_4 . .	0.0030	0.0090	0.0060	0.0060	—	—
H_2 . .	0.0142	0.0071	—	0.0142	—	—
CO . .	0.0055	0.00275	0.0055	—	—	—
CO_2 . .	0.0027	—	0.0027	—	—	—
O_2 . .	0.0032	0.0032	—	—	—	—
N_2 . .	0.0280	—	—	—	—	0.028
H_2S . .	0.0018	0.0027	—	0.0018	0.0018	—
		1.90155	0.9558	1.9052	0.0018	0.0280
Air required . . .	9.14	also furnished nitrogen				7.238
			Total N_2 =			7.266

The products formed will contain the heat generated and at the temperature t attained by the combustion of these gases. These products will contain the following amounts of heat:

		Cubic Meters		Sp. Heats		
N_2	=	7.266	$\times$	$(0.303 \times t$	+	$0.000027\ t^2)$
H_2O	=	1.9052	$\times$	$(0.34 \times t$	+	$0.00015\ t^2)$
CO_2	=	0.9558	$\times$	$(0.37 \times t$	+	$0.00027\ t^2)$
SO_2	=	0.0018	$\times$	$(0.444 \times t$	+	$0.00027\ t^2)$

Total heat $= 3.2044\,t + 0.00074057\,t^2 = 8203$ Cal. as determined above.

Solving, we find $t = 1806°$ the temperature of the flame attained when the gas and air employed are cold.

Now if the air is preheated to 1000°, we have 1 m.³ of air at $1000° = 0.303 \times 1000 + 0.000027 \times 1000^2$, or the heat in 1 cubic meter of air at $1000° = 330$ Cal., and in 9.14 cubic meters of air at $1000° = 3016$ Cal. Therefore, $3.2044\,t + 0.00074057\,t^2 = 8203 + 3016$ Cal., and solving we have $t = 2288°$ as the temperature of the flame providing air preheated to 1000° is employed.

It may be readily shown that if air in excess of the theoretical amount required to burn the gas be employed, the heat obtained by the combustion would be required to raise the temperature of this mass of material, and as a result the maximum temperature of the flame would be decreased by an amount depending upon the quantity of air used in excess.

Calorific Value of Foods. — The combustion of food, which consists of a mixed diet, is not exactly the same in the body as it is in a calorimeter. About 98 per cent of the carbohydrates and 95 per cent of the fats are digested — that is, absorbed by the body. In the case of these the products of combustion in the body are the same as in the calorimeter; but the products of combustion include urea, creatin, uric acid, etc., which are eliminated in this form from the body, hence the proteins are not completely burned as they are in the calorimeter. Therefore, it is evident that the physiological fuel value is smaller than the heat of combustion. This is apparent from the values of the heat of combustion and the physiological fuel values of a few foods given in Table LXXVI.

TABLE LXXVI

Food	Heat of Combustion per Gram	Physiological Fuel Value
Carbohydrates		4.0 Cal.
Cane sugar	3.95 Cal.	
Milk sugar	3.74	
Malt sugar	3.72	
Starch	4.20	
Fats		9.0 Cal.
Butter	9.2	
Olive oil	9.45	
Proteins		4.0 Cal.
Albumin	5.8	
Casein	5.86	

The summation of the physiological fuel value of the amounts of these three food types, namely, carbohydrates, fats, and proteins, present in a food constitutes what is termed the physiological fuel value of the food. The analysis of foods is expressed in terms of the three types of foods and moisture, and then from the physiological fuel value of these the fuel value of the food is calculated. In Table LXXVII are given the composition of a few typical foods and the physiological fuel value of the same:

TABLE LXXVII

Food Material	Chemical Composition Parts per Gram			Physiological Fuel Value
	Protein	Fat	Carbohydrates	
Roast beef as purchased	0.236	0.277	0.300	3.44 Cal.
Bread, white	0.093	0.012	0.527	2.50 Cal.
Eggs as purchased	0.119	0.093	—	1.31 Cal.
Milk, whole	0.033	0.040	0.500	0.69 Cal.
Peanut butter	0.293	0.465	0.171	6.04 Cal.
Peas, canned	0.036	0.002	0.098	0.55 Cal.
Strawberry as purchased	0.009	0.006	0.070	0.37 Cal.

Heat of Solution. — When a solute is dissolved in water, a change in temperature is usually obtained. If the quantity of water is just sufficient to produce a saturated solution of the solute, the heat change, or heat tone as it is sometimes termed, is called the *integral heat of solution.* The *heat of precipitation* is of the opposite sign and is the heat absorbed or evolved when the solute dissolves in a *nearly* saturated solution. If water be added to a saturated aqueous solution, there will be an additional heat effect; then if more solvent be added, the change becomes less with the successive additions of solvent until finally no further thermal change is noticed. So if one mole of the solute be added to an indefinitely large volume of solvent, the heat effect of solution is the maximum obtainable, and this is termed the *heat of solution.* When a solution of a specified concentration is diluted to an infinitely large volume, the heat tone of this reaction represents the difference between the heat of solution and the heat tone of the original solution, and this difference is termed the *heat of dilution*, that is, the heat effect obtained by diluting the solution to that of a solution of infinite dilution.

Table LXXVIII

	HCl		HNO_3	
Moles of Water	Heat of Solution Cal.	Heat of Dilution Cal.	Heat of Solution Cal.	Heat of Dilution Cal.
1	5.38	—	3.29	—
2	11.37	5.99	—	
5	14.96	3.59	6.67	3.38
10	16.16	1.20	7.32	0.65
20	16.76	0.60	7.46	0.14
50	17.12	0.36	—	
100	17.24	0.12	7.44	− 0.02
300	17.32	0.08	7.50	0.04

The heat effects obtained by diluting a solution with successive quantities of water are also designated heats of dilution with specified quantities of water, as the data in Table LXXV show. In many thermochemical tables the heat of solution is given as the heat tone obtained when one mole of the substance is dissolved in the specified amount of solvent. The heats of solution given are the values for the quantity of water designated in each case and the heats of dilution at these dilutions may be obtained by subtracting the value at any given dilution from that of the preceding one The values given under heats of dilution were obtained in this manner.

Heat of Hydration. — The combination of water with many substances with the production of hydrates is accompanied by a marked thermal change. If these hydrates are then dissolved in water, the heat of solution is much less than when the anhydrous salt is dissolved. In Table LXXIX the heat of hydration of a few common hydrates is given. The values which are expressed in kilogram calories (Cal.) represent the heat tone when one mole of the solid salt combines with the quantity of liquid water specified, forming the solid hydrate.

TABLE LXXIX

Substance	Water of Hydration	Heat of Hydration
$BaCl_2$	H_2O	3.6 Cal.
	$2\ H_2O$	7.0
$CuSO_4$	$5\ H_2O$	18.6
KF	$2\ H_2O$	4.6
K_2CO_3	$1.5\ H_2O$	7.0
Na_2CO_3	H_2O	3.4
	$7\ H_2O$	16.3
	$10\ H_2O$	21.8
Na_2HPO_4	$2\ H_2O$	6.0
	$7\ H_2O$	17.3
	$10\ H_2O$	28.5
$C_2H_4O_2$	$2\ H_2O$	6.2

Since the reaction of many substances takes place in solution, the products of the reaction dissolve, and the total heat of reaction includes the heats of solution and is then expressed as the heat of formation *in dilute solution.*

When dilute aqueous solutions of salts are mixed, there is practically no heat effect providing a precipitate is not formed. This is sometimes referred to as the Law of Thermal Neutrality of Salt Solutions. It is explained upon the basis of the complete ionization of the salts in dilute solutions, which results in the same state after mixing as before, and consequently the chemical reaction which is termed double decomposition (metathesis) takes place with no concomitant heat change. While in the case of such exceptions as noticed in mercury and cadmium salts, which are only partially dissociated, dilution takes place by mixing the solutions, and additional dissociation and reaction, accompanied by a thermal effect follow.

When precipitation takes place, there is assumed to be a change in the ionic concentration, and the heat effect produced is that of precipitation. The molecular heat of precipitation should be the same by whatever means the precipitation is accomplished in infinitely dilute solutions, *i.e.* for very slightly soluble substances such as silver chloride.

The neutralization of an acid by a base is accompanied by a large heat effect, and upon the ionic basis the equation representing the reaction would be

$$H^+Cl^- + Na^+OH^- = Na^+Cl^- + H_2O.$$

This indicates that the only change is the disappearance of the hydrogen and hydroxyl ions with the formation of water which remains in solution. The process of neutralization then consists of the formation of undissociated water, and the heat of neutralization should be the same per mole of water formed, irrespective of the acids or bases employed. The data in Table LXXX illustrates this for strong acids and bases.

TABLE LXXX — HEATS OF NEUTRALIZATION

REACTION	HEAT OF NEUTRALIZATION	REACTION	HEAT OF NEUTRALIZATION
HCl*aq* + NaOH*aq* . .	13.7 Cal.	HCl*aq* + NH_4OH*aq* . .	12.3
HCl*aq* + KOH*aq* . .	13.7	HF*aq* + KOH*aq* . . .	16.1
HCl*aq* + ½ $Ba(OH)_2$*aq* .	13.9	½ H_2CO_3*aq* + NaOH*aq* .	10.1
HNO_3*aq* + NaOH*aq*. .	13.7	½ H_2SO_4*aq* + NaOH*aq* .	15.7
HNO_3*aq* + KOH*aq* . .	13.8	HNO_3*aq* + NH_4OH*aq* .	12.6
HNO_3*aq* + ½ $Ba(OH)_2$*aq*	13.9	HCN*aq* + NaOH*aq* . .	2.9
HBr*aq* + NaOH*aq* . .	13.7	½ H_2SO_4*aq* + LiOH*aq* .	15.6

When the reaction involves a weak or moderately strong acid or base, there is not the uniformity as in the case of strong acids and bases, as is shown by the values in the right-hand part of the above table.

By replacing the hydrogen of polybasic acids successively, different heat effects are obtained. In this case there is the formation of acid salts as intermediate products. The data in Table LXXXI illustrate this and show that the maximum heat effect is obtained when all of the hydrogen is replaced.

TABLE LXXXI

MOLES BASE	H_2SO_4*aq*	H_2CrO_4*aq*	H_2CO_3*aq*	H_3PO_4*aq*
1 NaOH*aq* . .	14.3 Cal.	13.1 Cal.	11.2 Cal.	14.7 Cal.
2 NaOH*aq* . .	31.4	24.7	20.2	26.3
3 NaOH*aq* . .				33.6
4 NaOH*aq* . .	31.4	25.1	20.6	
1 KOH*aq* . .	14.7	13.4	11.0	
2 KOH*aq* . .	31.4	25.4	20.2	
3 KOH*aq* . .				
1 NH_4OH*aq* .	13.6	22.2	9.73	13.5
2 NH_4OH*aq* .	29.1	22.2	10.7	26.3
3 NH_4OH*aq* .				33.2

Heat of Ionization or Dissociation. — In the neutralization of weak acids and bases the heat of neutralization is quite different from the normal value of 13.7 Cal., as is illustrated by the values given in Table LXXX. In the process of neutralization, as the weak component is not completely dissociated, there must be a gradual dissociation taking place in order to furnish the ions of water which combine to form the undissociated water. Accompanying this process of gradual dissociation there is the concomitant heat change due to the dissociation, which is termed the heat of dissociation. Owing to the low concentration of the hydrogen and hydroxyl ions, there is an incompleteness of the process of neutralization. Hence this variation of the total heat effect from the value 13.7 Cal. is considered as the *heat of dissociation*. That is, $H_D = H_N - 13.7$, in which H_D is the heat of dissociation and H_N is the heat of neutralization. For example, in the case of HCN, where α is practically zero, this discrepancy amounts to 2.9 Cal. − 13.7 Cal. or − 10.8 Cal., while for HF we have $16.1 - 13.7 = +2.7$ Cal, which values are designated the heat of dissociation of HCN and HF respectively. That is, the quantity of heat, 13.7 Cal., is involved in the process of neutralization on the formation of one gram mole of the water from its ions; then the reverse operation or dissociation of water into its ions involves the absorption of the same quantity of heat. The heat effect is − 13.7 Cal.

The heat of ionization may be calculated from the change of the dissociation constants obtained from Ostwald's Dilution Law Equation for the same concentrations at two different temperatures; or direct from the change in the electrical conductance with the change in the temperature. The heat of ionization is then defined as the heat evolved during the dissociation of one gram mole of the electrolyte. The data in Table LXXXII give an idea of the magnitude of these values and show that ionization usually takes place with an evolution of heat and refer to the heat evolved in the ionization of substances already in solution.

TABLE LXXXII

SUBSTANCE	TEMPERATURE	VOL. IN LITERS	CAL.
KCl	35°	10	+ 362
NaCl	35	10	452
LiCl	35	10	399
NaOH	35	10	1292
HCl	35	10	1080
HNO_3	35	10	1360
HF	21.5	3.6	3110
Acetic acid	10–50	10	− 675
Salicylic acid	39	100	− 619
Phenol	11.5		− 6025

Ostwald has calculated the heat of ionization of metals from the thermochemical data obtained by the replacement of one metal by another. This consists of the transformation of an equivalent quantity of a metal from the metallic state into the ionic condition. The heat of ionization is then practically equal to the heat of solution of one gram-equivalent of the metal in a very dilute solution of an acid. The data in Table LXXXIII are some of Ostwald's values.

TABLE LXXXIII

ELEMENT	HEAT OF IONIZATION IN CALORIES	ELEMENT	HEAT OF IONIZATION IN CALORIES
Aluminium	+ 40,700	Potassium	+ 61,800
Lead	200	Magnesium	+ 54,400
Cadmium	+ 9,200	Mercurous Hg	− 19,800
Cuprous Cu	− 15,800	Nickel	+ 8,000
Cupric Cu	− 8,000	Silver	− 25,300
Ferrous Fe	+ 11,100	Hydrogen	0,0
Ferric Fe	− 3,100	Zinc	+ 17,500

CHAPTER XXXV

COLLOID CHEMISTRY

Diffusion. — We are familiar with the fact that if one gas is introduced into the space occupied by another, the two species will intermingle and they will soon thoroughly mix. The mixture will be uniform, and we say that the one gas has diffused throughout the other. If a bottle of perfume is opened in a room, the odor will soon be distinguished in all parts of it. The perfume has diffused throughout the air in the room. Similarly, if sugar is placed in a beaker of water and allowed to stand, the sugar will subsequently be found in all parts of the water. The same is true of other soluble substances, and we say that the substance diffuses throughout the water and will eventually occupy all of the space (volume of liquid) allotted to it as the gas occupies the volume in which it is confined.

We have seen that when gases are brought into contact with liquids, the amount absorbed depends upon the particular substances selected and also upon the temperature. The absorption is also accompanied by volume changes with the concomitant heat change. When a dry rope is wet with water, there is a marked decrease in volume accompanied by an evolution of heat. This fact is made use of in tightening the ropes of a sail. The water saturates the soil and rocks in a similar manner; we say that oil or rock absorbs the water, and this is an important property, making the supply available for plants. How does the water travel through the rocks and soil to the plants? We know that the oil passes up through the wick only when the "lamp is lighted," *i.e.* when there is a constant removal of the oil from the end through combustion. The oil passes through the fiber of the wick by a process termed imbibition, and the passage of the water through rocks is explained by the same process.

We have previously called attention to the passage of gases through solids, such as the passage of hydrogen through the walls of platinum tubes, of carbon monoxide through red-hot iron and through glass; and also of the diffusion of carbon into iron, and copper into platinum, as examples of diffusion of solids into solids.

The diffusion of solids through liquids is the most common and has been extensively studied. If $CuSO_4$ is placed in the bottom of a tall cylinder filled with water, the liquid becomes colored but very slowly, and it may take many days before the solution becomes uniformly colored. If a few crystals of $KMnO_4$ are placed on the bottom of another cylinder filled with water, the liquid is colored throughout quickly, thus showing the $KMnO_4$ diffuses very much more rapidly than does the $CuSO_4$. That is, different substances have different rates of diffusion.

Work of Graham. — Thomas Graham (1861) made an extensive study of the diffusion of a large number of acids, salts, bases, and organic substances, and determined their rates of diffusion. He found that the rate of diffusion is directly proportional to the concentration. By the diffusion coefficient[1] is understood in this case the number of grams of the substance that diffuses upwards per day when the concentration at each horizontal layer differs from that one centimeter above by 1 gram per cubic centimeter.

In Table LXXXIV are given the different rates of diffusion in water of a few substances.

[1] On the assumption of Frick's Law that the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations at two areas infinitely near each other, the *diffusion constant or specific diffusion rate* is "equal to an amount of the solution which would diffuse across the unit area under a concentration gradient of unity in unit time if the rate were constant during that time (days)."

TABLE LXXXIV

Substance	Days for Diffusion of Equal Quantities	Diffusion Coefficient in One Day (Stephane)
Hydrochloric acid	1	1.74 at 5°
Sodium chloride	2.23	0.76 at 5°
Cane sugar	7	0.31 at 9°
Magnesium sulphate	7	
Albumen	49	0.06 at 13°
Caramel	98	0.05 at 10°

That is, it takes 98 times as long for caramel to diffuse as it does for the same quantity of hydrochloric acid; or 7 times as long for cane sugar as for the same quantity of hydrochloric acid. The diffusion coefficient of cane sugar is 0.31 (9°), while that of HCl is 1.74 (5°), and of caramel 0.05 (10°).

Taking the amount of NaCl which diffuses in 24 hours at 10° – 15° through parchment, as the unit, the relative rates for a few other substances are given in Table LXXXV.

TABLE LXXXV

Substance	Relative Rates of Diffusion
NaCl	1.00
Alcohol	0.476
Glycerine	0.440
Mannite	0.349
Milk sugar	0.185
Cane sugar	0.214
Gum arabic	0.004

Graham emphasized from his data that these substances could be divided into two classes, and showed that of those that diffuse fairly rapidly practically all manifest the property of crystallization, which he called *crystalloids;* while those that diffused very slowly, which he called *colloids*, did not possess this property, but gelatinized on separating out, and if they crystallized at all it was only after a very long time.

Dialysis. — Graham showed that these crystalloids diffuse through jellies (gelatine, agar, etc.) or membranes of colloidal substances approximately as rapidly as through pure water, while by these the colloids are completely prevented from diffusing. This led Graham not only to emphasize a marked distinction between these two classes of substances, but also to utilize this property as a means of separation of crystalloids from colloids, thus giving a method for the preparation of solutions of colloids. " Of all the properties of liquid colloids, their slow diffusion in water and their arrest by colloidal septa are the most serviceable in distinguishing them from crystalloids."

The method of separation by diffusing the crystalloid through a septum of gelatinous matter, Graham termed *Dialysis*, while to the whole apparatus, which consisted of a glass vessel over one end of which the septum is drawn, or the septum itself in the form of a tube, he gave the name *Dialyzer*. One of the best and most extensively used dialytic septa is parchment paper.

One illustration of this method for the preparation of colloidal solutions will suffice. Graham says: " A solution of silica is obtained by pouring sodium silicate into dilute HCl, the acid being maintained in excess. But in addition to HCl, such a solution contains NaCl, a salt which causes the silica to gelatinize when the solution is heated, and otherwise modifies its properties. Now such soluble silica, placed for twenty-four hours in a dialyzer of parchment paper, to the usual depth of 10 mm., was found to lose in that time 5 per cent of its silicic acid and 86 per cent of its hydrochloric acid. After four days on the dialyzer, the liquid ceased to be disturbed by $AgNO_3$. All of the chlorine was gone, with no further loss of silica."

The preparation of colloid solutions of metals by Bredig's sparking electrode method consists of bringing the ends of the metal electrodes together under the surface of the liquid and then separating them so as to form an arc. By repeatedly touching the electrodes together and separating them a colloid solution of the metal may be formed. Colloid solutions may also be obtained by employing reducing agents according to the method used by Carey Lea.

General Character of Colloids. — In our consideration thus far we have defined a pure chemical compound as a substance that is chemically homogeneous. The method of ascertaining this is by process of analysis, and in the case of many very complex substances it is not a simple matter to determine whether the constituents present conform to the Law of Definite Proportions. We saw in the consideration of simple binary systems that by variation of the components we could obtain fusion curves and solubility curves which would manifest characteristic properties at certain points, from which we conclude the existence of a definite chemical compound, the evidence being the change of state without change in temperature, *i.e.* a constant fusion point, or a constant freezing point. As the methods have become more refined the increased accuracy of the measurements has revealed additional chemical compounds (hydrates in many cases). So by the use of new methods we are able to collect additional information concerning the relationship existing between the components.

In the discussion of binary systems we met a type of solutions designated solid solutions. These conform to our usual definition of solutions, which is, a phase in which the relative quantities of the components can vary continuously within certain limits, or a phase of continuously varying concentrations; while by phase we understand a mass that is chemically and physically homogeneous. So it is evident that the identification of any particular phase depends upon our ability to determine whether it is physically homogeneous and also chemically homogeneous, and this, of course, is dependent upon the degree of refinement of our methods.

Roozeboom defines a homogeneous system as one in which all of its mechanically separable parts show the same chemical constitution and the same chemical or physical properties. "Gases and liquids which have been well mixed possess this homogeneity of constitution because of the smallness of molecules and the grossness of our means of observation."

The attempts to determine whether a system is a solution have led to such definitions of a solution as "a homogeneous mingling"; as "physical mixtures the complexes of different substances in every part physically and chemically homogeneous," or, as Ostwald states it, "a homogeneous phase." The basis of the conception of solution, then, depends not upon the many properties of solutions that we have been discussing, but upon the question of the homogeneity or heterogeneity of the system, and consequently upon our conception of and our means of determining homogeneity.

From the process of diffusion we have seen how the solute becomes divided and subdivided and thus distributed throughout the whole of the solution. Here it exists in such a fine state of division that we are unable to distinguish any of the individual particles and the mass (solution) is said to be homogeneous. If we take a solution of colloidal $Al(OH)_3$, it appears perfectly clear, and from a casual observation looks like a clear solution of any crystalloid yielding a colorless solution. The same is true of many other colloid solutions, a microscopic examination of which would not reveal the presence of any of the diffused substance in the solution. If, however, a convergent ray of light were permitted to pass through these solutions, it would be possible to follow the ray through the solution in a manner similar to that when a bright ray of light passes into a darkened room through a small orifice in the curtain. The boundary surfaces of the particles of dust in the air reflect the light, and they are thus made visible to the naked eye; but if the strong ray of light passing through the solution is examined by a powerful microscope, very small particles can be readily recognized. These are termed ultramicroscopic particles, and an arrangement such as this, making use of the strong ray of light (the Tyndall effect) and the microscope, was designed by Siedentopf and Zsigmondy and is known as the Ultramicroscope. By use of this method a solution of sodium chloride would appear optically homogeneous, whereas in colloid solutions there would be a lack of homogeneity. It is conceivable that the particles may be of such a size that they would be recognizable without the aid of the microscope and the Tyndall method would render them visible. We might imagine the particles to be still larger and of such size that they would remain suspended in the liquid only a relatively short period. In this latter case of *mere suspension*, as it is termed, we would have a case readily designated as *heterogeneous*, for the boundaries of the components of the system could be readily recognized. It is therefore conceivable that we may have all degrees of division of matter and thus produce a continuous gradation of sizes of particles, from the one extreme of suspended particles through those of microscopic and ultramicroscopic size to the still finer ones, which we have at present no means of recognizing, on down to the ultimate molecular particles.

Zsigmondy says: "We see that, just as other investigators have said, when solutions are spoken of as homogeneous distributions, mixtures, etc., it cannot be meant that they are absolutely homogeneous mixtures. If such great homogeneity is demanded of solutions that we can detect no inhomogeneity in them by our most sensitive methods, we would thereby exclude altogether from this classification solutions not only of many colloids, but also of numerous crystalloids, for example, fuchsin, ferric chloride, chromic chloride, saccharose, raffinose, and solutions in the critical state. We would thus run a risk of reducing the sphere of solutions every time we increase the sensitiveness of our methods of investigation. The danger can be easily avoided if we use the word 'solution' in its usual chemical acceptance, meaning thereby subdivisions which appear clear in ordinary daylight and which cannot be separated into their constituents by the ordinary mechanical means of separation (filtration and decantation)." Wo. Ostwald emphasizes, "that it is *not* the presence of many more or less evident particles which may be recognized either macroscopically or microscopically that distinguishes a colloid from a true solution. It is rather the *intensity* of the unbroken light cone passing through the solution which betrays the state of the liquid. It is safe to say that *liquids which show no definite Tyndall light cone or show it only in high concentrations are true (molecular-disperse) solutions.* Practically all colloid solutions give a positive Tyndall effect."

It is generally accepted at the present time that colloid solutions are regarded as heterogeneous two-phase systems, and that their particular distinguishing properties are due principally to their very great specific surface, and thus it is evident that what we are considering is really a *state of matter* and should refer to this condition as the *colloid state.* This was fully recognized by Graham, for he states: "The colloidal is, in fact, a dynamical state of matter; the crystalloidal being the statical condition. The colloid possesses Energies. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element), may the characteristic protraction of chemico-organic changes also be referred."

Classification of Colloid Systems. — Various methods of classification of colloid systems have been used, but the classification of Zsigmondy is now generally employed. This is based upon the progressive subdivision of the given phase. Considering the system to consist of two phases, we have one phase being distributed throughout the other phase. The solvent or continuous phase is termed the *disperse means*, while the solute is termed the *disperse* phase, and the entire system is termed a dispersed system or a *dispersoid* (which is synonymous with *colloid*).

As the subdivision of the disperse phrase increases, the surface of the mass increases enormously. This is illustrated in Table LXXXVI given by Wo. Ostwald.

TABLE LXXXVI — INCREASE IN THE SURFACE OF A CUBE WITH PROGRESSIVE DECIMAL SUBDIVISION

Length of One Edge	Number of Cubes	Total Surface	Specific Surface
1 cm.	1	6 square cm.	6
1 mm. = 1×10^{-1} cm.	10^3	60 square cm.	$6 \cdot 10^1$
0.1 mm. = 1×10^{-2} cm.	10^6	600 square cm.	$6 \cdot 10^2$
0.01 mm. = 1×10^{-3} cm.	10^9	6000 square cm.	$6 \cdot 10^3$
1.00 μ (micron) = 1×10^{-4} cm.	10^{12}	6 square m.	$6 \cdot 10^4$
0.1 μ = 1×10^{-5} cm.	10^{15}	60 square m.	$6 \cdot 10^5$
0.01 μ = 1×10^{-6} cm.	10^{18}	600 square m.	$6 \cdot 10^6$
1.00 $\mu\mu$ = 1×10^{-7} cm.	10^{21}	6000 square m.	$6 \cdot 10^7$
0.10 $\mu\mu$ = 1×10^{-8} cm.	10^{24}	6 hectares	$6 \cdot 10^8$
0.01 $\mu\mu$ = 1×10^{-9} cm.	10^{27}	60 hectares	$6 \cdot 10^9$
0.001 $\mu\mu$ = 1×10^{-10} cm.	10^{30}	6 square km.	$6 \cdot 10^{10}$

The specific surface, which may be defined as

$$\frac{\text{the absolute surface of the entire disperse phase}}{\text{the total volume of the disperse phase}}$$

is one of the marked characteristics of a system. As the specific surface increases, the subdivisions become smaller and smaller, and we say that the dispersion becomes greater and greater. That is, the *degree of dispersion* increases, and instead of using the concept, specific surface, this other expression is frequently employed. The degree of dispersion is also used synonymously with the expression *colloidality*.

Hence we can use the degree of dispersion as our means of classification of dispersoids, and since there is a gradual successive subdivision, the colloidality will become gradually more pronounced as the subdivision of the particles increases. As there are no marked breaks or lines of demarcation, our classification must be made arbitrarily, and the basis of this is the relative sizes of the particles and our means of distinguishing them. There is, however, a gradual transition of one class into the other.

The following diagrammatic representation according to Wo. Ostwald illustrates the classification of dispersoids:

DISPERSOIDS

- *Molecular* and supermolecular *dispersoids* (Von Weimarn's solutoids)
  Size of particles of the disperse phase about 1 $\mu\mu$ or less
  Specific surface $> 6 \cdot 10^7$
- *Colloid Solutions*
  Size of the particles of the disperse phase between 0.1 μ and 1 $\mu\mu$
  Specific surface between $6 \cdot 10^5$ and $6 \cdot 10^7$
- *True or coarse dispersions* (suspensions, emulsions)
  Size of the particles of the disperse phase greater than 0.1 μ
  Specific surface $< 6 \cdot 10^5$

↓ Colloidality Decreases

↑ Degree of Dispersion Increases

The particles larger than about 0.1 μ in diameter — which represents the limit of microscopic visibility and which is taken as the *lower* limit of dispersion — constitute the Suspensions and Emulsions. Colloid solutions comprise the particles between 0.1 μ and 1 $\mu\mu$ in size. By the ultramicroscope particles smaller than about 6 $\mu\mu$ have not been recognized, and the lower limit has, therefore, been placed a little beyond the range of vision of our present instruments. Their degree of dispersion is between $6 \cdot 10^5$ and $6 \cdot 10^7$. Dispersoids with a degree of dispersion greater than $6 \cdot 10^7$ are known as *molecular dispersoids*, which comprise Graham's Crystalloids. The following illustrate the sizes of some of the molecular species: Hydrogen gas, 0.067 to 0.159 $\mu\mu$; water vapor, 0.113 $\mu\mu$; carbon dioxide, 0.285 $\mu\mu$; sodium chloride, 0.26 $\mu\mu$; sugar, 0.7 $\mu\mu$.

Additional Nomenclature. — Owing to different methods of classification of dispersoids a large number of terms appear in the literature, and it is necessary to become familiar with them. Depending upon which phases are taken for the disperse means and for the disperse phase, we have as in true solutions nine different combinations and possible "solutions."

I. Liquid as the disperse means; when the disperse phase is a
- (*a*) Solid, they are termed *suspensions.*
- (*b*) Liquid, they are termed *emulsions.*
- (*c*) Gas, they are termed *foams.*

II. Gas as the disperse means; we have when the disperse phase is
- (*a*) Solid — smoke (tobacco smoke); condensing vapors of metals (ammonium chloride, etc.); cosmic dust, etc.
- (*b*) Liquid — atmospheric fog, clouds, condensations of steam, etc.
- (*c*) Gas — no example known.

III. Solid as the disperse means; we have when the disperse phase is
- (*a*) Solid — known as solid solutions, mixed crystals, carbon particles in iron, etc.
- (*b*) Liquid — occlusion of water, inclusion.
- (*c*) Gas — solutions of gases in solids, gaseous inclusions in minerals.

This classification is then in harmony with Bancroft's definition: "Colloid chemistry is the chemistry of bubbles, drops, grains, films, and filaments."

Graham gave the name *sols* to those dispersoids which we usually designate *colloids*, the degree of dispersion of which lies between $6 \cdot 10^5$ and $6 \cdot 10^7$. If the degree of dispersion decreases below the lower limit of colloids, then the system becomes microscopically heterogeneous and the dispersoid is said to exist in the *gel condition*. There is, therefore, a loss of uniform distribution of the disperse phase throughout the disperse means. In the case of colloid silicic acid Graham called this solution a *sol;* after the silicic acid precipitated into a jelly-like mass he applied the term *gel* to the precipitate. Various terms are employed to express this change, which results in a decrease in the degree of dispersion, and the disperse phase is said to *coagulate*, *precipitate*, *gelatinize*, *clot*, *set*, etc. The reverse of this process was designated by Graham *peptization*, and represents the dispersion of the disperse phase throughout the disperse means. If for any dispersoid the degree of dispersion can be increased and also decreased at will, so as to change the state by reversing the conditions which brought about the change, it is said to be *reversible*. If this cannot be done, it is *irreversible*.

Depending upon the character of the disperse means we may have, when water is the disperse means, *hydrosols* and *hydrogels;* with alcohol, *alcosols* and *alcogels*. In general, when the disperse means is an organic liquid the dispersoid is termed an *organosol* or an *organogel*. And to designate the substance in the disperse phase a prefix is employed, *i.e.*, if gold is the disperse phase and water the disperse means, then we have gold-hydrosol, etc.

The Colloid State. — Hundreds of substances have been obtained as colloids, and these comprise elements as well as practically all types of chemical compounds; and it has been recently emphasized that the possibility of converting a substance into the colloidal state has no relation whatever to the chemical character of the substance. The conception that the colloid solutions are a special class of disperse systems leads to the acceptance of the universality of the colloid state. Just as we say that all substances are soluble, so with the proper conditions all substances can be sufficiently dispersed in the proper disperse means to have a degree of dispersion sufficient to produce particles of the size we define as belonging to the division designated colloid solutions. As there are different degrees of solubility, so there is a marked difference in the ease with which various substances assume the colloid state, for it is a state or condition of matter. The study of the colloid state comprises colloid-chemistry, which is an important division of physical chemistry and is assuming as prominent a place as electrochemistry, thermochemistry, actino-chemistry, and radio-chemistry. Wo. Ostwald states that, "Colloid-chemistry deals with *the relations of the surface energies to other kinds of energy as shown in an especially characteristic way in dispersed heterogeneous systems.*"

A number of substances are known to exist both as a colloid and as a crystalloid. Sodium chloride, which is usually known as a crystalloid, can be obtained in the colloid form, while albumen, which is usually classed as a colloid, may be crystallized

It is conceivable that the disperse means and the disperse phase could have the same chemical composition. In the case of a number of liquids the Tyndall effect is very marked, which shows the existence of a heterogeneous system, *i.e.* there is a disperse phase present. This has been noticed in the case of oils, waxes, different varieties of rubber, molten salts, phosphoric acid, arsenious acids, etc. These are designated *isocolloids;* and if the substance appears in allotropic modifications, the colloid system is termed an *allocolloid.* Sulphur, phosphorus, and selenium are *allocolloids.* Posnjak states that styrol, C_8H_8, polymerizes into $(C_8H_8)_n$ and becomes a jelly-like mass or glass-like (metastyrol), depending upon the degree of polymerization. "If one adds to pulverized metastyrol an equal weight of styrol, the former gradually absorbs the latter. In the process the originally opaque powder becomes translucent and gradually changes into a homogeneous, gelatinous or jelly-like, viscid, transparent mass. If less styrol is added to the metastyrol, — say only about a fourth as much of the former as of the latter, — a transparent mass results, which is not viscid, but glossy."

Two allotropic liquid modifications of sulphur, S_λ and S_μ, are recognized, and the system is designated an allocolloid, for over a certain range of temperature it is assumed that the dispersion of one form throughout the other conforms to a colloid condition.

If the substance exists in a number of different physical forms, then it is possible to have a large number of isocolloids. In the case of water, in addition to the vapor and liquid forms, there have been four or more different modifications of solid ice recognized. There are some sixteen different colloid types which have been investigated and described.

Suspensoids and Emulsoids. — In the case of two component systems in which the degree of dispersion is such that the disperse phase exists in the colloid state, the sols are termed *suspensoids;* if the disperse phase is liquid, the sols are termed *emulsoids*. These are synonymous with the two classes of sols termed *lyophobic* and *lyophilic* colloids. Since the classifications are based upon the degree of dispersion, it is evident that the lyophobic colloids approach on one side suspensions in liquid-solid systems, while the lyophilic colloids approach emulsions in liquid-liquid systems; and on the other hand they both approach very closely to the molecular dispersion or the condition of true solutions.

In this connection it is interesting to note that under certain conditions we have the transition of liquids to solids and *vice versa;* so, too, in the colloid state it is possible for a phase to pass from a solid to a liquid or a liquid to a solid. Under proper conditions certain emulsoids may be made to precipitate as a solid. We then have the transition of an emulsoid to a suspensoid and the subsequent enlargement of the particles, so that we may eventually have a suspension with the final precipitation, or it may even coagulate without assuming the microscopic dimensions. The transition of suspensions to emulsions and *vice versa* is also familiarly known, as in concentrated alcoholic solutions of rosin to which a little water has been added. These phenomena have led many to suggest that in the condensation of molecular dispersion we have the formation of droplets, *i.e.* the liquid phase, which changes to the solid phase; and further, that in all processes of crystallization or separation of the solid phase the liquid phase is first formed as an intermediate transitional stage. In some cases this transition stage exists for a very short time, while in other cases it exists for an appreciable time — days, in many cases.

Crystallization or Vectoriality. — That certain molecular disperse phases condense and eventually separate into crystalline masses indicates that there is a definite molecular arrangement of the molecules in space. The stage of the condensation process at which these vectorial properties manifest themselves is shown to be while the phase is still liquid, as a number of liquids are known to manifest the vectorial properties which characterize them as *crystals*. We have Lehmann's extensive researches in confirmation of the vectorial character of liquids. Von Weimarn even believes vectoriality is manifested by gaseous substances and in addition has presented evidence which he considers to be direct proof of the vectoriality of the colloid phases. In the case of colloid iodine and certain colloid dyes, L. Pelet and Wild claim to have observed the fusion of ultramicroscopic particles which assumed definite crystalline shapes. W. Ostwald says, "The precipitation of the insoluble from liquids seems always to occur primarily in the form of droplets, that is, in the state of an under-cooled liquid," and Wo. Ostwald concludes, "It, therefore, seems possible theoretically that a development of crystals may take place in that the ' crystal embryos ' are at first *liquid* and only later become solid as they enlarge because of a ' progressive ' coalition of molecularly dispersed particles."

Coagulation. — The degree of dispersion of colloids can be changed by a variety of methods and to such an extent that the disperse phase may become a mere suspension and eventually separate. Then, too, from suspensions and emulsions the disperse phase can be caused to deposit as a solid or liquid phase, and thus resembles the precipitate obtained from colloid solutions. The separated phase may be a granular precipitate, may be flocculent or gelatinous, or the whole mass may set to jelly. Depending upon the particular form assumed, various terms have been loosely applied to the phenomenon of separation — such as coagulation, precipitation, flocculation, gelatinization, setting, etc.

Among a few of the methods by which this phenomenon may be brought about we have: change in temperature; change in concentration; agitation, including centrifuging; addition of electrolytes; and addition of non-electrolytes.

If gelatin is dissolved in water and this solution is allowed to cool, it will set to a firm jelly. On adding more water and warming, the mass again becomes liquid, and we have the gelatin redissolved. That is, the process is reversible. If, however, a solution of colloid silicic acid is caused to gelatinize, one way to get this again into the form of a colloid solution is to fuse the precipitate with sodium hydroxide, dissolve the mass in water, decompose with acid, place in a dialyzer, and remove the salt. Colloids of this class are designated irreversible. Whether a colloid system is reversible or irreversible is determined many times by the treatment to which the system is subjected, and Zsigmondy suggests that this classification should be confined to the one factor of desiccation at ordinary temperature. That is, a reversible colloid is one which on addition of the original solvent or disperse means to the precipitated disperse phase will cause the formation of the original dispersoid system. According to this, then, most colloid metals, hydroxides, and sulphides are irreversible, while among the reversible colloids may be listed, molybdic acid, gum arabic, dextrin, and most albumens.

Addition of Electrolytes. — In general, it may be stated that electrolytes when added to colloid solutions cause the coagulation of the disperse phase. The amount of the electrolyte required to produce precipitation in the case of irreversible colloids is usually very small, while it is necessary to add large quantities to the reversible colloids, as they are not so sensitive.

A concentration of 24 per cent of ammonium sulphate is required, according to Kauder, before any precipitation of globulins begins, and 36 per cent is necessary for complete precipitation. This method of salting out is employed in separating many organic colloids, particularly the emulsoids such as albumens, etc. A 35 per cent solution of ammonium sulphate when added to blood serum separates the globulins, but a concentration of 70–80 per cent is necessary for the precipitation of the albumens. The kind of salt employed has a marked effect, and it has been shown that the precipitation of pure albumen increases for the cations in the order NH_4, K, Na, Li, and for the anions in the order CNS, I, Br, NO_3, Cl, $C_2H_3O_2$, and SO_4.

It has been shown by Linder and Picton that minute quantities of electrolytes cause the coagulation of most irreversible inorganic colloids, and this has been confirmed by numerous workers. Benton gives the following classification of colloid solutions and suspensions:

I. Anionic, solutions in water in which the particles move toward the anode, *i.e.* are negatively charged:
   1. The sulphides of arsenic, antimony, and cadmium.
   2. Solutions of platinum, silver, and gold.
   3. Vanadium pentoxide.
   4. Stannic acid and silicic acid.
   5. Aniline blue, indigo, molybdena blue.

6. Iodine, sulphur, shellac, rosin.
7. Starch, mastic, caramel, lecithin.

II. Cationic, solutions in water in which particles move toward the cathode, *i.e.* are positively charged:
1. The hydrates of iron, chromium, aluminium, copper, zirconium, cerium, and thorium.
2. Bredig solutions of bismuth, lead, iron, copper, and mercury.
3. Hoffmann violet, Magdala red, methyl violet, rosaniline hydrochloride, and Bismarck brown.
4. Albumen, hæmoglobin, and agar.

From the fact that the particles of the disperse phase may be either positively or negatively charged Hardy formulated a general statement, which is also known as the Linder-Picton-Hardy Law, expressed as follows: *The most active precipitants are those ions carrying a charge of opposite sign to that carried by the particles of the disperse phase.* The precipitating power also increases greatly with the *valency* of the ion.

The coagulative power of electrolytes, that is, the reciprocal of the concentration in moles per liter necessary to coagulate a given solution, increases greatly with the valency of the ion. Whetham points out that in order to produce coagulation of a sol a certain minimum electrostatic charge has to be brought into contact with the particle constituting the disperse phase. Through the velocity of these particles the number of collisions results in the union of the charges. As these charges are proportional to the valency of the ions and their number proportional to the conductance of the solution, the coagulative power of the electrolyte, as Linder and Picton showed, depends upon the electrical conductance of the solution. An equal number of electrical charges would be obtained from two trivalent ions, from three divalent ions, and from six monovalent ions.

Burton determined the velocity under electrical pressure of the positively charged copper of a copper colloid solution and the effect on the same when solutions of electrolytes of different concentrations were added. Some of his results are given in Table LXXXVII.

TABLE LXXXVII

Solution		Concentration Milli-moles per Liter	Velocity at 18° $\times 10^{-5}$	Solution		Concentration Milli-moles per Liter	Velocity at 18° $\times 10^{-5}$
KCl	1	0	+ 24.9	K_2SO_4	1	0	25.4
	2	17	25.7		2	7.7	25.3
	3	38	26.2		3	19.2	24.0
	4	74	22.8		4	38.4	21.8
	5	154	18.7		5	96.0	14.4
					6	153.0	0.0
K_3PO_4	1	0	25.4	$K_6(FeCN_6)_2$	1	0	30.4
	2	3.6	21.5		2	3.55	14.0
	3	7.2	16.8		3	7.15	3.8
	4	14.4	3.4		4	10.7	1.0
	5	21.6	− 4.8		5	14.3	− 1.5

The addition of Cl^- does not coagulate the copper, and even high concentrations of SO_4^{--} do not have much effect on discharging the colloid particles; but when trivalent ions, either PO_4^{---} or $(FeCN_6)^{---}$, are introduced there is a marked change at small dilutions, relatively a small amount producing the coagulation. The trivalent ions have the most marked effect, and Burton concludes "that the velocity results indicate that the ratios of the powers of various acid ions to reduce the velocity of the copper particles are not very far removed from the observed ratios of the powers of the same ions to produce coagulation." This confirms Linder and Picton's work on the coagulation of a colloid solution of arsenious sulphide by equivalent solutions of monovalent, divalent, and trivalent cations, their coagulative power being in the ratio 1 : 35 : 1023. This agrees with Schultze's 1 : 30 : 1650, and Whetham's theoretical ratio, 1 : 32 : 1024.

Cataphoresis and Endosmose. — We have seen that when suspensions, emulsions, and colloid solutions are subjected to electrical pressure, the disperse phase wanders to one of the poles, which shows that these particles possess an electric charge. This phenomenon is known as *cataphoresis* and is the reverse of *endosmose*, which denotes the passage of the liquid along the walls of the tube under electrical pressure. We could imagine the particles of the disperse phase to be so numerous as to form practically a continuous cellular structure such as in the fine unglazed china where the tubes are of microscopic size. The disperse phase would then be stationary and might be considered the disperse means, when the liquid would then become the disperse phase and would move under the electrical pressure to which it would be subjected.

Effect of Medium. — The effect of the medium may be well shown by a few typical examples. In acid solution albumen is positively charged, while in neutral solutions there is practically no motion under the electrical pressure; and if the solution is alkaline, the particles are negatively charged.

Platinum in chloroform was found by Billitzer to be positively charged and in water negatively charged. The addition of certain electrolytes to metallic hydrosols even changes the sign of the charge carried by the particles in solution.

Benton prepared Bredig solutions of lead, tin, and zinc in alcohol, in which all were positively charged, while bromine was negatively charged in the same solvent. In methyl alcohol Bredig solutions of lead, bismuth, iron, copper, tin, and zinc were found to be positively charged, while in ethyl malonate solutions platinum, silver, and gold were negatively charged. In aqueous solutions of starch, gelatin, agar, and silicic acid the charges on the particles could hardly be detected, as there was such a slight movement of them when subjected to electrical pressure.

Adsorption. — In the precipitation of colloids by electrolytes it is found in many cases that the electrolyte also appears with the precipitated colloid. By the process of washing, it cannot be removed from the gel. We say that the electrolyte has been *adsorbed*. When a colloidal solution of arsenious sulphide is coagulated by $BaCl_2$, it is found that there is considerable barium present in the gel, while the concentration of the chlorine in the solution remains constant. It has further been shown that the quantities of different metals which are adsorbed by any particular colloid are in the same ratio to one another as their chemical equivalents. These adsorbed metallic constituents cannot be removed by washing but can be removed by displacement with other elements and in equivalent quantities. This is, however, a mass action phenomenon, for the process of substitution may be reversed by changing the relative masses of the reacting substances. Linder and Picton found that when calcium chloride was employed, the calcium adsorbed by the gel could be replaced by cobalt; and if a salt of cobalt was employed as the coagulant, the cobalt adsorbed by the gel could be replaced by calcium.

From such experiments as these it has been concluded that chemical reactions take place and the resulting precipitate is a true chemical compound. In the case of many substances whose degree of dispersion is less than that of the disperse phase in colloid solutions, wherein we have mere suspension, suspensions such as clay manifest the same phenomenon. While in the case of many precipitates in analytic work we have the electrolyte adsorbed by the precipitate, as in the case of precipitation of $BaSO_4$, which adsorbs $BaCl_2$ readily, and in the precipitation of zinc and of manganese with the members of the preceding group, as well as in numerous other examples wherein the precipitates are washed free from impurities with difficulty. When two colloids of opposite signs electrically are mixed, the gel resulting will be a mixture of the two, the composition depending upon the original relative concentration of the colloid solutions. For example, when a colloidal solution of ferric hydroxide, which is electrically positive, is mixed with a colloid solution of arsenious sulphide, which is electrically negative, the resulting gel is a mixture of the two, and by varying the original concentration of the colloid solutions gels of continuously varying composition can be obtained, and when the electrical charges are just neutralized complete precipitation takes place. Some investigators, including van Bemmelen, even go so far as to consider many of the gelatinous precipitates, such as the hydroxides of iron, aluminium, etc., as oxides of the metals which have absorbed water, *i.e.* they are *adsorption compounds*. Many other substances which have been considered as true chemical compounds are now held to be adsorption products. For example, purple of Cassius (formally termed aurous stannous stannate) is considered by Zsigmondy to be an adsorption compound of colloidal gold and colloidal stannic acid.

From the foregoing we have seen that these adsorption compounds have been considered as true chemical compounds, and it is evident that we may also be dealing with solid solutions; but the tendency at present is to consider these products as the result of surface-tension phenomena, and they are designated as surface-tension condensation products.

Adsorption by charcoal is very pronounced and is commonly known in its use for the removal of the last traces of gases in the production of a high vacuum, for the purification of sirups and numerous other liquids by the removal of the coloring matter, as well as for the adsorption of metals from their aqueous solutions — all of which constitute many important technical processes. In the case of vapors of iodine, the amount adsorbed is proportional to the vapor pressure, and a final state of equilibrium results.

The amount of solute adsorbed is proportional to the surface of the adsorbent and is expressed by the following equation: $\frac{x}{m} = a c^{\frac{1}{n}}$, in which x is the weight of the substance adsorbed, m the weight of the adsorbent, c the volume concentration after adsorption, a and $\frac{1}{n}$ are constants. This has been confirmed by Walker and Appleyard, who obtained for the adsorption of picric acid from a 0.01 N solution in water and in alcohol by charcoal and by silk:

$$\frac{\frac{x}{m}\text{(charcoal)}}{\frac{x}{m}\text{ (silk)}} = \begin{array}{cc} \text{water} & \text{alcohol} \\ 7.3 & 5.2 \end{array}$$

For any substance the adsorption is proportional to the specific surface, which is closely related to the amount of chemical change. Since all surface energies and volume energies are interrelated, electrical energy, which is a surface energy, and surface phenomena, such as adsorption, must be related.

It is assumed that at the boundary surface, solution-solid, in these heterogeneous systems there is a surface concentration different from that within the solution, and that the greater the extension of the solid surface, *i.e.* of the disperse phase, the greater becomes the concentration on it. From extensive experimental evidence Lagergren has shown, by the application of Le Chatelier's theorem, that depending upon the change in solubility of the solute with change of pressure we may have either positive or negative adsorption, and from this experimental evidence it is concluded that the surface layer is in a state of high compression, which is due to the action of the cohesive forces. The heat evolved when insoluble powders are wetted would be due then to compression of the adsorbed solvent.

The absolute surface of substances does not consist of the external surface only, for all solids are more or less porous and therefore contain numerous capillary tubes which give the mass a cellular structure, increase greatly the absolute surface as well as the specific surface, and likewise the adsorbing power of the adsorbent. So this cellular or honeycomb structure, which is attributed by some authors to gels in general, is also assumed for all very finely divided substances as well. This is manifest particularly in the case of charcoal, which adsorbs metals from aqueous solutions, and in many cases the metal is completely removed, the solution becoming strongly acid while the adsorbed metal cannot be washed out from the charcoal. Not only is this phenomenon assumed to be one of adsorption, but even the formation (precipitation) of metals from metal ions need not be considered primarily a chemical reaction, but is explained upon the basis of the highly porous character of the substances, such as charcoal. In contact with water, the adsorbent becomes negatively charged[1] and the water positively charged, and a metal ion in attempting to diffuse into the body of the charcoal will pass into the capillary opening and may have its electrical charge neutralized by the negative charge of the charcoal and be deposited as the metal. This explanation is also given for the deposition of metals in very fine cracks in glass.

The adsorption of dyes by filter paper is explained in a similar manner, the fiber is negatively charged while the water is positive, and a positive sol will neutralize the charge on the paper, will become neutral, and be precipitated on the fiber. Similarly, a negative dye would not be precipitated, thus giving a method of separating and distinguishing them. The same is true of gels which are themselves strongly posi-

[1] Perrin has shown that for many cases this is not true. Coehn states that the substance with the higher dielectric constant is positive against the substance with a lower value for constant. Hence, as water has nearly the highest value known (81) all other substances would be electronegative toward water. Also see Briggs, *Jour. Phys. Chem.*, *21*, 198 (1917).

tive or strongly negative, and their strong adsorptive power is attributed to this. The adsorption results in the concomitant decomposition of the adsorbed salts.

We will not take up Gibbs' consideration wherein he has shown thermodynamically that if a dissolved substance had the property of lowering the surface tension of the solution, the substance would exist at a higher concentration in the surface layer than in the bulk of the solution. Nor must we lose sight of the fact that while many of these attempted explanations are purely physical, it is possible to apply the Distribution Law to them and show that the phenomenon is of the nature of solution, and giving rise in other cases to the so-called solid solution theory of dyeing. Then, too, in many of these purely physical theories we find no factors which account for the fastness of the dyes, a fact which emphasizes the chemical reaction between the dye and the fiber or the mordants employed. The same applies to the enzyme-action where some kind of combination takes place between the enzyme and the substance upon which it acts, thus demonstrating their colloidal character and their marked power as adsorbents.

With the increased dispersion of the disperse phase the absolute surface increases enormously, and since the amount of chemical change in unit time is proportional to the absolute surface, we should expect the reactions to occur much more slowly when the particles are coarse than when they are very fine. Hydrogen peroxide is decomposed slowly when smooth platinum foil is employed, but if this is covered with platinum black, which is metallic platinum in a very fine state of division, the decomposition is very much more rapid. Since in colloidal systems we have the disperse phase in a very fine state of division, the specific surface would be large and we should expect the colloids to have a very marked influence upon the speed of the chemical reaction. Such is the case, and we have the great increase in the speed of the chemical reaction through the mere contact of the finely disseminated colloid. This phenomenon is designated *catalysis*, and the substance which brings about this enormous change is designated a *catalyzer*. Bredig and his pupils have shown that not only are many inorganic substances in the colloidal state capable of producing catalysis, but the same results may also be accomplished by the organic ferments termed *enzymes*.

Protective Colloids — One would conclude from what has been said concerning the precipitating effects of electrolytes, that in order to have a colloid solution that is stable, it would be necessary, in the preparation of colloid solutions by chemical reaction and the subsequent removal of the electrolyte by dialysis, to remove all traces of the electrolytes. As a general thing this is true, but some authors believe that these minute traces are essential to the formation of a stable colloid solution and that they have a very pronounced stabilizing effect. Graham proved that colloid silicic acid solutions are more stable the longer they are dialyzed, but it is known that colloid solutions of ferric hydroxide are less stable if all of the hydrochloric acid has been removed. Numerous workers have presented a number of facts which show that both effects are produced, and that even some colloids have a stabilizing effect on other colloids. This is true particularly in the case of suspensoids where the stabilizing agent is an emulsoid. This is not due primarily to a change in the viscosity of the disperse means. Hydrosols of metals usually exist in very dilute solutions, but by the addition of albumen, dextrin, or starch very much more concentrated solutions can be obtained. It is stated that one milligram of gelatin will prevent the precipitation by sodium chloride of a liter of colloidal gold. Blood serum will do the same. Quincke has shown the protective action of gelatin in the system, mastic-gelatin-water. This is also pronounced in the case of suspensions as well as where the protective action is produced by organic as well as by inorganic colloids. Carey

Lea's colloid silver, which is produced by reducing silver salts with tartrates, ferrous salts, dextrin, carmin, or such substances, may be protected by either an electrolyte or a colloid, and a colloid silver content of over 90 per cent soluble in water can readily be obtained. Certain colloid silver solutions containing protein substances used in medicine contain as high as 75 per cent of silver upon this basis. Zsigmondy has devised a method for the identification and separation of various proteins, and these have been extended by the work of Biltz.

Physical Properties. — The change in volume of colloid solutions with pressure is but very little different from that of the pure disperse means and also from that of true *molecular* dispersoids. Gelatin at 100° is about 10 per cent less compressible than pure water, while a 30 per cent solution of KI according to Gilbant is even less compressible.

We have seen that as the degree of dispersion increases the specific volume (volume weight) increases enormously, and that at the intersurface contact there is a marked condensation of the disperse means. It has been found that water drops 0.3 mm. in diameter have a density 0.5 per cent greater than water in usual condition. So it follows that the density of colloid systems must be greater than when they are in a less dispersed condition. Molten and compressed gold has a density of 19.33; that precipitated by oxalic acid, 19.49; while that precipitated by ferrous sulphate is 19.55 to 20.71. That is, the greater the degree of dispersion of suspensoids the greater their density. In the case of emulsoids this is just as pronounced. Quincke observed a decrease in volume of more than 3.5 per cent in the system dried egg-albumen-water. The density of hydrogels is decidedly greater than that of the dry substance; for example, a 50 per cent solution of gelatin gave an observed density of 1.242, whereas the calculated value was 1.206.

If the volume of the disperse means, water, is calculated after this contraction, it will be found to be much less with increasing concentration of the disperse phase, as is shown by the following calculated value of the volume of 1 cc. of water after contraction:

In a 10 per cent solution of gelatin	0.96069 cc.
In a 25 per cent solution of gelatin	0.93748 cc.
In a 50 per cent solution of gelatin	0.90201 cc.

The same is true for the starch-water system; the contraction increases with the concentration, whether it be referred to the disperse means or to the disperse phase.

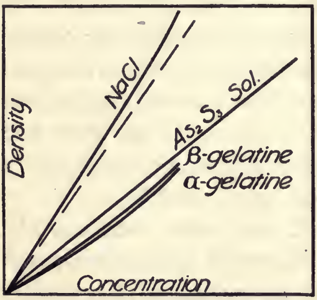


FIG. 93.

From Fig. 93 it will be seen that for the suspensoids such as As_2S_3 the density-concentration is a linear function, while for emulsoids such as gelatin there is a decided curve, which is concave toward the concentration axis. As illustrated by the curve for NaCl, we see that it is analogous to that for emulsoids and emphasizes the similarity of the true molecular disperse systems and the properties of emulsoids. The density-concentration gives us a means of distinguishing the two.

Colligative Properties of Colloid Solutions. — We have seen in the case of true solutions, *i.e.* molecular dispersed systems, that the vapor pressure of the disperse means is greatly modified by the addition of the second component, the disperse phase. The vapor pressure of the pure solvent is lowered by the addition of the solute. Likewise, there is a marked lowering of the freezing point and a rise of the boiling point produced by the addition of the solute. The amount of change in the vapor pressure, the freezing point, and the boiling point is proportional to the concentration of the solute, and is a function of the molar concentration.

The solute, *i.e.* the disperse phase, is molecularly dispersed. In dilute solutions the changes of these properties conform to the laws of solutions which we have previously considered, but we have seen that as the concentration of the disperse phase (solute) is increased and the solutions become concentrated, abnormal values are obtained for the data, for which explanations are attempted upon various assumptions, such as association of solute as well as of the solvent, combination of the solvent and solute (hydration), etc.

The measurements of the vapor pressure, the freezing point, and the boiling point of colloid solutions show that these properties of the disperse means are but slightly if at all affected by the addition of disperse phase of the degree of dispersion we designate colloid. Data from a large number of colloid solutions have been collected, and these show that the vapor pressure, freezing point, and boiling point are practically the same as those of the pure disperse means, nor are they changed appreciably by a large increase in the concentration of the disperse phase. The slight change observed in some cases is attributed to the presence of impurities in the materials used.

Osmotic Pressure. — In the discussion of the osmotic pressure of true solutions we have seen that by the use of a colloid septum, such as a precipitated copper ferrocyanide membrane, we have a semipermeable membrane which permits the passage of the solvent, *i.e.* of the disperse means. The hydrostatic pressure developed by the use of such a membrane in the osmotic cell we term the osmotic pressure of the dispersoid. It is stated that the disperse means passes through the membrane, diluting the solution contained in the osmotic cell. It was not stated, however, just how the disperse means "passed through" the membrane, whether it was due to the sieve-like character or the selective solvent action of the membrane.

Bancroft says:[1] "We can get osmotic phenomena in two distinct ways depending on whether we have a continuous film or a porous one. In the case of a continuous film it is essential that the solvent shall dissolve in the membrane and the solute shall not. Since the permeability is not dependent on adsorption, there is no reason why there should be any fundamental difference between the adsorption of a solute which does pass through the membrane and of one which does not pass through. If we have a porous film, we get osmotic phenomena only in case the pore walls adsorb the pure solvent and the diameter of the pores is so small that the adsorbed film of the pure solvent fills the pores full. Under these circumstances the dissolved substance cannot pass through the pores. On the other hand, if the dissolved substance can pass through the membrane, it must be adsorbed by the latter. There is therefore a fundamental difference between a solute which does pass through a porous membrane and one that does not in that the first is adsorbed by the membrane and the second is not."

If colloid solutions are employed in an osmotic cell, a small osmotic pressure is developed; but the question arises as to whether this small value may not be due to the impurities in the colloid solutions. For it will be remembered that by the process of dialysis it is exceedingly difficult to remove all of the electrolytes from them, owing to the marked adsorptive power of the colloid and also because of the stabilizing power of certain electrolytes. Numerous efforts have been made to determine whether the osmotic pressure developed was really due to the colloid or to the impurities present. This was accomplished by determining the electrolyte content of the colloid and then introducing the same content into the outer liquid so as to have the concentration of the electrolyte the same within the cell as on the outside, thus eliminating the osmotic effect due to the electrolyte. Then the

[1] *Jour. Phys. Chem.*, *21*, 450 (1917).

value obtained would be the experimental value of the osmotic pressure of the colloid itself.

Factors Affecting Osmotic Pressure. — The values obtained vary greatly, depending upon the method of preparation of the dispersoid and its previous treatment. The osmotic pressure of molecularly disperse systems soon reaches a maximum and remains at that value, whereas the osmotic pressure of colloid systems reaches a maximum and then a marked decrease takes place. Shaking or stirring the solution has a marked effect upon the osmotic pressure. In fact, the variability is a marked distinction between colloid solutions and molecular dispersoids and is attributed to a change taking place in the dispersion of the colloid system resulting in different states of aggregation and a change in viscosity. This is true particularly in emulsoids.

In molecular dispersoids Pfeffer showed that the osmotic pressure is proportional to the concentration of the disperse phase and also to the absolute temperature, but in the case of colloid solutions there is no such regularity manifest. According to Martin and Bayliss the osmotic pressure of albumen, hæmoglobin, and congo red varies directly with the absolute temperature. For gelatin solutions Moore and Roof found that the osmotic pressure increased much faster than the absolute temperature. Duclaux showed that the osmotic pressure decreased with the increase of temperature. The same marked irregularities are manifest with reference to the relation between the osmotic pressure and the concentration, — the value of the ratio of the osmotic pressure to the concentration is not a constant. This is well illustrated in Fig. 94. Congo red gives nearly a

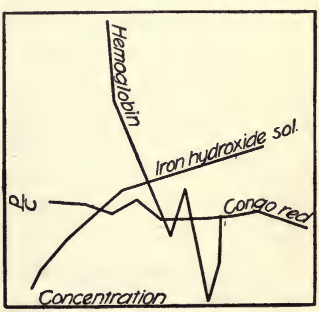


Fig. 94.

constant value for this ratio, iron hydroxide sol gives a marked increase in the values of the ratio with the increase in concentration, while in the case of hæmoglobin we have a decided decrease. The laws of solutions as developed from a consideration of the molecular dispersoids do not appear to be valid for colloid systems, for the attempt to apply them does not seem to be any more successful than in the case of osmotic pressure, which apparently demonstrates that we are not justified in applying the laws of molecular dispersoids to the colloid systems.

The addition of substances to colloid systems manifests the same erratic change in the osmotic pressure as we noticed with reference to the change in the concentration of the disperse phase. In molecular disperse systems the addition of another substance has an additive effect. The osmotic pressure of a highly dispersed congo red sol was found by Bayliss to be 207 mm. By replacing the water about the cell with water saturated with carbon dioxide, the osmotic pressure was 120 mm. The addition of alkali usually causes an increase in the osmotic pressure in certain cases, but in the case of egg albumen the osmotic pressure is always diminished.

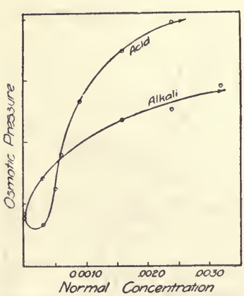


FIG. 95.

The disperse means enters the osmotic cell and there is the increased volume resulting in the so-called osmotic effect, or as some authors prefer, the "pseudo-osmotic" pressure. This pseudo-osmotic imbibition is not unlike the swelling phenomena in a solid colloid.

In Fig. 95 is given the effect of acid and alkali on the pseudo-osmotic pressure of a 1.5 per cent gelatin sol as determined by Lillie, while in Fig. 96 is illustrated the influence of acid and alkali on the swelling of gelatin according to the experiment of Wo. Ostwald. The analogy is very pronounced.

The relation between the viscosity of albumin sol as affected by the addition of acid and of alkali as shown in Fig. 97, according to Pauli, and the change of the pseudo-osmotic pressure according to Lillie, is very manifest by the shape of curves. The *increase* in internal friction (viscosity) corresponds to a *decrease* in the pseudo-osmotic pressure, and this holds completely not only in the case of viscosity and osmosis, but also for gelatinization, and as we have seen for swelling as well. We are then dealing with complex phenomena which are most intimately connected with one another.

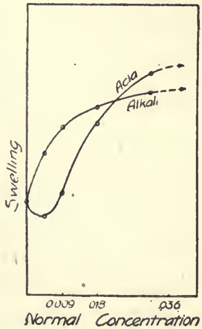


FIG. 96.

The addition of salts to sols of albumin and of gelatin has been found by Lillie to decrease the osmotic pressure. The magnitude of the decrease is less in the case of normal salts of the alkali metals than in the case of the alkaline earth metals, while the salts of the heavy metals produce the most marked decrease in the osmotic pressure. The acid or alkaline char-

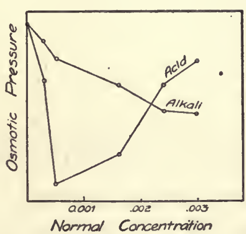


FIG. 97 *a*.

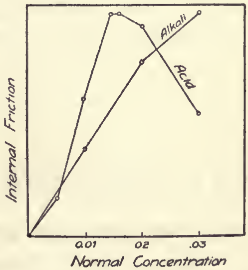


FIG. 97 *b*.

acter of a colloid system, as we have just seen, not only affects the pseudo-osmotic pressure but also the viscosity of the colloid system.

The Brownian Movement. — The English botanist R. Brown (1827) observed under the microscope that particles if not too large are always in rapid motion. Picton observed these movements in the microscopically visible particles in colloid metallic sulphide solutions, and Zsigmondy shows it to be very pronounced under the ultramicroscope. This is termed the Brownian movement. The particles recognizable in all dispersoids manifest this movement if they are not too large and if the disperse means, which may be either liquid or gaseous, does not offer too much resistance. The upper limit in size of particles is about 0.01 $\mu\mu$ in diameter. The movements of these larger particles, which are very small, are spontaneous and continuous and of a trembling or vibratory kind and in a curved path. With increased dispersity the motion is translatory in a zigzag fashion and Zsigmondy described it as "dancing, hopping, and skipping," as well as " translatory and progressive."

The viscosity of the disperse phase has a marked effect on the Brownian movement. The increase in temperature accelerates the Brownian movement and also decreases the viscosity of the disperse means. This has been investigated extensively by Seddig, who concludes that the movement of the particles, the amplitude A, is dependent on the temperature and expressed the relation as follows:

$$A = k\sqrt{\frac{T}{\eta}},$$

in which η is the viscosity; or $A^2 = k\frac{T}{\eta}$, which states that the path-length squared is directly proportional to the absolute temperature and inversely proportional to the viscosity of the liquid. Svedberg's law ($A\eta = k$) applied to this gives $A^2\eta = kT$ or $A \cdot A\eta = kT$ and since $A\eta = k$, we have $A = k_1T$, which states that when the viscosity is constant the path-length is directly proportional to the absolute temperature.

A very fine powder when placed in water becomes coated with the disperse means and soon becomes uniformly distributed throughout the water, thus showing that the Brownian movement overcomes the action of gravity. Perrin showed that mastic dispersoids under the influence of gravity become stratified. This is general, and he concludes that in the case of the larger particles the downward component in the irregular motion of the particles is augmented and previous uniform distribution results in the accumulation of the particles at the bottom.

Since electrolytes cause the coagulation of the disperse phase we should expect that the addition of electrolytes to colloid systems would have a marked influence on the Brownian movement. On adding N/10 NaOH to caoutchouc juice the movement of the gutta-percha particles was decreased to one half of their original rate, while N/10 HCl reduced the motion to only about one ninth of its original value. The original path length was 0.62 $\mu\mu$, while in the alkaline solution it was 0.3 $\mu\mu$, and in the acid solution it had decreased to 0.07 $\mu\mu$. Schulze states that the motion of the particles in opalescent liquids is caused to cease by the addition of small quantities of alum, lime, and acids with clumping, but in some cases the retardation of the Brownian movement may occur without clumping, particularly in the more highly dispersed systems. Although the Brownian movement will not prevent the stratification of the larger sized particles, it is considered as one of the chief stabilizing factors of sols. Perrin by observing the rate of fall of a cloud of gamboge particles under the influence of gravity was able to determine the number of particles per unit volume. By applying Stoke's Law of moving particles through a medium,[1] know-

[1] The velocity of a particle is proportional to the square of its radius and inversely proportional to the viscosity of the medium. Expressed mathematically it is $v = \frac{2}{9}\frac{\rho_1 - \rho}{\eta} gr^2$, where v is the velocity, ρ_1 the density of the particle, ρ the density of the liquid, η the viscosity, g the gravitational constant and r the radius of the particles.

ing the total mass, the viscosity, the density of the particles in the solid form and also in the emulsion, he was able to calculate the diameter of the particles as well as the Avogadro constant, *N*, which is the number of parts in one gram-equivalent of the disperse phase. The mean value for *N* he found to be 70.0×10^{22}. With other emulsions Perrin has repeated his experiments and obtained the value 68×10^{22}. Utilizing the mathematical deductions of Einstein, who assumed that the Brownian movement is due to the impacts of the molecules of the liquid on the particle, the value obtained is 68.6×10^{22}; from which he concluded that there is no essential difference between these particles and molecules, thus confirming the kinetic theory of Brownian movement.

Applications of Colloid Chemistry. — The phenomena of colloid chemistry which we have been considering include adsorption, surface tension, surface concentration, diffusion, etc. These factors control our so-called physical and chemical reactions. The applications of the principles embodying the phenomena are so broad in scope that they include practically all of the principal departments of chemistry. Since colloid chemistry deals with all degrees of dispersion in a system except that designated as molecular dispersion, the domain of colloid chemistry is practically coextensive with and comprises most of the industrial applications of chemistry. The list of industries which utilize the applications of these principles includes most of the commercial applications of chemistry, among which may be mentioned the wide field of biological chemistry, agriculture, plastics, ceramic industry, dyeing, tanning, rubber, sanitation, soap, photography, and metallurgy. It is beyond the scope of our presentation to consider these in detail, and we shall only refer to the application of the principles of colloid chemistry to the new metallurgical process of ore flotation. For a comprehensive consideration of the other industrial applications of colloid chemistry reference may be had to the current periodical literature, and to the following recent publications: *An Introduction to Theoretical and Applied Colloid Chemistry* by Wolfgang Ostwald, translated by M. H. Fischer, and *The Chemistry of Colloids* by Zsigmondy and Spear.

Ore Flotation. — In general, the process of ore flotation consists in employing a flotation machine in which are the ore, which is approximately 80 mesh, and water in the ratio of 3 to 1, together with small quantities of oil. Air is forced mechanically into this "pulp" by means of beaters. Then in this froth-flotation process we have the following systems present: two solid-liquid systems — (ore-water) and (ore-oil); liquid-liquid (water-oil); solid-gas (ore-air), and two liquid-gas systems — (water-air) and (oil-air). These various phases have existing at their respective surfaces their individual surface tensions, and these are referred to as interfacial tension.

It is known that the surface tension of water is changed by the addition of various solutes or soluble contaminants, as they are sometimes called. All acids lower the surface tension, and the same is true of oils, *i.e.* the oil will reduce the interfacial tension between the water-oil phases. We have seen that this change in surface tension is accompanied by adsorption, which results in the increased concentration of the contaminating or dissolved substance. We also have seen that the surface film might contain less of the contaminant than the solution, when we have negative adsorption. That is, we may have a condensation of the disperse phase upon the interfacial boundary, while in the case of negative adsorption the disperse phase would be rejected. So in the case of two non-miscible liquids, liquid-liquid system, we have the condensation of the disperse phase at the interface.

Substances placed in contact with water, and also with many other liquids, assume an electric charge. Most of these substances in contact with water become negatively charged, and we have seen that by the addition of electrolytes these charges can be changed and even reversed. These charges are found in particles of varying degrees of dispersion, from the ultramicroscopic particles to those occurring in coarse suspensions. Mineral gangues such as finely ground quartz, when suspended in water, are negatively charged, while sulphide minerals such as pyrite are positively charged. Oil drops are negatively charged, and the same is true of air bubbles, under certain conditions. In colloid systems these contact films are electrically charged, and in the case of the oil-water contact film the negative charge would tend to attract the positively charged sulphide particles of the ore, causing this to adhere to the interface of the oil-water system, while the gangue particles would be repelled.

Upon the basis of this electrical conception the flotation of ores by means of oil is considered to be an electrostatic process, and this electrical theory of Callow is stated as follows: "It is a scientific fact that when the solid particle is suspended in water, the water will form around the particle a contact film which generally possesses an electric charge, the amount and polarity depending upon the nature of the surface of the particle and the electrolyte in which it is suspended. The presence of these charges can be demonstrated by the fact that the particles possessing them will migrate when placed in an electric field. It has been demonstrated that flotable particles have charges of one polarity (positive), and that non-flotable particles have charges of the opposite polarity (negative); that the froth is charged negatively and so attracts the positively charged or flotable minerals and repels the negatively charged or non-flotable ones. It is this, it is believed, that causes the flotable minerals, galena, sphalerite, etc., to adhere to the froth, and the gangue minerals, silica, etc., to remain in the liquid where they can be discharged as tailings."

It is maintained by some investigators that as the electrostatic charges are small compared to the size of the particles, they are hardly sufficient to hold together the particles of sulphides and the gas. It is therefore necessary to seek other explanations for the flotation of minerals by the froth process. They attribute the phenomenon in the froth process to be due to the interfacial surface tension which determines the character as well as the formation of froths. A froth is defined "as a multiplicity of bubbles." As pure water will not produce a froth, it is necessary to introduce an impurity which will cause "a variable surface tension." The permanency of a froth is greatly affected by the viscosity, as the tenacity of the liquid film may be so modified by securing the proper viscosity and variable surface tension that the bubble can be made more or less resistant to bursting or rupture, which is due primarily to concussion, pressure, evaporation, and adhesive force.

Anderson says:[1] "Solutions in which the continuous phase is a solution of soap, various products from the saponification of albumens, etc., will froth voluminously even in a very dilute condition; frothing never occurring in pure liquids and is a definite proof that the solute or disperse phase lowers the vapor tension of the solvent. A froth which shows adsorption at the interfacial boundary of solution and gas, depends for its persistence on the production of a viscous film at that boundary; these viscous films are the direct result of surface adsorption of the disperse phase, *i.e.* dissolved contaminants, the amount of which is small — disappearingly so." The kind of oil and the amount of air are important factors in the production of a froth as well as in insuring its stability. "The most successful frothing oils include the pure oils, cresylic acid and turpentines, and other pyroligneous products from the distillation of wood . . . the coal tar phenols and their nearby derivatives, and almost all of the so-called essential oils are good frothers." Pure oil makes a brittle froth which dies immediately; creosote

[1] *Met. Chem. Eng.*, *15*, 82 (1916).

makes a stable elastic froth; coal tar products increase the viscosity but are poor frothing agents. An oil mixture of different oils will effect a better separation than a single oil, as in the case of zinciferous slimes, "the best combination consisted of pure oil as a frother, plus wood creosote as a froth and selector, plus refined tar oil as a froth stiffener." Anderson gives as the main and essential requirements for froth flotation: "(1) The production of a persistent froth by any means; (2) the attachment of the bubbles of air to the sulphides or other material to be floated; and (3) the maintaining of a selective action of the froth bubbles for the sulphides or other material to be floated."

Bancroft says: "We cannot get a froth with a pure liquid and air. There must be present a third substance in colloidal solution which will tend to form an emulsion of air in the liquid in question, for a froth is essentially a very concentrated emulsion of air in liquid. If the colloidal material is not present, it must be added. It has often been overlooked that what is needed for ore flotation is a froth of air in oil. The things which have proved successful are substances like sodium resinate, so called, which produce a froth of air in water in an alkaline solution but one of air in oil in an acid solution, because free rosin forms a colloidal solution in oil but not in water; . . . substances which form colloidal solutions in oil and not in water tend to emulsify water in oil."

The tendency of the practice is to reduce the quantity of oil used in the process, and if the amount is sufficiently decreased we have the particle of ore not surrounded by a film of oil, but merely wetted partially with the oil, while a part of it is in contact with the water and another part in contact with air. This gives then, in addition to the effect of the oil, the flotation effect of the air as well. "It is possible that the air film may surround the oiled particle of ore completely, so that the oil does not come in contact with the water. In that case we are back to a straight air flotation of oiled particles. This point calls for further study because, if established, it would have a very important bearing on the future development of the subject."

Preparation of Colloid Systems. — According to the classification of colloid systems upon the basis of the degree of dispersion of the disperse phase, all methods for preparing colloid solutions can be classified either as (1) *condensation* or (2) *dispersion* methods.

The condensation methods diminish the dispersivity to within the limits assigned arbitrarily to colloid systems. The disperse phase which exists in the molecularly disperse condition may be precipitated by double decomposition, hydrolysis, or reduction. In the case of $BaSO_4$ we have a case of double decomposition with the formation of very fine particles which have a strong adsorptive power. Aluminium hydroxide is precipitated, and in the presence of the ammonium salts it is converted into a gel; but if the ammonium salts are washed out, part of the hydroxide precipitate redissolves with the formation of the aluminium hydroxide sol. This same phenomenon is marked in the case of many precipitates, and the presence of electrolytes is necessary to prevent them from forming colloid solutions. Carey Lea employed, in the preparation of colloid solutions of silver, ferrous citrate as a reducing agent. Zsigmondy used formaldehyde to produce his gold sols from alkaline solutions of auric chloride; carbon monoxide and phosphorus are also employed in the preparation of gold sols, while Gutbier obtained red and blue gold sols with hydrazine.

The hydrolysis of salts is a special case of double decomposition. This is a reversible reaction and increases with the dilution as well as with the rise of the temperature. The preparation of hydrosols of the metallic hydrates of aluminium iron, tin, bismuth, cerium, thorium, and zirconium by hydrolysis and the removal of the free acid by dialysis are typical examples.

The dispersion methods increase the dispersivity of the disperse phase. There are a number of special methods by which this may be accomplished. Washing out precipitating reagents from finely divided precipitates causes the particles to " run through " the filter paper, thus demonstrating the necessity of the presence of the electrolyte to prevent the precipitate from "redissolving," that is, from its dispersivity being increased. By the addition of a suitable peptiser the dispersivity can be increased until a sol is produced, and a typical example of this method is peptisation. Some metallic sulphides are peptised with hydrogen sulphide. Zinc hydroxide and beryllium hydroxide form sols when treated with alkalies. Sols of many metals, such as chromium, manganese, molybdenum, tungsten, titanium, silicon, thorium, platinum, etc., can be obtained by using suitable peptisers, which include organic acids, phenols, aluminium, chloride, caustic alkalies, alkaline carbonates, potassium cyanide, and organic bases. The disperse means may be water, methyl alcohol, ethyl alcohol, or glycerine. By mechanical disintegration (grinding) many substances can be so finely divided that they form colloid solutions. The electric dispersion method of Bredig (1898) consists in producing by means of a direct current an electric arc between electrodes of the metal to be dispersed under the surface of the liquid employed as the disperse means. Many hydrosols as well as organosols have been prepared by this method. Svedberg, by using oscillating discharges instead of a direct current, has prepared pure metal sols in water and other liquids.

CHAPTER XXXVI

RATE OF CHEMICAL REACTIONS

In our discussion so far we have not considered that these various reactions require any time for their performance, but have rather assumed that the chemical reactions take place instantaneously. Such is not the case, however, for all reactions require a definite period of time for the substances taking part in the reaction to produce a system that is in equilibrium. While the transformations are themselves instantaneous, the conversion of all of one set of substances into another set depends upon many factors, one of which is the quantity of the substances to be transformed, that is, the mass of the reacting substances. In some cases the whole masses are transformed into new ones almost instantaneously, the time of the reaction being a small fraction of a second, while other reactions may require days or even longer periods for their completion. Connected with the completion of any reaction there are two opposing forces, one the moving power or the *affinity*, and the other the resistance to the reaction that comes into play. The latter can be varied considerably, in fact so much that the speed of a reaction can be decreased materially and made so slow that the reaction has practically ceased; while the *affinity* is definite for a given state of matter. The resistance to a reaction may be caused by the distance between the bodies reacting, by the viscosity of the medium in which the reaction is taking place, etc.

The reaction between zinc and sulphuric acid may be greatly decreased by subjecting the system to great pressure, where the evolution of hydrogen may cease entirely. A pressure of eighteen atmospheres stops the reaction, while a higher pressure, when 1.3 normal sulphuric acid is employed, reverses the reaction and causes zinc to be precipitated. Frowein found that the maximum vapor pressure of $ZnSO_4 \cdot 7\ H_2O$ at 18° C. is 8.406 mm., and a lower pressure produces a reversal of the reaction:

$$ZnSO_4 \cdot 6\ H_2O + H_2O \rightleftarrows ZnSO_4 \cdot 7\ H_2O.$$

In the case of evaporation we have a condition of equilibrium only when the maximum pressure of the body vaporizing is equal to the vapor pressure. The rate of evaporation will be proportional to the difference between the two vapor pressures. Noyes and Whitney found practically the same relation for the rate of solution of benzoic acid and of lead chloride, since the rate of solution proved to be proportional to the difference between the saturated concentration, C, and the concentration actually existing, *i.e.* the rate of solution is proportional to the difference in concentration $k(C - c)$.

Affinity. — The idea of the mutual attraction of the elements has been emphasized from very early times, and the property which causes the element to enter into chemical combinations is termed *chemical affinity*. It was Newton who first considered that this force was inherent in the element itself, and he showed that this chemical attraction decreased with the distance more rapidly than the law of gravitational attraction required. Various efforts were made to measure the magnitude of this attraction and represent the relative affinities of the various substances. Geoffroy (1718) was the first to compile a table of this character. The elements were arranged in the order of their decreasing attraction, and those above would replace the ones lower down from their compounds. Bergmann (1775) found that the conditions in which a substance existed affected its position in Geoffroy's table. These conditions were not only the state of aggregation (solid, liquid, or gas) of the substance, but also the temperature and the medium present The value of such a table of affinities therefore became practically negligible.

Wenzel in his discussion (1777) of the subject of affinity shows that the conditions under which the reactions proceded were dependent on the *masses* of the reacting substances, and he concluded that the chemical reaction is proportional to the concentration of the reacting substances. Berthollet confirmed this experimentally and in 1801 emphasized that the *masses* of the reacting substances must also be taken into consideration, for the effect of the mass may become such as to overcome completely the force of affinity. It follows then that the activity of substances must be measured by the masses which produce a definite reaction, and this Berthollet stated as follows: " The chemical activity of a substance depends upon the force of its affinity and upon the mass which is present in a given volume." But this idea of the influence of the mass received a great deal of opposition and was not accepted. It was not, however, until almost two decades later that Rose (1842) emphasized in a striking manner the action of the mass. The decomposition of silicates in the presence of water and carbon dioxide of the air illustrates the breaking down of very stable compounds by very weak chemical reagents when they are in large quantities acting for a long time. These reactions cannot be duplicated to any appreciable extent in the laboratory. Further, in the crystallization of acid sulphates of potassium from boiling solutions, a portion of the sulphuric acid is split off to combine with the water. On redissolving this crop and recrystallizing, the neutral salt is obtained, thus showing the further splitting off of the sulphuric acid by the mass action of the water. Other investigators now took up this work and presented a large number of experiments which show the marked effect of the mass of the reacting substances on the reaction. In the study of such reactions as the decomposition of barium sulphate by boiling in a solution of potassium carbonate, it was recognized that there are really two reversible reactions to be considered, and for a particular condition, a maximum amount of decomposition of barium sulphate.

It was not until 1850, when Wilhelmy published his data on the inversion of cane sugar, that we had the first method outlined by which the speed of the chemical reactions can be measured. Wilhelmy showed that by placing a sugar solution containing acid in a polarimeter tube and keeping the temperature constant, the progress of the inversion of the cane sugar could be readily followed by observing the optical condition at definite intervals of time. He studied the reaction carefully at different temperatures with different quantities of sugar, of acids, and with different acids, and concluded that the amounts of sugar inverted in a given time were proportional to the amounts of acid and of sugar present, and this also varied with the temperature.

Several years later (1862) Berthelot and Gilles studied the formation of esters from alcohols and acids, and these data emphasized the effect of the mass on the speed of these chemical reactions. They concluded that the amount of ester formed in unit time is proportional to the product of the concentrations (the masses) of the reacting substances and inversely porportional to the volume.

It, however, remained for Guldberg and Waage (1867) to formulate mathematically these ideas of affinity, the effect of mass, and the speed of the chemical reactions. "We must study the chemical reactions in which the forces which produce new compounds are held in equilibrium by other forces," and particularly is this true where the reactions do not run to an end but are partial.

Law of Mass Action. — If by the reaction of two substances, A and B, the two new compounds, C and D, are formed, the chemical equilibrium would be represented thus, $A + B \rightleftarrows C + D$. The substances A and B combine to produce C and D, while under the same conditions C and D react to produce A and B, and when equilibrium is established the four substances are present. There is, then, a force causing the union of A and B with the formation of C and D, thus resulting in the reaction going from left to right at a certain velocity. This velocity was shown by Guldberg and Waage to be proportional to the product of the active masses of the two substances, that is, the velocity $= k \cdot a \cdot b$, in which a and b are the active masses of A and B respectively, and k is the affinity coefficient. Similarly, in the reverse reaction in the re-formation of the substances A and B by the reaction of C and D, we have a velocity which is equal to $k' \cdot c \cdot d$, in which c and d are the active masses of C and D respectively, and k' is the affinity coefficient. As this is an equilibrium equation, it represents the reaction from right to left proceeding at the same rate as the reaction from left to right, and in unit time there are as many moles of A and B decomposed to form C and D as there are of C and D decomposed to re-form A and B. That is, the velocities of these two reactions are equal, and we then have $k \cdot a \cdot b = k' \cdot c \cdot d$.

If the reaction is in a state of equilibrium as just illustrated, then the velocity of the reaction represented by the reaction of the substances A and B must be equal to the velocity of the reaction of C and D, *i.e.* $v = v'$ and $v = k \cdot a \cdot b$ and $v' = k' \cdot c \cdot d$. But where the velocity in one direction is different from that in the opposite direction, the reaction is going to proceed more rapidly in that direction, and as a result the reaction as a whole proceeds in that direction. We speak of the reaction running to an end, *i.e.* until there is a complete predominance of one of the two systems. The velocity of the reaction V is defined as the difference between the individual velocities, *i.e.* $V = v - v'$, or $V = k \cdot a \cdot b - k' \cdot c \cdot d$, which is the fundamental expression for the velocity of reactions. In the expression $k \cdot a \cdot b = k' \cdot c \cdot d$ or $\frac{k}{k'} = \frac{c \cdot d}{a \cdot b}$ we recognize the Mass Law Equation, and the equilibrium constant $\frac{k}{k'} = K$. The Guldberg-Waage expression for the velocity of the reaction when the velocities of the two systems are equal is identical with the above expression, showing the reaction to be proportional to the products of the reacting masses.

Thermodynamic Deduction of the Law of Mass Action. — Lewis by means of an isothermal reversible cycle in which the "Equilibrium Box" of van't Hoff is employed gives the following thermodynamic deduction of the Mass Law Equation for a homogeneous gaseous system. In the reaction $A + B \rightleftarrows C + D$ let the four gaseous substances be in the two reservoirs, I, II, with the concentrations a, b, c, d, and a', b', c', d', respectively. The temperature of the two reservoirs is the same, and the substances are in equilibrium.

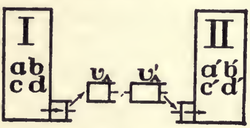


FIG. 98.

I. Isothermally and reversibly remove one mole of A from I at its partial pressure p_A, and the volume will be V_A. The work done by the system is $+ p_A V_A$. Now change p_A to p_A' reversibly, and simultaneously the volume changes from V_A to V_A'. The work done is then $+\int_{V_A}^{V_A'} p\,dV$. Now force the mass of gas, one molecular volume V_A', into II, the work is $- p_A' V_A'$. Then the summation of the work done is

$$+ p_A V_A + \int_{V_A}^{V_A'} p\,dV - p_A' V_A'.$$

Assume The Gas Law, $pV = nRT$; since T is constant, then $pV =$ a constant. As we have the same mass of gas it follows that $p_A V_A = p_A' V_A'$, hence the total work done is $\int_{V_A}^{V_A'} p\,dV$, which in this case is equal to $\int_{p_A'}^{p_A} V\,dp$.

II. Similarly and simultaneously with the transfer of A let one mole of B be transferred from I to II. Then

$$\text{the work per mole of } B = \int_{p_B'}^{p_B} V_B \, dp.$$

As the system is gaseous, assuming The Gas Law to hold, we have

$$p_A = RTa \text{ and } p_A' = RTa'$$

$$\text{hence the work on } A = RT \log \frac{a}{a'}$$

$$\text{and the work on } B = RT \log \frac{b}{b'}.$$

III. Now in equilibrium box II, assume that the moles of A and B added are changed into C and D and no external work is done.

IV. Finally transfer one mole of C and one mole of D from II to I in the above manner. Then

$$\text{work} = RT \log \frac{c'}{c} + RT \log \frac{d'}{d}.$$

Now let these molecules of C and D change into A and B in I and assume no external work is done. The initial conditions have been restored and the cycle is complete. Since this was accomplished isothermally and reversibly the summation of the work done is zero. Hence we have

$$RT \log \frac{a}{a'} + RT \log \frac{b}{b'} + RT \log \frac{c'}{c} + RT \log \frac{d'}{d} = 0 \text{ or}$$

$$\log a + \log b - \log c - \log d = \log a' + \log b' - \log c' - \log d'$$

which becomes

$$\frac{a \cdot b}{c \cdot d} = \frac{a' \cdot b'}{c' \cdot d'} = \text{a constant.}$$

This is the Law of Mass Action for a system following The Gas Law and is Guldberg-Waage's expression.

We have seen that when two substances A and B react to form C and D the velocity of the action of A on B is $v = k \cdot a \cdot b$; but it is apparent that this velocity must change as the reaction proceeds, since the concentrations of A and B, a and b respectively, are changing continuously. Let us assume that x moles of A and of B have been used up in the definite time t, then the concentrations of A and B at the end of this time will be $(a - x)$ and $(b - x)$ respectively, and we have for the reaction velocity

$$v \text{ (after time } t) = k(a - x)(b - x).$$

During this time t the concentrations of C and of D will likewise have increased to $(c + x)$ and $(d + x)$ respectively, and v' (after time t) $= k'(c + x)(d + x)$. We then state that the small amount of A changed, dx, in the small interval of time, dt, would be

$$\frac{dx}{dt} = k(a - x)(b - x) - k'(c + x)(d + x).$$

But if the reaction of the resulting products of the reaction is so slight that the speed of the reverse reaction can be neglected entirely, then the reaction velocity equation becomes

$$\frac{dx}{dt} = k(a - x)(b - x).$$

Or if there is only one substance, A, undergoing decomposition into products which do not react, then the equation takes the form $\frac{dx}{dt} = k(a - x)$, which is Wilhelmy's law that the velocity of the chemical reaction *at any moment* will be proportional to the amount of the substance, a, actually present. Or, as Harcourt and Esson state it, "the amount of chemical change in a given time is directly proportional to the quantity of reacting substance present in the system."

Equation for Monomolecular Reactions. — The differential equation $\frac{dx}{dt} = k(a - x)$ is then a mathematical expression of the theory of the speed of reaction. Reactions which correspond to an equation of this type are termed *monomolecular*. The equation contains the variables $\frac{dx}{dt}$ and x and the constants k and a. If different sets of corresponding values of these variables be determined experimentally, together with the value of a, and substituted in the equation, the computed values for k should agree. It is of course impossible to get instantaneous values of $\frac{dx}{dt}$, and the approximations that can be obtained do not give satisfactory results. It is therefore necessary to obtain another equation, the terms in which can be readily and accurately measured. It is possible to derive another equation involving the same constant, k, by integrating this differential equation.

The equation $\frac{dx}{dt} = k(a - x)$ may be written

$$\frac{dx}{a - x} = kdt, \text{ which on integration gives}$$

$$\int \frac{dx}{a - x} = \int kdt + C$$

which becomes

$$-\log_e (a - x) - kt = C.$$

At the initial conditions $t = 0$ and $x = 0$, the equation becomes

$$C = -\log_e (a - 0) - k0 = -\log_e a.$$

Substituting this value for C in the above equation and solving we have

$$kt = \log_e a - \log_e (a - x) \text{ or}$$

$$kt = \log_e \frac{a}{a - x} \text{ or}$$

$$k = \frac{1}{t} \log_e \frac{a}{a - x}.$$

It is customary to use the logarithms to the base 10, log, instead of the natural logarithms, $\log_e$; then the equation becomes

$$0.4343\ k = \frac{1}{t} \log \frac{a}{a - x}.$$

It is evident that since this is a constant it could be expressed directly in terms of log, and the equation takes the form

$$K = \frac{1}{t} \log \frac{a}{a - x}$$

which may be considered a special case of the general formula.

Equation for Bimolecular Reactions. — Reactions wherein there are two of the reacting substances changing in concentration during the reaction are termed *bimolecular* reactions. The reaction velocity at any moment is given by the differential equation $\frac{dx}{dt} = k(a - x)(b - x)$, in which a and b represent the concentrations of the two substances the concentrations of which are changing. Let x represent the amount of one substance that has changed in time t, then the same number of moles of the second substance will have changed during the same time. If we assume that there are the same number of moles of the two substances present at the beginning of the reaction, then $a = b$ and the equation becomes $\frac{dx}{dt} = k(a - x)^2$; or rearranging, $dt = \frac{dx}{k(a-x)^2}$. Integrating, we obtain $t = \frac{1}{k(a - x)} +$ constant. Evaluating the constant in the usual way by putting $x = 0$ and $t = 0$ and substituting, we have the integration constant $= -\frac{1}{ka}$. Substituting, we have

$$t = \frac{1}{k(a - x)} - \frac{1}{ka}$$

and simplifying

$$t = \frac{x}{ka(a - x)} \text{ or } k = \frac{1}{t}\frac{x}{a(a - x)}.$$

If, however, the quantities of A and B are not equal, then the equation is

$$\frac{dx}{dt} = k(a - x)(b - x)$$

which may be rewritten

$$\frac{dx}{a - b}\left(\frac{1}{b - x} - \frac{1}{a - x}\right) = kdt.$$

Integrating, we obtain

$$-\frac{1}{a-b}\left(\log\frac{b-x}{a-x}\right) = kt + \text{constant}.$$

If $x = 0$ and $t = 0$, substituting, we have

$$-\frac{1}{a-b}\log\frac{b}{a} = \text{a constant}.$$

Introducing this value, the equation becomes

$$-\frac{1}{a-b}\left(\log\frac{b-x}{a-x}\right) = kt - \frac{1}{a-b}\log\frac{b}{a}.$$

Solving,

$$k = \frac{1}{t}\left(\frac{1}{a-b}\log\frac{b}{a} - \frac{1}{a-b}\log\frac{b-x}{a-x}\right)$$

which simplifies to

$$k = \frac{1}{t(a-b)}\log\frac{(a-x)b}{(b-x)a}.$$

Equation for Trimolecular Reactions. — If there are three reacting substances and x represents the number of moles of each entering into the reaction in the time t, then $\frac{dx}{dt} = k(a-x)(b-x)(c-x)$. The simplest case is where the three reacting substances are in equivalent proportions. Then the equation takes the form $\frac{dx}{dt} = k(a-x)^3$, which on integration and by the evaluation of the integration constant gives

$$k = \frac{1}{t}\,\frac{x(2a-x)}{2a^2(a-\ )^2}.$$

Degree of the Reaction. — The number of different molecular species whose concentration changes during the course of the reaction is used as the basis for designating the order of the reaction. The reactions are termed monomolecular when only one molecular species changes in concentration; bimolecular, when two change; trimolecular, when three constituents change in concentration, etc. The three equations just derived are very different, and the question arises, how can they be used to determine the order of a chemical reaction? By substituting in the equations the different times, t, at which the concentrations, x, are determined, and knowing the initial concentration, the velocity constant can be calculated. The formula which gives a constant value would designate the order of the reaction. It is, however, necessary to make but a few determinations, for if the time in which one half of the material available for transformation is known, the relation between the time and the original concentration of the constituent is very characteristic for the different types of reactions. If $x = \frac{a}{2}$, on substituting this value in the equation for monomolecular reactions and solving for t, we find that the time is independent of the original concentration, *i.e.* substituting, we have

$$tk = \log 2.$$

As the original concentration does not appear in the equation, the time t is independent of the original concentration. This is known as the period of half change. Similarly, it may be shown that for bimolecular reactions the time is inversely proportional to the initial concentration, and for trimolecular reactions it is inversely proportional to the square of the initial concentration. In general, the time required to change one half of the substance present undergoing the chemical change is inversely proportional to the $(n - 1)$th power of the initial concentration. The order of the reaction is then readily established.

Reactions of different degrees of complexity are known, and those to the eighth order have been described. When the number of reacting substances is increased, reactions between the original constituents and the new constituents become possible as well as the reactions between the new constituents themselves. There will result a number of side reactions which will be of different orders, depending on the number of molecular species produced by the original reaction as well as by the secondary side reactions. Then there will be reactions which are opposite to the original reactions. These may take place at the same time as the original reaction, or they may be at a different time, thus giving rise to what is termed consecutive reactions. So the actual rate of a reaction, which is what we understand by the velocity constant, will be dependent upon the relative rates of the other reactions, and the value will be the sum of all the intermediate independent changes. Our discussion will be confined to a few examples of the simple cases free from these auxiliary reactions.

Monomolecular Reactions Running One Way. — Reactions of the first order are very common, and among these may be mentioned reduction of potassium permanganate; reduction of hydrogen peroxide; decomposition of diazo compounds; decomposition of chlor- and brom-acetates; formation of anilids; formation of esters in methyl alcohol; catalysis of sulphonic esters; the conversion of persulphuric acid into "Caro's" acid; decomposition of nickel carbonyl; hydrolysis of starch; hydrolytic action of yeast, and inversion of sugar.

The inversion of cane sugar by acids and salts in aqueous solutions is one of the important chemical reactions that fulfill the conditions for a reaction of the first order, since it has been found that the concentration of the hydrolyzing or inverting agents remains constant throughout the reaction. The equation representing the reaction is

$$C_{12}H_{22}O_{11} + H_2O \rightleftarrows \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6}.$$

This appears to be a bimolecular reaction, but the amount of the water that enters into the reaction is so small compared with the amount of solvent present that its concentration remains practically constant. This reaction may be carried out experimentally by placing equal volumes of a 20 per cent sugar solution and a fourth normal acid solution into a number of small flasks which have been freed from alkali by thorough steaming. These flasks are placed in a water bath, which is maintained at a constant temperature. At convenient intervals of time (about 30 minutes) one flask is removed and the sugar determined by the polarimeter. Having determined the initial concentration (polarimeter reading) at the time of mixing the acid and sugar solutions and the readings for several hours, the solution is permitted to stand for several days or is heated to obtain the end point of the reaction, that is, the point of complete inversion. The value obtained in this manner does not always agree with the value calculated from the weight of sugar employed. A number of experimenters have shown that the specific rotation is dependent on the concentration, time, temperature, and also upon the acid used. By substituting the data in the equation $k = \frac{1}{t} \log \frac{a}{a - x}$ and solving for k, the values for the velocity constant or coefficient may be obtained as illustrated in Table LXXXVIII. It is immaterial in what units the concentration a, of the substance changing is expressed. So it is usually convenient to employ the values as expressed by the scale of the polarimeter for designating the values of a and of x. In Table LXXXVIII t represents the time in minutes, after the solutions of sugar and acid were mixed, when the polarimeter reading was taken; α the reading on the scale; x the difference between the initial reading and the reading at the given time. In the last column are given the values for k, which indicate a good constant value.

From an inspection of the equation it will be seen that there are no factors that take into account the concentration of the sugar or of the hydrolyzing agent. Ostwald from his experimental results showed that the concentration did have an effect on the velocity coefficient. Cohen, however, considered that the molecules in a concentrated sugar solution have a shorter free path of motion than those in less concentrated solutions, and since the speed is proportional to the free path it is proportional to the actual space occupied by the sugar molecules. By applying the proper correction for this, he concluded that the concentration did not affect the velocity constant, *i.e.* it is independent of the concentration of the sugar.

TABLE LXXXVIII — INVERSION OF CANE SUGAR

a (total change) = 65.50

t	α Reading	x	k
0	46.75°	——	——
30	41.00	5.75	0.001330
60	35.75	11.00	1332
90	30.75	16.00	1352
120	26.00	20.75	1379
150	22.00	24.75	1321
210	15.00	31.75	1371
330	2.75	44.00	1465
510	− 7.00	53.75	1463
630	− 10.00	56.75	1386
	− 18.75	a = 65.50	——

Inversion of Cane Sugar by Acids. — It is only in the presence of acids that the inversion of sugar proceeds at a marked velocity. The concentration of the acid does not change during the reaction. The action of the acid is said to be *catalytic*. The greater the concentration of the acid the greater the velocity of inversion of the sugar. The nature of the acid has a marked effect on the velocity of the inversion. The so-called *strong* mineral acids cause the inversion to proceed rapidly, while under the effect of weak organic acids the action is much less pronounced. It will be recalled that the definition of an acid is that it is a substance in aqueous solutions that yield hydrogen ions. The strength of an acid is attributed to the hydrogen ions present due to the dissociation of the acid, that is, the greater the degree of dissociation the greater the hydrogen ion concentration. In the case of the inversion the greater the concentration of the hydrogen ions the quicker the inversion of the cane sugar. Trevor (1892) used the inversion of cane sugar as a means of determining the concentration of the hydrogen ions, *i.e.* of the degree of dissociation of the acids. This method has been employed extensively for establishing the relative strength of acids and in Table LVIII, page 356, is given in one column the relative values referred to hydrochloric acid taken as 1.000. These values give an excellent idea of the variability of the inversion coefficients of the various acids.

It will be remembered that certain organic salts undergo hydrolytic dissociation with the formation of hydrogen ions. Trevor employed the inversion of cane sugar as a method for the determination of the degree of dissociation of a number of the sodium salts of organic acids, and W. A. Smith also determined the hydrolytic dissociation of organic salts by this method and compared the values with those obtained by the electrical conductivity method. Long published the results of his experiments on the inversion of cane sugar by inorganic salts. His results, given in Table LXXXIX, will illustrate the type of reactions and the constancy of the value, k, obtained for the velocity constant.

The data show that in the solutions employed the normal solution inverted the sugar but little more rapidly than the half normal solution. From the data obtained he calculated the degree of hydrolytic dissociation of these salts.

The addition of normal binary salts with a common ion to an acid has a marked effect upon the velocity of inversion of cane sugar. For example, potassium chloride added to a solution of cane sugar containing hydrochloric acid greatly increases the velocity of inversion, while the addition of a salt to a weak organic acid with a common ion greatly decreases the velocity. Arrhenius says, "The catalytic activity of hydrogen ions is greatly stimulated by the presence of other ions."

TABLE LXXXIX — INVERSION OF CANE SUGAR BY $FeSO_4 \cdot 7\ H_2O$

0.5 NORMAL $a=17.12$				NORMAL $a=17.10$			
t	α	x	k	t	α	x	k
0	12.97	—	—	0	12.95	—	—
15	12.48	0.49	0.00084	15	12.45	0.50	0.00086
45	11.50	1.47	0.00086	45	11.26	1.69	0.00100
75	10.40	2.57	0.00094	75	10.08	2.87	0.00106
135	8.43	4.54	0.00099	135	8.07	4.88	0.00108
195	6.72	6.25	0.00101	195	6.30	6.65	0.00110
255	5.21	7.76	0.00102	255	4.70	8.25	0.00112
375	2.87	10.10	0.00103	375	2.25	10.70	0.00114
495	1.03	11.94	0.00105	495	0.15	12.80	0.00121
		Average	0.00099			Average	0.00107

The inversion of cane sugar can then be utilized in the determination of the degree of electrolytic dissociation as well as of hydrolytic dissociation.

Bimolecular Reactions Running One Way. — Chemical reactions in which two molecular species are simultaneously undergoing change are common. A few of the different bimolecular reactions may be mentioned: the esterfication of the chloracetic acids; bases and esters in aqueous as well as in alcoholic solutions; formation of methyl orange; ammonium cyanate into urea; oxidation of formaldehydes; hydrolysis of amids; the action of bromine on the fatty acids; formation of esters.

One of the best-known examples of a reaction of the second order is the saponification of esters. By mixing a base and an ester in aqueous solution there are gradually formed an alcohol and a salt of the corresponding organic acid. This may be illustrated by the following chemical equation:

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{sodium hydroxide}}{NaOH} \rightleftarrows \underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{sodium acetate}}{CH_3COONa}$$

In order to determine the velocity of this reaction equal volumes of ester and the base of the same molecular concentration are mixed in a flask and placed in a constant temperature bath. At convenient intervals of time, t, a definite quantity of this mixture is pipetted into a definite excess quantity of standard acid. The excess is determined by titration, and the alkali at this time can be calculated; and if the original concentration, a, is known, the velocity can be calculated by means of the bimolecular reaction equation

$$k = \frac{1}{t} \frac{x}{a(a - x)},$$

since the two substances changing simultaneously were taken in equal molecular quantities.

This equation contains no term designating the nature of the ester or of the saponifying agent, and the question has been raised whether they do affect the velocity of saponification and also whether an excess of either would have any influence. Reicher attempted to answer this and obtained data which show that different bases give different values for the constant. This is illustrated by the following data for methyl acetate, using bases of the same concentration:

Base	Constant
NaOH	2.307
KOH	2.298
$Ba(OH)_2$	2.144
$Ca(OH)_2$	2.285
$Sr(OH)_2$	2.204
NH_4OH	0.011

The strong bases all give practically the same value for the constant coefficient, while the saponification by ammonium hydroxide takes a much longer time.

That the alcohol radical has a marked influence is shown from the following data, which give the constant for the saponification of these various acetates by solutions of sodium hydroxide of the same concentration:

Ester	Constant
Methyl acetate	3.493
Ethyl acetate	2.307
Propyl acetate	1.920
Isobutyl acetate	1.618
Isoamyl acetate	1.645

The more complex the radical the less the speed of saponification, and that the same is true for the acid radicals is shown from the following, which illustrate the saponification of the esters by sodium hydroxide:

Ester	Constant
Ethyl acetate	3.204
Ethyl propionate	2.816
Ethyl butyrate	1.702
Ethyl isobutyrate	1.831
Ethyl isovalerate	0.614
Ethyl benzoate	0.830

The work of Reicher has been confirmed by Bugarsky and others, including Ostwald, who further emphasize the fact that the speed of saponification of esters is a function of the concentration of the hydroxyl ions and is therefore dependent on the degree of dissociation of the base. Conversely, the saponification of esters may be employed as a method for the determination of the degree of electrolytic dissociation, that is, the concentration of the hydroxyl ions. The rate of saponification can be followed by the conductivity method, and the values of the velocity constant as found by different investigators agree well.

Saponification of esters by weak bases, such as ammonium hydroxide, methylamine, ethylamine, etc., proceeds slowly and gives a small velocity constant which varies with the time. Ammonium hydroxide gives, for example, the values 1.76 : 1.21 : 1.01 : 0.845 : 0.501. Ostwald showed that neutral salts have a marked effect upon the rate of saponification by weak bases particularly, and attributed their variations to this cause.

It has also been shown that saponification can be produced by substances that on hydrolysis yield alkaline solutions, and since the rate is proportional to the concentration of the hydrogen ions, this method may be employed as a means of determining the degree of hydrolytic dissociation. See Table LXVI, page 393.

Other Molecular Reactions. — There are numerous reactions of a higher order than those in which only two molecular species take part. In many of these there are secondary reactions which are not only reverse reactions which prevent the major reaction from going to completion, but also side reactions which result from the inter-reactions with the products of the reaction. These side reactions may be simultaneous with the main reaction or they may be consecutive. When a number of substances are present, they may react so that there is a series of consecutive reactions. The most pronounced example of consecutive reactions probably is the formation of radium emanations. This is true not only in the case of homogeneous reactions but we may also have reactions of different orders in the case of heterogeneous chemical changes wherein the reacting substances are in different states of aggregation. For a discussion of these the student is referred to special texts on advanced Physical Chemistry.

Factors which Influence the Velocity of Reactions. — Iron exposed to air combines slowly with the oxygen at ordinary temperature. If a piece of iron picture wire is heated and introduced into oxygen, the iron burns very rapidly with an evolution of much heat and light. The reaction is of such velocity at this higher temperature that the heat developed is greater than can be conducted or radiated away, so that the heat in turn accelerates the reaction. Similarly, for many other substances there is no reaction between them, or the reaction proceeds slowly at the lower temperatures. On increasing the temperature the speed of the reaction increases until a temperature is reached at which the heat generated exceeds that conducted or radiated away, and the mass becomes incandescent, breaks into a flame, or ignites. With liquids such as oils we designate this the *flash point*, with gases it is the *temperature of explosion*. This minimum temperature at which combustion or explosion takes place is designated the *ignition temperature*, or the *kindling temperature*.

When phosphorus is placed in air, the reaction with the oxygen is slow; but when the temperature is raised above 60° C., the phosphorus ignites. There is some reaction taking place below the ignition temperature, but it is slow, and in most cases the reaction is so slow that it cannot be observed. The reaction velocity at the ignition temperature is so great that the heat evolved is sufficient to maintain this temperature and even increase it with the accompanying increase in the speed of the reaction. In many cases a small rise in temperature may then give an enormous increase in the velocity of the reaction. Cane sugar is inverted about five times as fast at 55° as at 25°. According to Berthollet an ester may be formed about twenty-two thousand times as fast at 200° as at 7°. Many empirical formulations of the change of the velocity of a reaction with the temperature have been made. The relation seems to be, that the velocity is nearly proportional to the square root of the absolute temperature.

The *influence of pressure* on the velocity of reaction is practically negligible in the case of reactions of the first order, but for reactions of the second order the effect is nearly a linear function of the pressure. The velocity of decomposition of hydriodic acid is, according to Bodenstein, practically proportional to the pressure to which the gas is subjected. The reaction between metals and acids with the liberation of hydrogen ceases above a certain pressure, according to Nernst and Tammann.

The *nature of the medium* in which a chemical reaction takes place has a marked effect on the velocity of the reaction. Menshutkin gives the data in Table XC for the velocity constant in a number of solvents for the reaction of ethyliodide on triethylamine,

$$C_2H_5I + (C_2H_5)_3N \rightleftarrows (C_2H_5)_4NI$$

TABLE XC

SOLVENT	VELOCITY	DIELECTRIC CONSTANT OF SOLVENT
Xylene	0.00287	2.6
Benzene	0.00584	2.26
Ethyl alcohol	0.0366	20.5
Methyl alcohol	0.0516	33.2
Acetone	0.0608	21.5
Acetophenone	0.1294	18.1
Benzyl chloride	0.1330	10.6

This illustrates the marked change in the velocity of the reaction with change of solvent. Various efforts have been made to connect this with the different physical properties of the solvent, — such as the dielectric constant, viscosity, dissociation power, etc. The value of the dielectric constant for the solvents is given in the last column of the table. The velocity constants do not appear to bear any relation to the dielectric constant of the solvent or to the viscosity changes. From the evidence available the physical properties of the solvents alone do not seem to determine the reaction velocity, but it is to be noted that those solvents with high dissociative power are the ones in which the reaction of dissolved substances is the most pronounced.

In the reaction of hydrogen and oxygen, as in the case of the ignition of other gases, there is a definite rate at which the flame travels throughout the mass of gas. The ignition is started at one point and owing to the intense heat developed, due to the chemical reaction of the gases, there is an increase in pressure. The time required to develop the maximum pressure is then a measure of the explosiveness and is the *time of explosion*. The explosion is considered complete when maximum pressure is reached. Bunsen found that for oxygen and hydrogen maximum pressure was attained in $\frac{1}{4000}$ of a second and the high temperature lasted for at least $\frac{1}{65}$ of a sceond. The temperature obtained by calculation necessary to produce this pressure was 2500°. But making corrections for steam condensed the value found was 3897°, but on further corrections for heat evolved by the combustion, which was assumed complete before maximum pressure was reached, constant specific heat of steam at constant volume, etc., assuming ideal conditions, the value of 9000° was found. But these ideal conditions are unattainable, and the maximum temperature ranges between 2500° and 3900°, which, however, does not account for all of the heat evolved. As the ignition of the mixture takes place from particle to particle, the heat due to the reaction causes an expansion, which in turn causes the projection of the ignited into the unignited particles and increases the rate of ignition.

The formation of these gases is so violent that their quick expansion produces another blow on the surrounding mass, which causes complete explosion of the entire mass. The rise of pressure is exceedingly rapid and produces not only a forward wave of detonation but also a sudden backward wave of compression which hastens this residual combustion. The explosive or detonating wave set up is comparable to a sound wave passing through a gaseous mixture. It results, however, from "an abrupt change in chemical condition which is propagated in the explosive wave and which generates an enormous force as it passes through successive layers of the media." Berthelot considers that the main velocity of translation of the molecules of the products of combustion, retaining kinetic energy corresponding to the heat developed in the reaction, may be regarded as the limiting maximum rate of propagation of the explosive wave. Berthollet and Vieille found the rate of propagation of the explosive wave in pure electrolytic gas to be 2810 meters per second, and Dixon's value, 2819 meters per second, confirmed this.

Catalysis. — The inversion of cane sugar is much more rapid in the presence of acids than in pure aqueous solution, and we have seen that the rate of inversion is proportional to the concentration of the acid, *i.e.* to the concentration of the hydrogen ions. The hydrogen does not enter into the products of the reaction, but its presence greatly accelerates the progress of the reaction. Berzelius introduced the term *catalytic agent* and defined it as follows: "A catalytic agent is a substance which, merely by its presence and not through its affinity, has the power to render active, affinities which are latent at ordinary temperature." The agent which causes the catalytic action or *catalysis* is called a *catalyzer* or a *catalyst*. Ostwald defines a catalytic agent as a substance which affects the velocity of a chemical reaction without itself appearing in the final product.

A catalyzer cannot start a reaction, but it merely modifies the velocity of the reaction. It does not change the equilibrium point, as it affects the velocity of the inverse reactions to the same degree. There is no change in the concentration of the catalyst, for if in the inversion of cane sugar by means of acid, the concentration of the acid be ascertained at different stages of the reaction, the values will all be the same. An infinitely large quantity of the reacting substances can be transformed by a very small quantity of the catalyzing agent. Titoff says that the rate of oxidation of a solution of sodium sulphite is noticeably increased by even dipping a strip of clean copper into the solution for a few seconds. The reduction of mercuric chloride by oxalic acid is greatly increased by the addition of potassium permanganate to a concentration of 0.000001 gram in ten cubic centimeters. The nature and the quantity of the catalyst does not affect the final state of an equilibrium. There are a large number of catalytic agents and reactions, and Ostwald goes so far as to state that "there is probably no kind of chemical reaction which cannot be influenced catalytically, and there is no substance, element, or compound which cannot act as a catalyzer." Although there have been several efforts to classify catalytic reactions, we shall not present any of these, but shall consider a few of the marked examples of catalysis and mention a few technical applications of catalytic reactions.

On placing a platinum wire heated to redness in various mixtures of gases and vapors combination results. This was shown by Humphry Davy (1817), and this fact was utilized by Hempel for the analysis of mixtures of gases. By passing a mixture of oxygen with hydrogen, carbon monoxide, methane, and nitrogen over spongy platinum at 177°, only the hydrogen and the carbon monoxide are oxidized. Phillips in 1831 patented the method for manufacturing sulphuric acid by the process of oxidizing SO_2 with the use of platinum wire or platinum sponge. But owing to the fact that certain impurities destroyed the catalytic action of the platinum the process was abandoned. A number of substances such as hydrogen sulphide, ammonia, ethylene, etc., have been found to destroy or inhibit the activity of the platinum.

The more highly dispersed the catalyst is, the greater its chemical activity. For example, platinum black is more active than sheet platinum, *i.e.* there is more surface exposed. Mitscherlich concludes that "the layer of carbon dioxide which condenses on the walls of wood charcoal is about 0.00005 cm. thick," and that at least one third of the carbon dioxide so condensed is in the liquid state. That perfectly dry gases do not unite has been demonstrated by a number of investigators. Dixon (1880) demonstrated that the reaction takes place only in the presence of moisture and showed that at 100° sulphur dioxide and oxygen will not unite in the presence of *water vapor*, but that a particle of *liquid* water produces oxidation. This condensation theory of combustion proposed by Faraday has been supported by many others and particularly by Dixon, who attributes to water vapor the rôle of an "oxygen carrier." This was stated by Mrs. Fulhame in 1794, nearly a century before, as follows: "Water is essential for the oxidation, and it is always decomposed in the process; . . . carbon monoxide unites with the oxygen of the water, while the hydrogen of the latter seizes the oxygen of the air." Dixon showed that when the vapors such as hydrogen sulphide, ammonia, formic acid, ethylene, etc., were mixed with oxygen and carbon monoxide the explosion would take place, while if carbon dioxide, nitrogen monoxide, and carbon bisulphide were employed no explosion resulted. Hence, *not only steam but all substances which will form steam under the conditions of the experiment* will cause the reaction to take place.

A minute portion of the solid phase of the solute introduced into a supersaturated solution of this particular solute may cause the mass to crystallize; the blow by a trigger causes the materials in the detonator to react; and similarly the addition of small amounts of material or small amounts of energy in various forms such as heat, light, etc., may result in chemical changes which produce enormous quantities of energy in other forms. These results are not at all commensurate with the initial inaugurating effect and are independent of it. Phenomena of this type must be clearly different from what is termed catalysis, but it is not an easy matter to distinguish the differences.

Catalytic Processes. — There are a large number of reactions which we term catalytic for which no very satisfactory explanation had been presented, and the method of the reaction has been "explained" by stating that it was catalytic, which of course does not "explain." Efforts have been made to show how the catalyst actually takes part in the reaction, and the "combination hypothesis" as employed by Dixon is extensively used. This is analogous to the explanation of the electrolytic decomposition of water. We use, however, either an acid or an alkaline solution and obtain hydrogen and oxygen, the constituents of water. In the *catalytic action* of *dilute* acids Kastle and other workers state that the hydrogen ions react first to form addition products, and these subsequently are decomposed into the final products. In the *Friedel and Crafts' reaction* anhydrous aluminium chloride is used as the catalytic agent. The reaction is explained usually by assuming the formation of additive intermediate compounds, which then react to reform the catalytic agent aluminium chloride. The reaction between benzene and ethyl chloride is explained as follows:

$$Al_2Cl_6 + C_6H_6 = Al_2Cl_5 \cdot C_6H_5 + HCl$$

and $$Al_2Cl_5 \cdot C_6H_5 + C_2H_5Cl = Al_2Cl_6 + C_6H_5 \cdot C_2H_5.$$

The aluminium chloride reacts with the benzene, and this intermediate compound then reacts with the ethyl chloride with the reformation of aluminium chloride.

The manufacture of chlorine by the *Deacon Process* is usually explained chemically by assuming the formation of intermediate products. Thus,

$$CuSO_4 + 2\ HCl = CuCl_2 + H_2SO_4$$
$$2\ CuCl_2 = 2\ CuCl + Cl_2$$
$$4\ CuCl + O_2 = 2(CuCl_2 + CuO)$$
$$CuCl_2 + CuO + 2\ HCl = 2\ CuCl_2 + H_2O$$

The copper acting as a carrier of the chlorine, we have the formation of cupric chloride, its decomposition into cuprous chloride with liberation of chlorine, and then its subsequent regeneration in the presence of hydrochloric acid. The explanation that the copper salt is a "contact agent" which aids in attaining the equilibrium $2\ HCl + O_2 \rightleftarrows H_2O + 2\ Cl_2$ is also offered.

Metallic Catalysts. — Platinum in a very fine state is employed in many catalytic processes, and it has been found that numerous other metals as well as their oxides can be employed in a large number of reactions in order to increase the velocity of the reaction to such an extent that it can be carried on under normal conditions (which include lower temperature) with the insurance of a large yield of the desired product and the financial success of the process.

In addition to platinum may be mentioned finely divided indium, palladium, osmium, copper, iron, nickel, cobalt, vanadium, ruthenium, and the oxides of the same; colloidal suspensions of metals have proved excellent catalyzers. Cerium was used as catalyst for combining hydrogen and nitrogen to make ammonia, but iron is extensively used for that purpose. Electrolytic cerium, mixed with about two per cent of potassium nitrate when employed as a catalytic agent for the combination of hydrogen and nitrogen, gave about three times the yield of the untreated cerium. Substances of this type are designated *promoters*. In general, the compounds of the metals of the alkali and the alkaline earths are promoters of catalytic action, as well as the oxides of the rare earth metals tantalum and niobium, as well as silica, while the metalloids, sulphur, selenium, tellurium, arsenic, phosphorus, and easily fusible and easily reducible metals such as zinc, lead, and tin, usually act as *contact poisons*.

There are two of these used in extensive industrial processes which will be considered in some detail. They are platinum in the contact process for the manufacture of sulphuric acid and nickel in the hydrogenation of oils.

The Hydrogenation of Oils. — The addition of hydrogen to oleic acid ($C_{18}H_{34}O_2$) with the formation of stearic acid ($C_{18}H_{36}O_2$) has been one of the problems of the chemist for years. Oleic acid is a liquid and stearic acid is a solid at ordinary temperatures. This fact, in addition to the great abundance of oleic acid, made it desirable to utilize oleic acid as a source of hard fats. Lewkowitsch as late as 1897 states that while the lower members of the oleic acid series can be converted into saturated acids, "oleic acid itself has resisted all attempts at hydrogenation." It was not until about ten years later (1907) that Bedford and Williams published the first description of a method of exposing oil to the action of hydrogen by forming the oil in a spray or film in an atmosphere of hydrogen in contact with a catalyzer of nickel. They converted linseed oil into a hard fat melting at 53°, oleic acid into stearic acid with a melting point of 69°, and the solidifying point of paraffin wax was raised 3°. While this is still the general method employed in the hydrogenation of oils, many detailed mechanical devices have been introduced.

Various catalyzers have been tried, but the one used principally is metallic nickel, and numerous patents have been issued on methods for the preparation of the catalytic agent. An effective nickel catalyzer may be prepared by either igniting nickel nitrate to obtain the oxide, or by precipitating the nickel hydroxide from a sulphate solution by an alkali. This oxide or hydroxide is then reduced by hydrogen at a temperature between 250° and 500° or until water is no longer formed. The lower the temperature at which the reduction takes place, the more sensitive it is; a good working range is between 300° and 350°. The catalyzer is more efficient when the active surface is increased by employing a carrier. So there are employed a large number of carriers and extenders, such as pumice stone, kieselguhr, charcoal, and sawdust. The catalyzer should be protected from the air to prevent oxidation. It is claimed by various investigators that a short period is required for the nickel catalyzer to become acclimated, as it were, before reaching its maximum efficiency or activity, after which there is then a period of decline. The most active period is generally very long, and the period of decline is usually attributed to the action of poisons. For treating liquids, superficially treated or coated carriers are most desirable, while for the hydrogenation of gases or vapors porous impregnated catalyzers are better.

The Mechanism of Hydrogenation. — The methods by which the various catalytic metals transfer the hydrogen during the process of addition or hydrogenation of numerous bodies, as well as the reduction by hydrogen of other bodies, has led to many attempted explanations. The prevalent ones are the adsorption method and the hydride formation. Whether the hydrogen is adsorbed, absorbed, or occluded, there is difference of opinion, as Firth shows that adsorption of hydrogen by wood charcoal takes place in a few minutes, while hours are required for an equilibrium to be realized by absorption. That many metals dissolve hydrogen has been demonstrated by many workers, and in Table XCI are given the volumes of hydrogen under normal conditions that are adsorbed by one volume of the metal.

The adsorption of hydrogen by palladium and by platinum is very pronounced, and the same is true for cobalt, nickel, and iron. The solubility increases with a rise in temperature, and the metals copper, iron, and nickel in the liquid state manifest a very marked increase in solubility with increase in temperature. On solidifying at 1084°, copper gives up twice its volume of hydrogen, iron at 1510° about seven times its volume, and nickel at 1450° about 12 times its volume. They all "spit" when allowed to freeze in an atmosphere of hydrogen.

TABLE XCI — ADSORPTION OF HYDROGEN

(Abegg and Auerbach) Anorganischen Chemie

METAL	VOLUME OF HYDROGEN
Reduced cobalt	59–153
Precipitated gold	37–46
Reduced nickel	17–18
Reduced iron	9.4–19.2
Cast iron	0.57–0.8
Sheet aluminium	1.1–2.7
Magnesium	1.4
Silver powder	0.91–0.95
Reduced copper	0.6–4.8
Copper wire	0.3
Silver powder	0.91–0.95

Contact Process for Manufacture of Sulphuric Acid. — The reaction between sulphur dioxide and oxygen takes place slightly at about 350° to 375° without the aid of a catalyzer; but, in the presence of a catalyst, platinum black, the reaction begins at 325° and the rate of reaction increases so that at about 375° to 450° the sulphur dioxide and oxygen combine readily with practically the theoretical yield of sulphur trioxide. Ferric oxide at higher temperatures is less efficient as a catalyst, while other catalysts, such as ferric oxide containing a little copper oxide, chromium oxide, hot silica, and quartz, are even less efficacious.

According to the law of mass reaction we have, from the equilibrium equation, $2\,SO_2 + O_2 \rightleftarrows 2\,SO_3$, $K_p = \dfrac{p_{SO_3}}{p_{SO_2}\sqrt{p_{O_2}}}$

in which K_p is the equilibrium pressure constant. The values of this constant with increase in temperature are given (by Bodenstein) as follows:

Degree C. .	450	528	579	627	680	727	789	832	897
K_p . . .	188	31.3	13.8	5.54	3.24	1.86	0.956	0.627	0.358

By the use of platinum black as a catalyst the reaction can be noticed at a temperature as low as 200°; the rate of reaction becomes very rapid above 450°. The heat of this reaction is 21.6 calories, and the heat obtained from the rapid formation of SO_3 results in the rise of temperature unless proper provisions are made to keep the temperature constant at about 450° by dilution of gases and absorption of heat, otherwise there will be reversal of the reaction. The values of K_p indicate that the dissociation of the SO_3 increases rapidly with rise of temperature, and a small rise in temperature reduces the yield of SO_3. This reversal of the equilibrium and the inhibiting or poisoning action of the impurities in the gases from the burners used in producing the SO_2 from iron pyrites were two factors which retarded the successful commercial utilization of this method for the manufacture of sulphuric acid.

APPENDIX

To supply the data for numerous problems such as are required for use with large classes necessitates many duplications, and in most lists of problems but few of the same type are given. To multiply these as usually stated requires considerable space, and as this has not been done there is a demand for more illustrative material. We have endeavored to provide this material in the tables compiled in this Appendix, which affords material for the problems illustrating the fundamental principles given in the text.

The principal formulæ have been collected under the different headings, and as supplementary to the subject matter of the text are used to indicate the method of solution of the problems, instead of giving type solutions.

Instead of expressing in words the conditions of a problem, the data have been arranged in tabular form, and the instructor can clothe the data in the form he may desire. This method of presentation has several advantages, one of which is compactness, and another is that the answers appear as one of the terms in the table. For instance, in the Gas Law Equation $pV = nRT$, there are five terms, any one of which may be assumed unknown; with the others known the value of the one unknown is the answer to the specified problem formulated in any appropriate terms.

Another illustration will suffice to represent the general plan of the arrangement and the method of employing the data tabulated. Take the first problem in Table XX, C, page 534, which as stated in the usual manner would read:

The specific conductance of a 5 per cent solution of HCl at 18° is 0.3948 mho. If the equivalent conductance at infinite dilution Λ_∞ is 376, calculate the degree of dissociation. Also calculate the freezing point of the solution. Calculate the vapor pressure.

As tabulated there are the following terms: the specific conductance κ, the per cent composition, the density ρ, the value of Λ_∞, all of which may be considered the known data from which the degree of dissociation α, the freezing point, and the vapor pressure may be calculated, and may be termed the answers.

1. To calculate the degree of dissociation α, Λ_V must first be obtained from V and κ; but V is obtained from ρ and the per cent composition. Now knowing Λ_V and Λ_∞, α is readily calculated.

2. With the data given, the freezing point and the vapor pressure of the solution may be calculated.

Now, considering these answers as part of the given data, other problems which illustrate the principles involved equally as well as the above problems may be formulated, and the answers appear in the table. A few of these may be outlined.

3. Given the vapor pressure and the concentration, calculate the degree of dissociation and the freezing point of the solution.

4. Given the freezing point and the concentration, calculate the degree of dissociation and the vapor pressure of the solution.

5. Select the proper data and calculate the concentration of the solution from the freezing point, the vapor pressure, and the electrical conductance of the solution.

6. Calculate the specific conductance, given the concentration of the solution.

From the data tabulated in these ten problems, we not only have thirty problems on the basis that the values in the last three columns are the answers, but as indicated above, we could have all together over one hundred problems. The same holds for the other tables. We have a great variety offered, with the answers in one of the columns.

Table I

Percentage Composition and Formulæ

The formula of a compound is a combination of symbols that represents the percentage composition of the compound and such that the formula weight in grams of the compound in the gaseous state occupies 22.4 liters of space under standard conditions. If the compound cannot be obtained in the gaseous state, then other facts are used, such as the effect of the compound upon a solvent in lowering the vapor pressure, lowering the freezing point, raising the boiling point. In general, the formula of a compound is obtained by the following rule:

Use the simplest combination of symbols that represents the percentage composition of the compound and agrees with the known facts.

	Percentage Composition			Approximate Wt. of 1 Liter as Gas under Standard Conditions	Calculate Formula
1.	Ba = 58.9	S = 13.7	O = 27.4		$BaSO_4$
2.	Mg = 21.8	P = 27.8	O = 50.4		$Mg_2P_2O_7$
3.	Pb = 64.1	Cr = 16.1	O = 19.8		$PbCrO_4$
4.	K = 16.0	Pt = 40.4	Cl = 43.6		K_2PtCl_6
5.	C = 64.9	H = 13.5	O = 21.6	3.33 g.	$(C_2H_5)_2O$
6.	C = 54.5	H = 9.1	O = 36.4	3.96	$CH_3CO_2C_2H_5$
7.	C = 92.4	H = 7.6		3.51	C_6H_6
8.	C = 77.5	H = 7.5	N = 15.0	4.19	$C_6H_5NH_2$
9.	C = 62.1	H = 27.6	O = 10.3	2.62	CH_3COCH_3
10.	C = 22.7	H = 6.6	As = 70.7	4.87	$(CH_3)_2AsH$
11.	C = 28.1	O = 37.5	Ni = 34.4	7.70	$Ni(CO)_4$
12.	C = 38.8	H = 8.2	Zn = 53.0	5.54	$Zn(C_2H_5)_2$

TABLE II

The Gas Law Equation

The Gas Law Equation $pV = nRT$ which expresses the relationship of the mass, pressure, temperature, and volume of a gas may be utilized in solving problems involving these variables.

For a given gas we then have

$$pV = nRT, \text{ or } pv = rT, \text{ in which } R = mr \text{ and } n = \frac{g}{m}$$

$$\frac{g}{V} = \rho \text{ and } \frac{\rho}{\rho_s} = s$$

(*a*) Or if any three of the values g, V, T, and p are known, the other may be calculated.

(*b*) For a constant mass of gaseous substances which would occupy a volume of V, at the temperature t, and pressure p, either V_2, t_2, or p_2 may be readily obtained if the other two are known.

The data for problems given in the following tables are arranged so that the values describing the conditions under which the gas exists are designated by the same subnumbers.

In Table II problems might read:

1. What will be the volume of — grams of — at 20° C. and under a pressure of 750 mm.?

2. At what temperature will — grams of — occupy a volume of — liters under a pressure of 750 mm.?

3. Under what pressure will — g. of — occupy a volume of — liters at temperature t?

4. How many grams of — will be required to occupy a volume of — liters at 20° C. under a pressure of 750 mm.?

Or these same problems, assuming that the condition designated by the subscript 1 are known, *1.* To what t_2 must the gas be raised so that it will occupy a volume V_2 at the pressure p_2?

2. If the gas is heated to a temperature t_2, what volume will it occupy, V_2, if the pressure is p_2?

3. To what pressure must the gas be subjected so that its volume will be V_2 at t_2?

Or the values indicated by the subscript 2 may be assumed to be the known values and in the manner just indicated the values marked by the subscript 1 calculated.

Substance	Grams	p_1	V_1 Liters *	t_1	p_2	V_2 Liters	t_2
1. Methane	0.163	745 mm.	250 cc.	20°	760 mm.	29.1 cc.	75°
2. Ammonia	8.20	750 mm.	12	27	740 mm.	15.1	100
3. Sulphur dioxide	1.018	740 mm.	500 cc.	100	755 mm.	42.1 cc.	47
4. Argon	15.8	5 atmos.	2	35	25 atmos.	3.74	15
5. Oxygen	20.9	2 atmos.	10	100	15 atmos.	2.76	500
6. Hydrochloric acid	164.6	5 atmos.	35	200	2 atmos.	74.0	127
7. Nitrogen	0.2713	725 mm.	250 cc.	27	755 m.	298 cc.	100
8. Hydrogen	1.211	725 mm.	15	15	545 m.	18.0	−13
9. Carbon dioxide	1.275	742 mm.	750 cc.	35	760 m.	130.8 cc.	277
10. Air	17.5	755 mm.	15	17	275 m.	49.4	87

Table III

The Gas Law Equation

Substance	g_1	p_1	V_1 Liters	t_1	g_2	p_2	V_2 Liters	t_2
1. Air	12.02	1 atmos.	10	20°	30.05	25 atmos.	10	20°
2. Air	83.9	3.5 atmos.	20	21	121.0	5 atmos.	20.2	21
3. Hydrogen	22.55	745 mm.	300	45	16.6	745 mm.	200	15
4. CO_2	9.13	750 mm.	5	17	10.5	800 mm.	5.5	20

Types. — Given mass at p_1 T_1 V_1, find change in one term when changes in other three are known.

* Volume in liters unless otherwise specified.

TABLE IV

The Specific Gas Constant

Given the weight of one liter of the following gases, calculate the specific gas constant, r, and express the same in liter-atmospheres per degree and in gram-centimeters per degree:

GAS	WEIGHT OF 1 LITER IN GRAMS	r	
		In Gram-cm. per Degree	In Liter-atmos. per Degree
Nitrogen	1.2514	3025	.00292
Argon	1.782	2124	.00205
Hydrochloric acid . . .	1.6398	2310	.00223
Nitric oxide	1.340	2825	.00273
Sulphur dioxide	2.9266	1293	.00125
Oxygen	1.429	2652	.00256

TABLE V

Specific Gravity and the Specific Gas Constant

Given the specific gravity of the following gases, calculate the specific gas constant, r, and express as in preceding:

GAS	SPECIFIC GRAVITY (AIR = 1)	r	
		In Gram-cm. per Degree	In Liter-atmos. per Degree
1. Xenon	4.526	647.5	.000626
2. Chlorine . . .	2.491	1177.0	.001137
3. Ethane	1.0494	2790.0	.00270
4. Arsine	2.696	1087.0	.001050
5. Methane . . .	0.5576	5255.0	.00508

Table VI

Molecular Weight and Formula

Calculate the molecular weight or obtain the formula. These may all be solved from $pV = nRT$ and $n = \frac{g}{m}$.

Substance	Weight	V_1	p_1	t_1	m
1. Acetone	0.1845	81.5 cc.	732.3	26.8°	57.8
2. Ether	0.6520	244.2	747.3	59.8	74.2
3. Benzene	0.6550	242.1	754.4	76.0	77.9
4. Chloroform	0.6111	147.2	754.6	72.6	118.5
5. Ethyl alcohol	0.1390	76.5	735.6	27.2	46.2
Percentage Composition					Formula
1. C = 92.3 H = 7.7 . .	0.1123	36.0	741.2	24.8	C_6H_6
2. C = 62.07 O = 27.59 H = 10.34	0.5535	272.0	761.4	76.8	CH_3CH_2CHO
3. C = 62.1 O = 27.6 H = 10.3	0.788	255.6	754.5	180	$C_5H_7O_2CH_3$
4. C = 83.73 H = 16.27 .	0.6590	232.5	759	98.6	C_6H_{14}
5. C = 10.05 H = 0.85 Cl = 89.1	1.039	252.5	760.9	78.2	$CHCl_3$

Table VII

Dissociation of Gases

By employing the Mass Law Equation and Dalton's Law, together with the equations $m = s \times m_s$ and $\alpha = \frac{s - s_1}{s_1(f - 1)}$, calculate the degree of dissociation and the final partial pressures. Then from the gas equation $pV = nRT$ calculate the final concentrations.

Dissociation of PCl_5 *under Atmospheric Pressure*

Temp.	s (air)	α	Partial Pressures Atmospheres		Concentrations Moles per Liter	
			PCl_5	PCl_3 and Cl_2	PCl_5	PCl_3 and Cl_2
1. 182	5.08	0.417	0.4110	0.2945	0.0110	0.0079
2. 190	4.99	0.443	0.3860	0.3070	0.0102	0.0081
3. 200	4.85	0.485	0.3470	0.3265	0.0089	0.0084
4. 230	4.30	0.675	0.1940	0.4030	0.0047	0.0098
5. 250	4.00	0.800	0.1111	0.4444	0.0026	0.0104
6. 274	3.84	0.875	0.0667	0.4665	0.0015	0.0104
7. 288	3.67	0.962	0.0194	0.4903	0.0004	0.0107
8. 300	3.65	0.973	0.0137	0.4931	0.0003	0.0105

Table VIII

Gaseous Equilibrium

Equilibrium equations involving problems of the type when a given mass of gas occupies a specified volume at a certain pressure and temperature to calculate degree of dissociation and partial pressures.

Equilibrium Equation	Grams	V_1 Liters	p_1	t_1	ρ g. per Liter	α	Partial Pressures		
							p_1	p_2	p_3
								NH_3	CO_2
1. $NH_4CO_2NH_2$ (solid) $\rightleftarrows$ $2\ NH_3 + CO_2$	6.71	8.8	745	180	0.763	0.85		496.8	248.4
							N_2O_4	NO_2	
2. $N_2O_4 \rightleftarrows 2\ NO_2$	3.29	6.65	182.7	49.7	0.495	0.69	33.5	149.2	
	1.30	855 cc.	497.8	49.7	1.527	0.49	170.3	327.5	
	0.762	12.0	26.8	49.7	0.0635	0.93	0.97	25.83	
							NO_2	NO	O_2
3. $2\ NO_2 \rightleftarrows 2\ NO + O_2$	2.18	2.35	737.2	279	0.928	0.130	602.2	90	45
	4.05	7.25	742.5	494	0.559	0.565	251.7	327.2	136.6

TABLE IX

Dissociation of NH_4HS

Assuming NH_4HS to be a solid and the part vaporized to be completely dissociated:

1. From the mass V and t calculate the partial pressures.
2. Now by introducing a given mass of one of the products of dissociation compute the partial pressures and the percentage of the original NH_4HS which remains dissociated.
3. Calculate the specific gravity with respect to air of each of the mixtures.

REACTION	MASS IN GRAMS	V LITERS	t	GRAMS ADDED		PARTIAL PRESSURES		PER CENT DISSOCIATED α	$s_{(AIR)}$
				NH_3	H_2S	NH_3	H_2S		
$NH_4HS \rightleftarrows$		2	25.1°	0	0	251.8	251.8	100	0.534
(solid)	1.382				1.17	318	458	54.9	0.745
$NH_3 + H_2S$				0.495		417	146	59.2	0.508
					0.315	208	294	84.2	0.570

TABLE X

Dissociation of Hydriodic Acid

Assume that one mole of the original substance taken and that when equilibrium is established x moles have been dissociated. Since one mole is assumed, the value of x is the same as α, the degree of dissociation, and from any number of moles, n, the number of moles dissociated, x, would equal αn. The equilibrium equation for the dissociation of hydriodic acid is $2\ HI \rightleftarrows I_2 + H_2$ or $HI = \frac{1}{2}\ I_2 + \frac{1}{2}\ H_2$. Show that the dissociation constant is $k_1 = \dfrac{\alpha^2}{4(1 - \alpha)^2}$ and

$k_2 = \dfrac{\alpha}{2(1 - \alpha)}$ respectively. The equilibrium equation for the dissociation of N_2O_4 is $N_2O_4 \rightleftarrows 2\ NO_2$ or $\frac{1}{2}\ N_2O_4 \rightleftarrows NO_2$. Show that the dissociation constant is $k_1 = \dfrac{4\ \alpha^2}{1 - \alpha}$ and $k_2 = \dfrac{2\ \alpha}{(1 - \alpha)^2}$ respectively, in which one is the square root of the other.

From the following data for hydriodic acid calculate the degree of dissociation α, or the equilibrium constant k_2 at the different temperatures, assuming that the value of α is known:

t	α	k_2
520	0.245	0.162
500	0.238	0.156
480	0.232	0.152
460	0.225	0.145
440	0.219	0.141
420	0.213	0.135
400	0.208	0.132
380	0.202	0.127
360	0.197	0.122
340	0.192	0.119

Table XI

The Law of Mass Action and Gaseous Equilibrium

Whitaker and Rittman (*Jour. Ind. Eng. Chem.*, *6*, 383 (1914)), give the following practical illustration of the significance of equilibrium conditions in the manufacture of blue water gas. Assume a theoretically ideal mixture consisting of 50 per cent H_2 and 50 per cent CO. Pass the two gases through a chamber heated to 700° C. (1290° F.) until they reach the equilibrium at this temperature; what are the resulting gases? K at this temperature is in the neighborhood of 0.32.

$$3\ CO + H_2 = CO_2 + H_2O + 2\ C + 67750 \text{ cal.}$$

Under equilibrium conditions

$$\begin{aligned} \text{Let } x &= \text{volume } CO_2 \\ \text{then } x &= \text{volume } H_2O \\ 0.5 - x &= \text{volume } H_2 \\ 0.5 - 3\,x &= \text{volume } CO \\ \hline \therefore 1 - 2\,x &= \text{total final volume} \end{aligned}$$

$$\frac{x}{1 - 2\,x} = p_{CO_2} \qquad \frac{0.5 - x}{1 - 2\,x} = p_{H_2}$$

$$\frac{x}{1 - 2\,x} = p_{H_2O} \qquad \frac{0.5 - 3\,x}{1 - 2\,x} = p_{CO}$$

$$K = \frac{p_{CO_2} p_{H_2O}}{p^3_{CO} p_{H_2}} = \frac{2\,x^2(1 - 2\,x)}{(0.5 - 3\,x)^3} = 0.32$$

Solving, $x = 0.069 = 6.9$ per cent

$2\,x =$ gas lost in reaction $= 13.8$ per cent

$$\frac{x}{1 - 2\,x} = \frac{0.069}{0.862} = 8 \text{ per cent } CO_2$$

$$\frac{x}{1 - 2\,x} = \frac{0.069}{0.862} = 8 \text{ per cent } H_2O$$

$$\frac{0.5 - 3\,x}{1 - 2\,x} = \frac{0.293}{0.862} = 34 \text{ per cent } CO$$

$$\frac{5 - x}{1 - 2\,x} = \frac{0.431}{0.862} = 50 \text{ per cent } H_2$$

I. From the principles illustrated in the solution of the problem above, apply these to a mixture of 1000 cubic feet each of carbon monoxide and hydrogen, assuming that no hydrocarbons are formed and that there is a net loss of 13.8 per cent due to the reaction; what is the number of cubic feet of the gaseous constituents and the number of pounds of carbon formed? What is the percentage composition of the permanent gas and how many cubic feet of the original constituents remain?

II. If 1 liter of carbon dioxide is passed over carbon heated at 600°, calculate the composition of the resulting mixture assuming the reaction to be $CO_2 + C = 2\,CO$.

$$K_{P_{600}} = \frac{(CO)^2}{CO_2} = 0.1$$

Let $2x$ = volume of CO
$1 - x$ = volume of CO_2

$1 + x$ = final volume

Ans. Final volume = 1.156 liter
volume CO = 0.312 liter
percentage CO = 26.99
percentage CO_2 = 73.01

III. If 1 liter of CO forms CO_2 and carbon at 750°, calculate the percentage composition of the resulting mixture and the degree of dissociation. $K_P = \frac{(CO)^2}{CO_2} = 3.94$

Ans. Percentage dissociation = 0.27 Percentage CO = 77.3
Percentage CO_2 = 22.7

IV. Ethylene dissociates into acetylene and hydrogen. The values for the equilibrium constant $K_P = \frac{C_2H_2 \cdot H_2}{C_2H_4}$ at the temperatures 600°, 750°, and 900° C. are 0.00018, 0.0093, and 0.0178 respectively. Calculate the volume of acetylene and the total gas volume at the different temperatures.

		600°	750°	900°
Ans.	Volume of acetylene . . .	0.01342	0.09602	0.1323
	Total volume	1.01342	1.09602	1.1323

V. If 0.5 liter of NO and 0.5 liter of O_2 are allowed to come to equilibrium at 2195° C., find the percentage composition of the mixture.

$$K_P = \frac{p_{NO}}{p^{\frac{1}{2}}_{O_2}\, p^{\frac{1}{2}}_{N_2}} = 0.0242$$

Ans. Degree of dissociation α = 0.0119 NO = 1.19 per cent
O_2 = 20.4 per cent
N_2 = 77.4 per cent

VI. The percentage composition of mixtures of N_2, H_2, and NH_3 is given in the following table:

Temp.	Volume Per Cent of		
	H_2	N_2	NH_3
27°	2.76	0.92	96.32
327	73.75	24.58	1.67
627	74.97	24.99	0.039
930	75.00	25.00	0.0065

Calculate K_P at 27° C. and at 930°. Why is not 27° used in technical practice?

$$K_P = \frac{p_{NH_3}}{p^{\frac{1}{2}}_{N_2} p^{\frac{3}{2}}_{H_2}}$$

Ans. 27 $K_P = 2.19 \times 10^3$
930 $K_P = 2.00 \times 10^{-4}$

VII. Derive an equation showing how the degree of dissociation of ammonia may be calculated at any other pressure if K_P at one pressure for a given temperature is known. K_P at 930° under 1 atmosphere is 2.00×10^{-4}. Calculate α the degree of dissociation for 930° at 100 and at 200 atmospheres. $2\ NH_3 = N_2 + 3\ H_2$

Ans. $\alpha = 0.9875$ at 100 atmos.
$\alpha = 0.9753$ at 200 atmos.

VIII. In the formation of SO_3 according to the equilibrium equation $SO_2 + \frac{1}{2} O_2 \rightleftarrows SO_3$, calculate the ratio $\frac{SO_3}{SO_2}$ if the partial pressures of the oxygen in the initial mixture of SO_2 and O_2 are respectively 0.25, 0.50, 1.00, 2.00, and 3.00 atmospheres.

$$K = \frac{p_{SO_3}}{p_{SO_2} p^{\frac{1}{2}}_{O_2}} = 100$$

Assume $\frac{SO_3}{SO_2} = x$ and solve.

Ans. 50, 70.7, 100, 141, 173.

IX. The following are the values of $K_P = \frac{p_{SO_3}}{p_{SO_2} p^{\frac{1}{2}}_{O_2}}$ from Bodenstein's measurements for the reaction
$SO_3 \rightleftarrows SO_2 + \frac{1}{2} O_2$. Calculate the degree of dissociation, α, for the values of K_P.

Temp.	K_P	Ans. α
528	31.3	0.119
579	13.8	0.192
627	5.54	0.313
680	3.24	0.403
727	1.86	0.516
789	0.956	0.653
832	0.627	0.713
897	0.358	0.807

In order to calculate the degree of dissociation, first assume values of α and calculate K_P. Now plot these values of α against K_P on a very large scale about two by three feet. From the curve obtain the values of α which correspond to the given values of K_P at the designated temperature. The following table illustrates the assumed values of α which may be selected with the corresponding value of K_P:

Assumed Values of α	K_P	Assumed Values of α	K_P
.1	40.26	.5	2.00
.12	29.95	.6	1.22
.15	20.68	.7	0.723
.2	12.65	.8	0.395
.3	6.03	.9	0.166
.4	3.36		

Table XII

Surface Tension and Association Factors

1. By employing the equation $\gamma = \frac{gr\rho h}{2}$ the value for any one term may be calculated, providing the others are known. The values of these terms are given in Table XIII, from which calculate γ.

2. The constant of the equation $\gamma(mV)^{\frac{2}{3}} = k_1(\tau - d)$ (where $\tau = t_c - t$, $d = 6$) is required in order to calculate the association factor x (from the equation $x = \left(\frac{2.12}{k_1}\right)^{\frac{3}{2}}$), and k_1, which has a value of 2.12 for normal liquids, is obtained by solving two simultaneous equations for different temperatures. In the table are given the data at a number of different temperatures, from which calculate the value for k_1, then calculate the association factor.

Tate's Law is $\gamma = kw$, in which w is the weight of a drop of the liquid and k is a constant for a given tip of the capillary tube from which the liquid drops. In calculating the association factor from the falling drop data, the same general formula as was used above is employed; but instead of 2.12, the constant for normal liquids, the constant k_w, obtained from the following relation, must be employed, $\gamma : w :: 2.12 : k_w$. Solving, we have $k_w = \frac{2.12\ w}{\gamma}$. Calculate the association factor, using the weight of the drop.

3. The capillary constant or the specific cohesion is represented by a^2, and by definition we have $a^2 = rh$. From the equation $\gamma = \frac{grh\rho}{2}$, we then have, since $g = 981$, $\gamma = \frac{981\ a^2\rho}{2}$, and when a^2 is expressed in millimeters we have $\gamma = \frac{a^2\rho}{0.204}$,

or $a^2 = \frac{0.204\ \gamma}{\rho}$. Calculate the values for a^2 from the data in the accompanying table.

Table XIII

Relation of Latent Heat of Vaporization and a^2, and Trouton's Law

Substance		ρ	t	Weight of Drop mg.	γ	h cm.	r cm.	Association Constant a	a^2 mm²
1. Acetone . . .		0.80177	15.0°	25.674	23.49	3.100	0.0193	1.34	5.99
B. Pt.	56.5°	0.78348	30.1	23.610	21.64	2.917		1.24	5 63
L_V	125.3 cal.	0.74962	60.0	19.642	17.97	2.539			4.90
2. Acetonitrile . .		0.7929	10	32.545	29.50	4.120	0.01843	1.78	7.6
B. Pt.	80.5°	0.7607	40	28.385	25.73	3.741		1.97	6.9
L_V	173.6 cal.	0.7500	50	27.015	24.50	3.618			6.67
3. Benzaldehyde .									
B. Pt.	179.9°	1.0349	30.2	42.358	37.42	4.843	0.01522	1.22	7.38
L_V	86.6 cal.	1.0169	50.0	39.914	35.27	4.650		0.90	7.08
4. Benzene . . .		0.8043	90	21.40	19.225	3.772	0.01294	1.00	4.88
B. Pt.	80.3°	0.8171	78	23.06	20.75	2.810	0.01843		5.18
L_V	93.5 cal.	0.8565	41	28.08	25.27	3.122	0.0193		6.026
5. Hexane . . .									
B. Pt.	70.0°	0.67795	0.0	22.404	20.7	3.995	0.0156	0.89	6.232
L_V	79.4	0.65213	30.0	19.152	17.5	3.490			5.449
6. Prophyl alcohol .		0.8035	20	26.046	23.01	4.108	0.01425	2.35	5.85
B. Pt.	97.3°	0.7875	40	24.274	21.45	3.919		2.40	5.58
L_V	166.3 cal.	0.7700	60	22.503	19.88	3.688			5.26
7. Water		0.99987	0.0	84.325	75.87	12.00	0.0129	2.88	15.49
B. Pt.	100°	0.99913	15.0	81.643	73.50	11.62	0.0129	2.81	15.03
L_V	535.8 cal.	0.99567	30.0	78.940	71.03	11.29	0.0129	2.81	14.57
		0.98324	60.0	73.148	65.80	9.58	0.01425	2.68	13.65
		0.97781	70.0	71.068	63.97	9.37	0.01425		13.34

Walden showed that the latent heat of vaporization, L_V, divided by a^2, is a constant, *i.e.* $\frac{L_V}{a^2} = 17.9$. In the table the necessary data are given so that the constant can be calculated, or either of the values may be calculated by assuming the others known. It will be observed that the values in this table are not the constant value 17.9, but if the value found from the latent heat of vaporization and a^2 be divided by the constant, the result is a value that approximates very closely to that given for the association factor in the last

Substance	Boiling Point	L_V Cal.	a^2	$\frac{L_V}{a^2}$	$\frac{mL_V}{T_V}$	Association Factor	
						$\frac{L_V}{17.9\,a^2}=x$	$\left(\frac{2.12}{k_1}\right)^{\frac{3}{2}}=x$
1. Carbon tetrachloride	76.2°	46.4	2.59	17.9	20.4	1.00	1.01
2. Carbon bisulphide	46.2	86.67	4.90	17.7	20.6	0.99	1.07
3. Chloroform	60.9	58.4	3.20	18.2	20.8	1.02	1.03
4. Ether	34.8	84.5	4.72	17.9	20.4	1.00	0.99
5. Ethyl iodide	71.3	46.0	2.58	17.8	20.8	0.99	0.96
6. Phosphorus chloride	78.5	51.42	2.67	19.2	20.1	1.07	1.02
7. Acetone	56.6	125.38	5.00	25.2	22.1	1.41	1.26
8. Acetonitrile	81.5	170.6	5.93	29.4	20.4	1.64	1.67
9. Allyl alcohol	96.5	163.3	4.88	33.5	25.6	1.87	1.86
10. Aniline	183.0	113.9	5.73	19.9	20.8	1.11	1.05
11. Chlorbenzene	130.0	74.24	4.02	18.4	20.7	1.08	1.03
12. Ethyl alcohol	78.2	216.5	4.74	45.8	28.4	2.56	2.43
13. Methyl alcohol	60.0	269.4	4.33	61.7	25.4	3.45	3.43
14. Methyl ethyl ketone	79.5	103.8	4.65	22.3	21.2	1.24	1.15
15. Methyl propyl ketone	94.0	88.7	4.63	19.2	20.8	1.07	1.06
16. Nitrobenzene	151.5	79.2	5.32	14.9	23.0	0.83	1.13
17. Propionitrile C_2H_5CN	97.2	134.4	5.24	25.7	20.0	1.43	1.57
18. Propyl alcohol	97.3	166.3	4.66	35.7	27.0	1.98	2.40
19. Water	100.0	535.8	12.41	43.2	25.9	2.41	2.68

column. So the values for the association factor obtained from the formula $\frac{L_V}{17.9\,a^2} = x$ are given in the next to the last column.

Trouton's Law is $\frac{mL_V}{T_V} = 20.6$, in which m is the molecular weight; L_V, the latent heat of vaporization; and T_V, the temperature on the Absolute scale at which the heat of vaporization was determined. The boiling point under 760 mm. pressure is usually given in the formula. The value of the constant can be calculated if the other values are given, or assuming all values known but one, this may be calculated.

Table XIV

Construction of Temperature-Concentration Diagrams

From the data for each of the following systems, plot the *liquidus* and *solidus* curves on a temperature-concentration diagram, and draw the horizontals at the transition points and at the eutectic points. Indicate the solid phase separating along each liquidus curve, and the components of the systems in equilibrium in the various areas into which the curves divide the diagram.

System	Melting Points	Composition Weight Per Cent *	Solid Phase Separating
1. Mg – Bi . . .	650.9°	0	
	552	65	Eutectic composed of Mg – Mg_3Bi_2
	715	85	Mg_3Bi
	268	100	
2. Au – Sb . . .	1064	0	
	360	25	Eutectic Au – $AuSb_2$
	460	55	$AuSb_2$
	631	100	
3. Bi – Te . . .	267	0	
	261	2	Eutectic Bi – Bi_2Te_3
	573	48	Bi_2Te_3
	388	85	Eutectic Bi_2Te_3 – Te
	428	100	

* The value in this column is the per cent of the member of the system named last.

System	Melting Points	Composition Weight Per Cent	Solid Phase Separating
4. Cu – Mg . .	1084	0	
	730	9	Eutectic Cu – Cu_2Mg
	797		Cu_2Mg
	555	33	Eutectic Cu_2Mg – $CuMg_2$
	570		$CuMg_2$
	485	68	Eutectic $CuMg_2$ – Mg
	650	100	
5. Si – Mg . . .	1408	0	
	950	42.5	Eutectic Si – Mg_2Si
	1102		Mg_2Si
	646	96	Eutectic Mg_2Si – Mg
	661	100	
6. $NaNO_3$ – KNO_3	308	0	Eutectic consists of two solid solutions containing 20 and 87 per cent of KNO_3 respectively
	218	52	
	339	100	
7. Au – Sn . .	1064	0	
	280	20	Eutectic: solid solution 5 per cent Sn — AuSn
	440		AuSn
			$AuSn_2$ transition point
	309		
	252		$AuSn_4$ transition point
	217	90	Eutectic $AuSn_4$ – pure Sn
	232	100	
8. Au – Co . .	1064	0	
	997	10	Eutectic: two solid solutions containing 5 and 97 per cent of Co respectively
	1493	100	

System	Melting Points	Composition Weight Per Cent	Solid Phase Separating
9. $Li_2SiO_3 - BaSiO_3$	1169 880 1490	0 58 100	Eutectic consists of two solid solutions containing 16 and 84 per cent of $BaSiO_3$ respectively
10. $PbF_2 - PbCl_2$	824 570 554 601 454 495	0 24 90 100	 $4\,PbF_2 \cdot PbCl_2$ — transition point Eutectic: $4\,PbF_2 \cdot PbCl_2$ and solid solution containing 42 per cent $PbCl_3$ $\cdot\, PbF_2 \cdot PbCl_2$ Eutectic: solid solutions containing 53 per cent and 97 per cent $PbCl_2$ respectively

Table XV

Index of Refraction

From the data in the following table calculate the molecular refractivity by the Gladstone-Dale formula and also by the n^2 formula, from which the values given in the table were obtained.

Then compare these values with those obtained by calculating the molecular refractivity by employing the atomic refractivities given in Table XIX, page 127.

Given the experimental value for the index of refraction, n, for toluene and the atomic refractivities, calculate the number of double bonds.

Similarly, the structural relation of compounds containing oxygen may be ascertained by determining whether the oxygen has the value for carbonyl oxygen, hydroxyl oxygen, etc., and from this determine whether the compound is a ketone, alcohol, etc. Or, assuming the value for one element to be unknown, calculate its atomic refractivity from the other known values.

The molecular refractivity for either the D line or for the hydrogen line may be calculated. By calculating both of these values the molecular dispersion may be obtained.

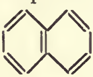
	$\rho_{4°}$	n	Line	Temp.	Molecular Refraction
1. Cymene	0.8619	1.4926	D	13.7	45.18
$CH_3 \cdot C_6H_5 \cdot CH(CH_3)_2$.		1.5111	Hγ		46.62
2. Naphthalene	0.9621	1.58232	D	98.4	44.46
 $C_{10}H_8$		1.57456	Hα		43.97
3. Toluene	0.8707	1.4992	D	14.7	31.06
$C_6H_5 \cdot CH_3$		1.4944	Hα		30.80
4. Acetophenone	1.0293	1.53427	D	19.1	36.28
$C_6H_5 \cdot CO \cdot CH_3$		1.52837	Hα		35.95
5. Benzaldehyde	1.0455	1.54638	D	20	32.15
$C_6H_5 \cdot CO \cdot H$		1.57749	Hγ		33.64
6. Methyl ethyl ketone . .	0.8087	1.38071	D	15.9	20.67
$CH_3 \cdot CO \cdot C_2H_5$		1.37844	Hα		20.56
7. *n*-Butyric acid	0.9587	1.39789	D	20	22.16
$CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$					
8. *i*-Butyric acid	0.9490	1.39300	D	20	22.15
$\begin{matrix}CH_3\\CH_3\end{matrix}\rangle CH \cdot COOH$ . .					
9. Ethyl acetate	0.9007	1.37257	D	20	22.25
$CH_3COOC_2H_5$					
10. Methyl propionate . .	0.9166	1.37767	D	18.5	22.13
$CH_3 \cdot CH_2 \cdot COOCH_3$ . .					
11. Benzal alcohol	1.0456	1.53938	D	22.1	32.41
$C_6H_5 \cdot CH_2 \cdot OH$					
12. *n*-Butyl alcohol	0.8099	1.39909	D	20	22.13
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$					
13. Ethyl alcohol	0.8000	1.36232	D	20	12.78
$C_2H_5 \cdot OH$		1.36997	Hγ		13.02
14. Ethyl trichloracetate . .	1.3826	1.45068	D	20	37.25
$CCl_3COOC_2H_5$		1.44802	Hα		37.06
15. Propargyl alcohol	0.9715	1.43064	D	20	14.92
$CH \vdots C \cdot CH_2 \cdot OH$ . .		1.44277	Hγ		15.28
16. *n*-Propyl alcohol	0.8044	1.38543	D	20	17.52
$CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$ . .		1.39378	Hγ		17.85

TABLE XVI

Calculation of Osmotic Pressure

Calculate the osmotic pressure from the data given in the following table. Or, assuming the osmotic pressure known, calculate the apparent molecular weight, m_A, and then the degree of dissociation, α.

For additional problems see tables of data, page 534.

SOLVENT	SOLUTE	CONCENTRATION	P_O IN ATMOS.	α	m_A
		grams in 1000 cc. solution			
H_2O . .	Cane sugar				
$t = 0°$ . .	$C_{12}H_{22}O_{11}$	2.02	0.134		337.5
		20.	1.32		339.
		93.75	6.18		339.5
		300.	26.8		250.4
		750.	134.7		124.5
		n in 80 liters			
H_2O . .	K_2SO_4	5.0	2.82	.449	91.9
$t = 17°$. .		4.0	2.19	.415	94.7
		3.0	1.705	.456	91.3
		2.0	1.01	.35	102.4
		1.0	0.66	.610	78.5
		n in 160 liters			
H_2O . .	K_4FeCN_6	8.0	3.44	.473	127.5
$t = 17°$. .		4.0	1.92	.5565	114.1
		2.5	1.27	.6045	107.9
		2.0	0.95	.549	115.4
		1.0	0.50	.591	109.4
		1 mole in 20 liters			
H_2O . . .	KNO_3		1.68	.414	71.5
$t = 17°$. .	$NaNO_3$		1.79	.51	56.5
	NH_4NO_3		1.48	.245	64.3
	$Mg(NO_3)_2$		2.12	.391	83.3
	$Ca(NO_3)_2$		1.67	.202	116.9
	$Sr(NO_3)_2$		1.58	.165	158.9
	$Ba(NO_3)_2$		2.04	.359	152.0

Table XVII

Osmotic Pressure, — Comparison of Normal Weight and Normal Volume Concentrations

Check the values for ρ_0 in the following table by interpolation from density tables of sugar solutions such as given in Landolt and Börnstein's *Tabellen*. Then express the concentration in moles per liter (molal volume concentration) and in moles per 1000 grams of solvent (molal weight concentration). Calculate the osmotic pressure, using each of these values for the concentration and ascertaining which set of results conforms more nearly to the observed values.

Grams in 1 Liter of Solution	ρ_0	Osmotic Pressure in Atmospheres						
		Observed	Calculated Values					
		Berkeley & Hartley's	Conc. Molal Volume n	p_0 in Atmos.	Conc. Molal Weight n	p_0 in Atmos.	Assuming both Association Hydration
10.0	1.0000	0.66	0.02922	0.654	0.02952	0.661	0.663
45.0	1.0180	2.97	0.1315	2.94	0.1354	3.025	3.07
150.8	1.0597	11.80	0.4405	9.86	0.4847	10.85	11.4
180.1	1.0713	13.95	0.5262	11.8	0.5904	13.22	14.0
420.3	1.1634	43.97	1.228	27.5	1.652	37.0	43.7
540.4	1.2086	67.51	1.579	35.35	2.364	52.9	68.0

The data in this table may also be employed in the calculation of the osmotic pressure by the modified formula (page 363) wherein correction is made for association of the solvent and hydration of the solute. On the basis that the association factor of water is $x = 1.65$, calculate the osmotic pressure on the normal weight basis, then calculate the value of the osmotic pressure, assuming the hydration is $C_{12}H_{22}O_{11} \cdot 6\ H_2O$, and then calculate the osmotic pressure, assuming both hydration and association. The values are given in the last column in the table.

Table XVIII

Vapor Pressure Calculations

In order to determine the molecular weight from the lowering of the vapor pressure Raoult's modified formula for the vapor pressure is used:

$$\frac{p - p_1}{p} = \frac{\frac{g}{m_A}}{\frac{S}{m} + \frac{g}{m_A}}$$

Solving $$m_A = \frac{mgp_1}{S(p - p_1)}$$

Since $i = \dfrac{m}{m_A}$, solve for i.

Since $\alpha = \dfrac{i - 1}{(f - 1)}$, solve for α.

The following data are for aqueous solutions wherein 100 grams of the solvent were employed in each case. The vapor pressure of water at 0° C. is 4.62.

Solute	Grams	Vapor Pressure of Solution p_1	m_A
Cane sugar	3.971	4.612	412
$t = 0°$	8.72	4.600	361
$C_{12}H_{22}O_{11}$	17.31	4.579	348
	33.89	4.533	318
	68.2	4.439	301
Urea	0.810	4.611	74.7
$CO(NH_2)_2$	1.614	4.603	78.7
$t = 0°$	2.964	4.586	71.9
	5.976	4.550	69.9
	12.0	4.485	71.7
	24.0	4.356	71.5
	36.0	4.212	67.0
	60.0	3.968	65.7

Solute	t	Vapor Pressure of Solvent p	Vapor Pressure of Solution p_1	a	m_A
Sodium chloride	19.14	16.61	14.4	1.474	23.6
NaCl	32.07	35.88	31.1	1.483	23.5
g = 20.08 gr.	41.24	59.29	51.3	1.518	23.2
	50.00	92.54	79.6	1.625	22.3
	59.99	149.46	129.7	1.465	23.7
	69.37	227.79	196.7	1.555	22.9
	79.50	348.34	300.3	1.583	22.6
	89.72	520.04	449.7	1.533	23.1
	95.12	636.34	553.4	1.423	24.1
Potassium chloride	14.2	12.15	11.2	0.755	42.5
KCl	25.6	24.63	22.2	1.260	33.0
g = 20.04	29.7	31.29	28.4	1.100	35.5
	40.5	56.83	51.3	1.236	33.5
	49.7	91.18	83.1	1.010	37.1
	60.9	155.8	140.7	1.220	33.6
	68.9	222.9	201.1	1.240	33.3
	77.2	317.0	287.5	1.120	35.2
	85.4	440.6	399.3	1.138	34.9
	94.7	627.0	570.1	1.060	36.2
Calcium chloride	17.5	15.0	13.5	1.219	32.38
$CaCl_2$	29.3	30.58	26.9	1.609	26.31
g = 19.99	39.5	53.88	47.1	1.720	25.00
	50.2	93.47	81.6	1.744	24.74
	74.2	279.8	245.8	1.636	25.99
g = 15.10	20.3	17.87	16.2	1.605	26.37
	31.2	34.09	30.9	1.608	26.33
	44.1	68.64	62.6	1.469	28.18
	56.8	128.7	117.2	1.504	27.70
	72.0	254.8	232.2	1.487	27.93

Table XIX

Lowering of the Freezing Point and Rise of the Boiling Point

Calculate the apparent molecular weight of the solute in water from the following data. In the case of electrolytes, calculate the degree of dissociation. Assuming the formula weight, m, calculate the apparent molecular lowering, K_A, or the apparent molecular rise. For additional problems see tables of data, page 534.

Solute	Grams in 100 Grams of Water	Lowering of Freezing Point Δ	Calculated Values		
			$K = 18.6$		m
			m_A	a	K_A
Cane sugar	0.04825	0.00264	340.		18.7
$C_{12}H_{22}O_{11}$	0.6878	0.0378	338.3		18.8
	9.778	0.5387	336.		18.9
	26.008	1.466	330.		19.3
	29.82	1.768	314.		20.3
	34.20	2.07	307.		20.7
Acetone	0.1191	0.0372	59.6		18.12
$(CH_3)_2CO$	0.5851	0.1846	59.0		18.3
	3.007	0.920	60.8		17.8
	6.221	1.930	60.0		18.0
	22.19	6.55	63.0		17.2
	45.30	12.35	68.2		15.8
NaCl	0.01047	0.006403	30.4	.922	35.8
	0.03738	0.02339	29.8	.960	36.6
	0.1250	0.07584	30.7	.903	35.4
	0.690	0.4077	31.5	.855	34.6
	3.099	1.759	32.8	.780	33.2
	5.770	3.293	32.6	.792	33.4
$NaNO_3$	0.1970	0.0817	44.8	.896	35.2
	0.5224	0.2124	45.7	.858	34.6
	1.620	0.6318	47.7	.781	33.2
	4.328	1.621	49.6	.712	31.9
	8.526	3.040	52.2	.628	30.3
KCl	0.00192	0.000953	37.47	.991	37.02
	0.07632	0.03674	38.63	.931	35.92
	1.123	0.5140	40.64	.835	34.14
	2.526	1.1311	41.54	.795	33.41
	7.46	3.2864	42.22	.767	32.86

Solvent	Solute	Grams in 100 Grams of Water	Rise of Boiling Point Δ	Calculated Values		
				$K = 5.2$		$m =$
				m_A	a	K_A
H_2O	NaCl	0.4388	0.074	30.8	.895	9.86
$K = 5.2$		2.158	0.351	31.9	.830	9.52
$m_F = 58.45$		7.27	1.235	30.6	.908	9.92
		12.17	2.182	29.0	1.012	10.48
		18.77	2.866	25.2	1.317	12.04
H_2O	KNO_3	0.505	0.051	51.5	.965	10.21
$K = 5.2$		2.789	0.248	58.5	.730	9.00
$m_F = 101.1$		9.22	0.797	60.2	.681	8.76
		35.54	2.710	68.2	.484	7.72
		53.37	3.795	73.2	.382	7.21
H_2O	$CaCl_2$	0.585	0.091	33.4	1.162	17.26
$K = 5.2$		2.405	0.302	41.4	.841	13.95
$m_F = 111.$		5.35	0.643	43.2	.782	13.34
		10.89	1.481	38.2	.953	15.11

Table XX

Electrical Conductance

From the data in the following tables calculate the degree of electrolytic dissociation, the osmotic pressure, the freezing point, and the vapor pressure of the solution.

Table A

Specific Conductance κ	Temp.	Moles Liter n	Electrolyte	Ionic Conductance		Degree of Dissociation a Per Cent
1. .2586	18°	2.924	NH_4Cl	$NH_4 = 64.7$	$Cl = 65.5$	67.9
2. .1231	18	2.168	$SrCl_2$	$\frac{1}{2}Sr = 51.9$	$Cl = 65.5$	24.2
3. .0296	18	0.387	LiI	$Li = 33.3$	$I = 66.6$	76.7
4. .1303	18	2.688	$NaNO_3$	$Na = 43.4$	$NO_3 = 61.8$	46.1
5. .0718	18	1.000	K_2SO_4	$K = 64.5$	$\frac{1}{2}SO_4 = 68.5$	27.0
6. .1061	18	8.052	$MgCl_2$	$\frac{1}{2}Mg = 45.9$	$Cl = 65.5$	5.91
7. .0508	18	0.790	$(COOH)_2$	$H = 314.5$	$\frac{1}{2}C_2O_4 = 63.$	8.52

TABLE B

Equivalent Conductance Λ_v	Temperature	Volume Liters V	Equivalent Conductance Λ_∞	Electrolyte	Degree of Dissociation α	Osmotic Pres. Atmospheres
1. 18.1	18°	0.1	133.0	K_2CO_3	.136	153.7
2. 42.7	18	0.2	109.0	NaCl	.392	166.2
3. 53.1	18	0.5	98.9	LiCl	.537	73.3
4. 46.0	18	0.33	105.33	$NaNO_3$	.437	102.8
5. 28.9	18	1.0	109.9	$MgSO_4$	.263	15.08
6. 70.0	18	0.1	368.0	H_2SO_4	.190	164.8
7. 21.5	18	0.2	111.9	$Ca(NO_3)_2$	.192	82.6
8. 38.4	18	0.5	111.7	$Sr(NO_3)_2$	.344	40.25
9. 26.3	18	1.0	82.3	$Ca(C_2H_3O_2)_2$	.320	19.55
10. 42.2	18	0.25	118.7	$SrCl_2$	.356	81.7
11. 56.6	18	2.	115.3	$Ba(NO_3)_2$	.491	11.82

TABLE C

Specific Conductance κ	Temp.	Conc. Per Cent	Density Grams per cc. ρ	Λ_∞	Electrolyte	Degree of Dissociation Per Cent α	Freezing Point	Vapor Pressure mm.
1. .3948	18°	5	1.0242	376	HCl	74.8	− 4.70	14.70
2. .1211	18	10	1.0707	109	NaCl	60.6	− 5.68	14.59
3. .0389	18	5	1.0445	117	$BaCl_2$	66.0	− 1.09	15.21
4. .1728	18	20	1.1794	115.2	$CaCl_2$	35.22	− 7.14	14.38
5. .0469	18	50	1.5102	112	$Ca(NO_3)_2$	15.2	− 14.80	13.45
6. .0458	18	5	1.0395	130.7	K_2SO_4	50.2	− 1.125	15.22
7. .1505	18	20	1.133	126.5	KNO_3	53.0	− 7.04	14.39
8. .0651	18	20	1.104	76.4	$NaC_2H_3O_2$	31.62	− 7.46	14.33
9. .001081	18	40	1.0496	107.0	CH_3COOH	0.145	− 23.66	12.50
10. .0783	18	7	1.0326	235.2	$(COOH)_2$	20.7	− 2.20	15.08

(Vapor Pressure of water at 18° is 15.383 mm.)

TABLE XXI

Ionic Product

The calculation of the solubility of difficultly soluble substances, either alone or in the presence of a more soluble salt containing a common ion, introduces a number of cases depending upon the assumptions made. Two of the simple cases may be illustrated by a consideration of uni-univalent or bi-bivalent and of uni-bivalent salts as $PbSO_4$ and $PbCl_2$.

1. $PbSO_4 \rightleftarrows [Pb^{++}]+[SO_4^{--}]$ then from the Law of Mass Action $[Pb^{++}] \cdot [SO_4^{--}]=L_0$. But the concentration of the $[Pb^{++}]$ = the concentration of the $[SO_4^{--}] = \sqrt{L_0}$ or $[Pb^{++}]^2 = L_0$. Now assume that a definite concentration, c, of $(NH_4)_2SO_4$ is added to a specified quantity of the saturated solution of $PbSO_4$. What will be the concentration of the Pb^{++} present? We would then have $[Pb^{++}] \cdot [SO_4^{--} + c] = L_0$; but $[Pb^{++}] = [SO_4^{--}]$ in concentration, hence

$$[SO_4^{--}] \cdot [SO_4^{--} + c] = L_0 \text{ or } [SO_4^{--}]^2 + c[SO_4^{--}] = L_0$$

or
$$[SO_4^{--}]^2 + c[SO_4^{--}] - L_0 = 0.$$

Solving this quadratic equation for $[SO_4^{--}]$ gives the ionic concentration from which the solubility of $PbSO_4$ is readily obtained.

2. $PbI_2 \rightleftarrows [Pb^{++}] + [2\ I^-]$ and then $[Pb^{++}] \cdot [I^-]^2 = L_0$. But there are twice as many $[I^-]$ as $[Pb^{++}]$, hence $[I^-] = [2\ Pb^{++}]$. Then $[Pb^{++}] \cdot [2\ Pb^{++}]^2 = L_0$ or $4\ [Pb^{++}]^3 = L_0$ or $[Pb^{++}] = \frac{\sqrt[3]{L_0}}{4}$ and $[I^-] = \sqrt[3]{2\ L_0}$, from which the solubility of the PbI_2 can be calculated or the concentration of the individual ions. Now if an electrolyte with a common ion is added to a saturated solution a cubical equation is obtained. Show the form of this expression and how it may be employed in determining the solubility of the difficultly soluble salt. It must be remembered in solving the cubical equation that since the root is a very small decimal the terms involving the second and the third powers are practically negligible with respect to the first power, hence a very close approximation may be obtained by employing the term involving the first or the second power and solving. This method of approximation was utilized to obtain the values in the last column.

From the data presented in the table, calculate the Ionic Product. This is obtained by expressing the concentration of the ions in terms of gram-ions per liter and the solubility obtained from these values would be expressed in gram-molecules or moles per liter.

To 100 cc. of a saturated solution of the substance listed in the first column add 100 cc. of the designated solution of an electrolyte containing a common ion. This substance is assumed to be completely dissociated, and the solution of the original substance is to remain saturated. Calculate the concentration of the original substance and express the same in moles per liter.

Substance	Temp.	Solubility	Ionic Product	Substance Added Concentration	Concentration Moles per Liter Original Substance
1. Ag_2CO_3 . . .	25	3.2×10^{-3} per cent	6.25×10^{-12}	Na_2CO_3 1.5 gr.	4.70×10^{-6}
2. $Ag_2C_2O_4$ . .	18	1.2×10^{-4} moles per liter	$6.9\ \times10^{-12}$	$(NH_4)_2C_2O_4 \cdot H_2O$ 5 gr.	3.13×10^{-6}
3. Ag_2CrO_4 . .	25	2.0×10^{-3} per cent	$0.9\ \times10^{-12}$	$AgNO_3$ 0.1 N	$3.5\ \times10^{-10}$
4. $BaCrO_4$ . . .	18	3.5×10^{-4} per cent	$1.9\ \times10^{-10}$	K_2CrO_4 0.5 N	$3.8\ \times10^{-10}$
5. $BaC_2O_4 \cdot 2\ H_2O$	18	0.0086 gr. per 100 g·H_2O	1.44×10^{-7}	$(NH_4)_2C_2O_4 \cdot H_2O$ 0.6N	0.96×10^{-6}
6. $BaSO_4$ . . .	25	2.3×10^{-4} per cent	0.97×10^{-10}	$(NH_4)_2SO_4$ 0.2 N	1.94×10^{-9}
7. CaC_2O_4 . . .	18	4.35×10^{-5} moles per liter	1.89×10^{-9}	$(NH_4)_2C_2O_4 \cdot H_2O$ 0.5 N	3.88×10^{-9}
8. PbI_2	25	1.65×10^{-3} moles per liter	1.80×10^{-8}	NaI 12.0 gr.	1.12×10^{-7}
9. $Pb(IO_3)_2$ . .	25	1.9×10^{-3} gr. per 100 gr. H_2O	1.59×10^{-13}	$Pb(NO_3)_2$ 10 gr.	5.13×10^{-6}
10. $SrSO_4$ . . .	18	1.14×10^{-2} gr. per 100 gr. H_2O	0.37×10^{-6}	$(NH_4)_2SO_4$ 3.3 gr.	2.96×10^{-6}
11. TlBr	25	5.7×10^{-2} gr. per 100 gr. H_2O	$4.0\ \times10^{-6}$	NaBr 4.53 gr.	1.80×10^{-5}

Table XXII

Ionic Product, Solubility and Specific Conductance

From the data in the following table and the equivalent ionic conductances given in Table L, page 320, calculate the solubility in moles per liter. Assume the conductance of the water to be 1.2×10^{-6} mhos in all cases. Calculate the ionic product. Or assuming the solubility calculate the specific conductance of the solution.

Substance	Temp.	Specific Conductance	Solubility Moles per Liter	Ionic Product L_0
1. AgCl	18°	2.4×10^{-6}	1.00×10^{-5}	1.0×10^{-10}
2. $Ag_2C_2O_4$	18	2.55×10^{-5}	1.04×10^{-4}	4.5×10^{-12}
3. BaC_2O_4	16.3	67.7×10^{-6}	2.925×10^{-4}	1.1×10^{-7}
4. $PbSO_4$	18	3.24×10^{-5}	1.57×10^{-4}	2.46×10^{-8}
5. TlCl	25	1680×10^{-6}	1.105×10^{-2}	1.22×10^{-4}
6. Tl_2SO_4	20	149.4×10^{-4}	0.53×10^{-1}	5.96×10^{-4}

By employing the data in Tables LVI and LVII additional problems can be readily formulated.

Table XXIII

Degree of Dissociation of Water

From the data given in Table LXIII calculate the degree of dissociation of water at each of the given temperatures.

Table XXIV

Hydrolysis Constant and Per Cent of Hydrolysis

Draw a curve representing the change of the Ionic Product (Dissociation Constant) of water with the change in temperature. Making the proper correction for the temperature for the dissociation constant and employing the data given in Table LVI calculate the hydrolytic constant for the substances in the following table and then calculate the per cent of hydrolysis at the specified temperature.

Substance	Temp.	Vol. in Liters	Hydrolysis Constant K_h	Per Cent Hydrolysis
1. Acetanilid HCl	40°	10	0.78	89.7
2. Acetamid HCl	25	10	3.36	97.2
3. Aniline acetate	40	39.32	3.86	66.2
4. Ammonium acetate . .	100	40.13	17.95×10^{-4}	4.06
5. Ammonium chloride .	25	32	0.578×10^{-9}	0.013
6. Butyronitril	25	10	5.78	96.7
7. Urea HCl	25	10	0.694	88.5
8. Potassium cyanide . .	42.5	9.63	0.5×10^{-4}	2.2

Table XXV

Speed of Reaction; Affinity Constant

In the transformation of ammonium cyanate into urea a decinormal solution was employed. Calculate the value of the affinity constant k assuming the reaction to be monomolecular. Calculate the per cent transformed at each reading and in what time one half will be transformed at each temperature.

25° $a = 23.5$			64.5° $a = 22.9$			80.1° $a = 22.9$		
t in min.	x	k	t in min.	x	k	t in min.	x	k
1325	5.6	0.000236	20	7.0	0.0220	7	9.0	0.093
1970	7.0	0.000214	37	10.3	0.0221	17	14.6	0.103
2725	9.0	0.000228	50	12.1	0.0224	37	17.9	0.097
5640	13.3	0.000231	65	13.8	0.0233	57	19.5	0.101
	mean	0.000227	95	16.0	0.0244	97	20.9	0.108
			150	17.7	0.0227		mean	0.100
				mean	0.0228			

Table XXVI

Table of Atomic Weights

The values given in this Table of Atomic Weights are the ones that have been used in the problems.

Aluminium	Al	27.1	Manganese	Mn	55.0
Antimony	Sb	120.2	Mercury	Hg	200.6
Argon	A	39.9	Molybdenum	Mo	96.0
Arsenic	As	75.0	Neon	Ne	20.2
Barium	Ba	137.4	Nickel	Ni	58.7
Bismuth	Bi	208.0	Nitrogen	N	14.0
Boron	B	11.0	Oxygen	O	16.0
Bromine	Br	79.9	Palladium	Pd	106.7
Cadmium	Cd	112.4	Phosphorus	P	31.0
Cæsium	Cs	132.8	Platinum	Pt	195.2
Calcium	Ca	40.1	Potassium	K	39.1
Carbon	C	12.0	Selenium	Se	79.2
Chlorine	Cl	35.5	Silicon	Si	28.3
Chromium	Cr	52.0	Silver	Ag	107.9
Cobalt	Co	59.0	Sodium	Na	23.0
Copper	Cu	63.6	Strontium	Sr	87.6
Fluorine	F	19.0	Sulphur	S	32.0
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.0	Thallium	Tl	204.0
Hydrogen	H	1.0	Tin	Sn	118.7
Iodine	I	127.0	Titanium	Ti	48.1
Iron	Fe	55.8	Tungsten	W	184.0
Krypton	Kr	82.9	Uranium	U	238.2
Lead	Pb	207.2	Vanadium	V	51.0
Lithium	Li	7.0	Xenon	Xe	130.2
Magnesium	Mg	24.3	Zinc	Zn	65.4

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