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AN INTRODUCTION
TO
PHYSICAL CHEMISTRY

INTRODUCTION

TO

PHYSICAL CHEMISTRY

BY

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PREFACE TO THE FIRST EDITION

THIS book makes no pretension to give a complete or even systematic survey of Physical Chemistry; its main object is to be explanatory. I have found, in the course of ten years' experience in teaching the subject, that the average student derives little real benefit from reading the larger works which have hitherto been at his disposal, owing chiefly to his inability to effect a connection between the ordinary chemical knowledge he possesses and the new material placed before him. He keeps his everyday chemistry and his physical chemistry strictly apart, with the result that instead of obtaining any help from the new discipline in the comprehension of his descriptive or practical work, he merely finds himself cumbered with an additional burthen on the memory, which is to all intents and purposes utterly useless. This state of affairs I have endeavoured to remedy in the present volume by selecting certain chapters of Physical Chemistry and treating the subjects contained in them at some length, with a constant view to their practical application. In choice of subjects and mode of treatment I have been guided by my own teaching experience. I have striven to smooth, as far as may be, the difficulties that beset the student's path, and to point out where the hidden pitfalls lie. If I have been successful in my object, the student, after a careful perusal of this introductory text-book, should be in a position to profit by the study of the larger systematic works of Ostwald, Nernst, and van 't Hoff.

As I have assumed that the student who uses this book has already taken ordinary courses in chemistry and physics, I have devoted little or no space to the explanation of terms or elementary notions which are adequately treated in the text-books on those subjects. I have throughout avoided the use of any but the most elementary mathematics, the only portion of the book requiring a rudimentary knowledge of the calculus being the last chapter, which contains the thermodynamical proofs of greatest value to the chemist.

Since it is of the utmost importance that even beginners in physical chemistry should become acquainted at first hand with original work on the subject, I have given a few references to papers generally accessible to English-speaking students.

J. WALKER.

August 1899.

PREFACE TO THE THIRD EDITION

THE present edition differs from those that have preceded it in many points of detail. Where recent researches have afforded more accurate numerical values or better illustrative examples than those formerly available, the newer data have as far as possible been substituted. Numerous additions have been made both to text and references, and in particular the book has been enlarged by the inclusion of a chapter on Electromotive Force (Chapter XXVII.), and an extension of the chapter on Thermodynamical Proofs (Chapter XXVIII.) which deals with the same subject. Although the matter is perhaps not very readily intelligible to the ordinary chemical student, the increasing importance of Electro-chemistry has necessitated its inclusion.

J. W.

August 1903.

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CHAPTER I

UNITS AND STANDARDS OF MEASUREMENT

To express the magnitude of anything, we use in general a number and a name. Thus we speak of a length of 3 feet, a temperature difference of 18 degrees, and so forth. The name is the name of the unit in terms of which the magnitude is measured, and the number gives the number of times this unit is contained in the given magnitude. The selection of the unit in each case is arbitrary, and regulated solely by our convenience. In different countries different units of length are in vogue, and even in the same country it is found convenient to adopt sometimes one unit, sometimes another. Lengths, for example, when very great are expressed in miles; when small, in inches; and we also find in use the foot and yard as units for intermediate lengths. Such units as these British measures of length were fixed by custom and convention, and for the purposes of everyday life are convenient enough. When we come, however, to the discussion of scientific problems, we find that they are unsuitable and inconvenient, leading to clumsy calculations the greater part of which could be dispensed with if the units of the various magnitudes were properly selected. There is, for instance, no simple relation between any of the British units of length and the usual British standard of capacity—the gallon. It is true that the cubic inch and cubic foot are sometimes used as measures of capacity, but not generally for liquids. Now lengths, volumes, and weights often enter in such a way into scientific calculations that the existence of simple relations between the units of these magnitudes enables us to perform a calculation mentally which would necessitate a tedious arithmetical operation were the units not thus simply related.

The first requirement of a convenient system of measurement is that all multiples and subdivisions of the unit chosen should be **decimal**, in order to be in harmony with our decimal system of numeration. For scientific purposes the decimal principle of measurement is uniformly accepted, save in circular measure and in the measurement of time, where the ancient sexagesimal system (of counting by sixties) still in part prevails. The unit of length is subdivided into tenths, hundredths, and thousandths if we wish to use the smaller derived units; if we desire a larger derived unit we take it ten, a hundred, or a thousand times greater than the fundamental unit. The choice of this fundamental unit is, as has been already stated, quite arbitrary. At the time of the French Revolution, when a decimal system was first adopted in a thoroughgoing manner, the unit of length, the **metre,** was selected because it was of a convenient length for practical measurement, and in particular because it was supposed to have a natural relation to the size of the earth, ten million metres measuring exactly the quadrant of a circle through the poles. The value of the fundamental length therefore depended theoretically on the determination of the length of the earth's meridional quadrant. But the degree of accuracy with which this determination can be made is far inferior to that obtainable in comparing two short lengths (say a metre) together. If the metre then were strictly defined by the earth's dimensions, the fundamental unit of length would change with every fresh determination of the polar circumference. For practical purposes the metre is legally defined as the distance, under certain conditions, between two marks on a rod of platinum-iridium preserved in Paris, and the supposed exact relation to the earth's circumference has been given up.[1] Copies of this standard have been made and distributed, and the relation between them and similar standards of length, such as the yard, have been determined with great exactness.

For many scientific purposes, the hundredth part of the metre, the centimetre, is a convenient unit, and in what follows we shall frequently make use of it in calculations.

The unit of mass (or weight),[2] the **gram,** was primarily defined as the mass (or weight) of 1 cubic centimetre of water at the temperature at which its density is greatest, viz. 4° C. Here we depend on the constancy of the properties of an arbitrary substance (pure water) to establish a relation between the units of weight and of cubical capacity, or volume. The original **standard kilogram** was constructed in accordance with this relation, being made equal to 1000 grams as above defined, *i.e.* equal in weight to a cubic decimetre of water at its maximnm density point. Since it is possible, however, to compare weights with each other with much greater accuracy than is attainable in the measurement of volumes, the exact relationship between the two units has been allowed to drop,

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[1] According to recent measurement, the ten-millionth part of the earth's quadrant is nearly 0·2 millimetres longer than the standard metre.

[2] When a chemist uses an ordinary balance he directly compares *weights*, but, since at any one place weight is proportional to mass, he indirectly compares the *masses* of the substances on the two pans. So far, then, as measurement of quantity of material by means of the balance is concerned, the terms are interchangeable.

and for exact purposes the kilogram is defined as the weight of the platinum standard kilogram kept in Paris.[1] For the purposes of the chemist the relation between the units of weight and volume as originally defined may be looked upon as exact, since the error is not greater than 0·01 per cent, a degree of accuracy to which the chemist attains only in exceptional circumstances. For measuring the volume of liquids, the **litre** is defined, not as a cubic decimetre, but as the volume occupied by a quantity of water which will balance the standard kilogram in vacuo at 4° C.

The unit of time seldom enters into chemical calculations. The standard for the unit is derived from the length of time necessary for the performance of some cosmical process—for example, the time taken by the earth to perform a complete revolution on its axis. For chemical purposes, the minute, as measured by a good-going clock or watch, is the practical unit.

The units of length, weight, and time being once fixed, a great many derived units may be fixed in their turn. The C.G.S. system, which takes, as the letters indicate, the centimetre, the gram, and the second for the fundamental units, is very frequently employed, especially in theoretical calculations, and we shall often have occasion to use it. For example, instead of expressing the average atmospheric pressure as that of a column of mercury 76 cm. high, it is expedient in many calculations to give the pressure in grams weight per square centimetre. The conversion may easily be performed as follows. Suppose the cross section of the mercury column to be 1 sq. cm., then if the height of the column is 76 cm., the total volume of mercury is 76 cc., and the pressure per square centimetre is the weight of 76 cc. of mercury, viz. 1033 g.[2] The average pressure of the atmosphere, then, is equal to 1033 g. per square centimetre.

The **specific volume** of a substance may be defined as the number of units of volume which are occupied by unit weight of the substance. In the above system it is therefore the number of cubic centimetres occupied by one gram. The specific weight, or **density,** of a substance is the number of units of weight which occupy unit volume: in the

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[1] To give an idea of the difficulty of accurate measurement when volumes are concerned, the following example may suffice. By Act of Parliament a gallon was defined as equal to 4·543458 litres, this number being derived from the weight of a cubic inch of water in grains, and the relation between the inch and the decimetre, a litre being supposed equal to a cubic decimetre. The original definition of the gallon is "the volume at 62° F. of a quantity of water which balances 10 brass pound weights (true in vacuo, and of specific gravity 8·143) in air at 62° F. and 30 inches pressure (barometer reduced to the freezing point) and two-thirds saturated with moisture." From this definition, and the relation of the pound to the kilogram, Dittmar calculated that 1 gallon is equal to 4·54585 litres, a value which differs from this statutory relation by 1 part in 2000. By an Order in Council of May 1898, the gallon is equivalent to 4·54596 litres.

[2] This value is obtained by multiplying 76 by the specific gravity of mercury, viz. 13·59.

above system, the number of grams which occupy one cubic centimetre.

These definitions are directly derived from the units of weight and volume, and are independent of the properties of any substance save that considered. For purposes of measurement in the case of solids and liquids, however, it is much more convenient and accurate to compare the density or specific volume of one substance with that of another arbitrarily chosen as standard, than to effect an absolute determination by measuring both weight and volume of one and the same substance. The substance usually chosen as the standard of comparison is water, and that for two reasons. In the first place, water is easily obtained and easily purified; in the second place, water is a standard substance in other respects; in particular it is the substance which was used to fix the relation between the units of weight and of volume. From this relation the density of water in our units is 1 (cp. p. 2), so that if we take water as our standard, and refer all densities to it as the unit, we have what are really relative densities, although if measured at 4° the numbers obtained do not differ greatly from the absolute densities of the substances. The actual comparison is made in the case of liquids by weighing the same tared vessel filled with water, and filled with the liquid whose density is to be determined. Although the actual volume is unknown, it is known to be the same in both cases, so that the quotient of the weight of liquid by the weight of water gives the relative density of the liquid.

In order to specify with exactness the density of a substance, it is necessary to indicate at what temperature the determination or comparison has been made. As substances change in temperature they invariably change in volume, so that the absolute density varies with the temperature. In specifying the relative density, or specific gravity, it is not only necessary to give the temperature at which the substance is weighed, but also the temperature at which the equal volume of water is weighed. Thus we meet with such data as the following, ${}_{15\cdot5}S_4 = 1\cdot0653$, which indicates that the weight of the substance at 15·5° is 1·0653 times as much as the weight of the same volume of water at 4°. As a general rule, the weights are both for the same temperature, say 15°; or the substance is weighed at this temperature and referred either directly or by calculation to water at 4°, its maximum density point. In the latter case the density given is very nearly equal to the absolute density of the substance at the specified temperature.

Quantities of matter may always be expressed in terms of the unit of weight irrespective of the form in which the matter may exist. When we come to measure energy we find no such common unit in which its amount may be expressed. Each form of energy, such as heat, work, electrical energy, has its own special unit, but according to the Law of Conservation of Energy, a given amount of any one form of energy is under all circumstances equivalent to constant amounts of the other kinds of energy; we have therefore merely to ascertain the relation between the different special energy units in order to express a given amount of energy in terms of any one of these units. Thus electrical energy is usually expressed in volt-coulombs for practical purposes, but it may easily be expressed in terms of the mechanical or heat units, the numbers then indicating the amounts of mechanical or thermal energy into which the electrical energy may be converted.

The "absolute" unit of mechanical energy, the **erg,** is the product of the unit of length into the "absolute" unit of force, or **dyne,** *i.e.* the force necessary to impart to a mass of 1 g. in a second a velocity of 1 cm. per second. For our purposes, however, it will be more convenient to use gravitation units, in the definition of which the value of the earth's gravitational attraction for bodies on its surface is involved. The unit of force thus defined is the weight of 1 g., and is equal to 981 dynes. The unit of mechanical energy is therefore the product of this unit into the unit of length, *i.e.* the **gram-centimetre.**

To obtain the unit of heat and a scale of temperature it is again necessary to refer to the properties of some arbitrarily-chosen substance or substances. In the construction of a scale of temperature it is customary to fix two points by means of well-defined and presumably constant properties of some standard substance, and divide the range between these two points into equal arbitrary units as measured by the change in property of some substance caused by change of temperature. Thus in the **centigrade scale** the two points which are fixed are the freezing point of the standard substance water, and secondly, its boiling point under a pressure of 76 cm. of mercury. When we use a mercury thermometer it is assumed that equal changes in volume of the mercury correspond to equal changes of temperature,[1] so by dividing the whole change of volume of the mercury between the freezing and boiling points of water into 100 equal portions, we obtain an ordinary centigrade thermometer. Similarly, if we use an air thermometer, we assume that equal increments of volume correspond to equal increments of temperature. In each case we depend for our measurement of temperature on the properties of some particular substance, and it does not at all follow that the temperature as measured by one substance will exactly coincide with the temperature as measured by another. In point of fact, the temperatures registered by the mercury and air thermometers never exactly agree except at the point at which the two thermometers were originally made to correspond when their fixed points were determined. In theoretical calculations **absolute temperatures** are frequently employed. The absolute scale of tempera-

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[1] In mercury and other liquid thermometers we really deal with the difference of the volume change of the liquid and of the vessel containing it.

ture has degrees of the same size as centigrade degrees, but starts from a point 273 degrees below zero centigrade. The absolute temperature is therefore obtained by adding 273 to the temperature in the centigrade scale.

The usual unit of heat for chemical purposes is the "small calorie" or **gram calorie.** It is roughly defined as the quantity of heat required to raise the temperature of one gram of water through one degree centigrade. This quantity is not exactly the same at all temperatures, *e.g.* the amount of heat necessary to warm a gram of water from 0° to 1° is somewhat different from that required to heat it from 99° to 100°. It is therefore necessary to specify the temperature at which the heating takes place. Practically the calorie measured at the ordinary temperature, say from 15° to 16°, is the most convenient. The great or **kilogram calorie** is 1000 times the small calorie. A **centuple calorie** has also been proposed, and its definition is a practical one. It is the quantity of heat required to raise a gram of water from 0° to 100°, and is very nearly equal to 100 small calories. It is usually denoted by the symbol K, and we have thus the following relation of heat units:—1 Cal. = 10 K = 1000 cal.

Another unit of heat has recently been proposed for thermochemical purposes. It is called a **joule,** is equivalent to 10,000,000 ergs, and is denoted by the letter j. A larger unit, equal to 1000 joules, is called the kilojoule, and may be denoted by the symbol Kj. The relations between these and the older units are given by the equations

$$1 \text{ cal.} = 4{\cdot}183 \text{ j.} \qquad 1 \text{ j} = 0{\cdot}2391 \text{ cal.}$$
$$1 \text{ Cal.} = 4{\cdot}183 \text{ Kj.} \qquad 1 \text{ Kj} = 0{\cdot}2391 \text{ Cal.}$$

It is a matter of importance to fix the relation of the mechanical unit of energy to the heat unit, *i.e.* to determine the **mechanical equivalent of heat.** Mechanical energy, *e.g.* the energy of a falling body, is converted by friction or otherwise into heat, the amount of mechanical energy and the amount of heat resulting from it being both measured. In this way it has been found that 42,650 gram centimetres are equivalent to 1 gram calorie, *i.e.* 42,650 grams falling through a centimetre will generate enough heat in a friction apparatus to raise the temperature of a gram of water one degree at about 18°. In the sequel we shall denote this value by J.

The relations between the units employed in electrical measurements have been the subject of many accurate experimental investigations. The units have been chosen theoretically so as to give a unit of electrical energy which bears a simple relation to the absolute unit of mechanical energy. The theoretical unit of resistance, the **ohm,** may be practically defined as the resistance at 0° of a column of mercury 1 sq. mm. in section, and 1·0630 metres long. A convenient practical unit, the Siemens mercury unit, is the resistance of a similar column exactly a metre long. The unit quantity of electricity, the **coulomb**, can be defined as the quantity of electricity which will deposit 1·118 mg. of silver from a solution of a silver salt under properly chosen conditions. The unit of potential difference or electromotive force, the **volt**, is so related to the previous units that when the potential difference between the ends of a resistance of 1 ohm is 1 volt, a current of 1 coulomb per second (**1 ampère**) will pass through the resistance. For purposes of comparison the difference of potential between the electrodes of a normal galvanic cell is used as standard. Thus a Clark's cell, which is frequently employed for this purpose, has a potential difference between its electrodes equal to 1·433 volts at 15°. The unit of electrical energy, the **volt-coulomb**, is the product of the volt into the coulomb, and is equivalent to 10^7 ergs, 10,200 gravitation units, or 1 j.

In connection with the subject of units, the student is strongly recommended to read CLERK-MAXWELL, *Theory of Heat*, Chaps. I.-IV.

CHAPTER II

THE ATOMIC THEORY AND ATOMIC WEIGHTS

CHEMISTS have for long been in the habit of expressing their experimental results in terms of the Atomic Theory propounded by Dalton at the beginning of this century. At the time of its inception the facts which this theory had to explain were comparatively few in number and simple in character. Nowadays, the experimental data are numberless, and often of great complexity, yet the atomic theory is still capable of affording an easy and convenient mode of formulation for them, and is therefore to be pronounced a good theory. It is true that in the course of years the notions associated with the term "atom" have undergone many changes, but Dalton's fundamental idea is unaltered, and seems likely to persist for many years to come.

The results of chemical analysis show that most substances can be split up into something simpler than themselves, but that a few, some eighty, resist all attempts at decomposition, and are incapable of being built up by the union of any other substances. These undecomposed bodies we agree to call **elements,** and to express the composition of all other bodies in terms of them. It does not, of course, follow that because we have hitherto been unable to decompose these elements, methods may not at some later time be found for effecting their decomposition. In the sequel we shall see, however, that the elements form a group of substances, singular not only with respect to the resistance which they offer to decomposition, but also with respect to certain regularities displayed by them and not shared by the substances which go under the name of compounds.

The atomic theory as at present understood affords a simple explanation of the manner in which elements unite to form compounds. Each element is assumed to be not infinitely divisible, but to consist rather of minute indivisible particles—the **atoms**—all alike amongst themselves, especially with respect to their weight. The atoms of different elements are supposed to differ in weight and in other properties. Compounds must, on our assumption, be built up of these atoms, the mode of their hypothetical union being chosen in accordance with the observed facts. In the first place, the atoms must be supposed to retain their weight unchanged, no matter in what state they may exist; for all our chemical experience shows that chemical change is unaccompanied by any change in the total weight (or the total mass) of the reacting substances. Again, the same kinds of atoms in the same proportions go to the formation of any particular compound. This must be assumed to bring the theory into harmony with the constant composition exhibited by all compounds. Further, as the number of compounds actually existing is vanishingly small compared with the possible combinations of the different atoms, various rules have had to be devised regarding the nature and relative number of atoms which may unite with each other, in order that under these restrictions the number of possible combinations may agree more closely with the number of existing compounds. In these rules of "valency," etc., other properties of atoms besides their weight are indicated, and of late years it has been found necessary with regard to the carbon atom in particular to make very specific assumptions as to its nature, and its mode of combination with other atoms.

From what has just been said, it is evident that our conception of the atom is made to accommodate itself to the facts it has to explain. Beyond the constancy of weight of each atom, nothing had to be assumed in Dalton's time except that the atoms united in proportions expressible by the simple whole numbers, and these assumptions were made in order that the theory might be in harmony with the laws of constant and of multiple proportions. It should be noted that at the present time we can scarcely speak of a law of simple multiple proportions existing. We know well-defined substances whose composition we are obliged to express by means of such formulæ as $C_{20}H_{23}N$, $C_{13}H_{14}O_5$—to choose two examples at random from organic chemistry. Here there is no approximation to simple multiples.

When Dalton's theory had led to the adoption of a simple system for expressing the numerical proportions by weight in which elements combine and substances in general enter into chemical action, the conception of atom was practically allowed to drop, and its place was taken by the purely numerical conception of **equivalent weight** or **combining proportion**. The necessity of attaching any other significance to the atom than a constant weight was not generally felt, as the facts were not sufficiently well known to require any extension of the idea. Although the name "atom" continued to be used, the conception was practically that of a number. Laurent, for instance, in his *Chemical Method* (1853) says: "By the term 'atoms,' I understand the equivalents of Gerhardt, or, what comes to the same thing, the atoms of Berzelius." Again, "In order to avoid all hypotheses, I shall not attach to the term 'atom' any other sense than that which is included by the term 'proportional number.'"

For each element there existed a number which expressed its combining weight, and the composition of any compound was expressed in terms of these weights as standards. It was therefore of extreme importance to fix the standard weights relatively to each other, in order that no dubiety or ambiguity should exist in the formulation of the compounds. Had there been no law of multiple proportions the task would have been easy. The weight of one element would have been chosen as ultimate standard to which all others would be referred, and as in that case each element would have united with each other element in one proportion only, no ambiguity could possibly exist. But the law of multiple proportions expresses the fact that a given weight of one element may unite with more than one weight of another element to form more than one compound, and that then the ratios of the weights of the second element are expressible by means of the simple whole numbers. Taking the combining weight of hydrogen as standard and unit, the combining weight of oxygen might be either 8 or 16, for 1 g. of hydrogen unites with 8 g. of oxygen to form water, and with 16 g. to form hydrogen peroxide. So it is with most of the other elements. The choice becomes still more complex when the element to be considered forms no compound with the standard element hydrogen (as is often the case) and various compounds with the element oxygen, itself of doubtful combining weight. Some principle had therefore to be adopted for obtaining a consistent system of combining weights, only one for each element, to which all other weights might be referred.

The extraordinary insight and acumen of Berzelius enabled him to arrive at a system of numbers not greatly differing from those in use at the present day, although he had little to guide him but the principles of analogy and simplicity of formulation. A better guide was gradually recognised in the uniformity displayed by substances in the gaseous state.

When the atomic theory was first propounded, no distinction was made between the ultimate particles of elements and the ultimate particles of compounds; both were alike called atoms. By the atom of a compound was meant the smallest particle of it that could exist, any further subdivision resulting in the splitting of the compound into its elements, or into simpler compounds. It referred, therefore, to an ultimate particle which might be decomposed chemically, but not mechanically. On the other hand, the ultimate particle of an element was an atom which could not be decomposed either mechanically or chemically. There was thus a slight difference in the sense in which the term "atom" was used in regard to the two classes of substances; and until this difference was recognised, little help was afforded to systematic chemistry from the study of gases. It had been observed by Gay-Lussac that gases entered into chemical actions in simple proportions by volume, the volumes of the different gases being of course measured under the same external conditions of temperature and pressure. Now, according to Dalton, gases (like all other substances) also entered into chemical action in simple proportions by atoms. There was thus necessarily a simple connection between the atoms of gases and the volumes they occupied. Dalton himself, led by other speculations, tried the assumption that equal volumes of different gases contained the same number of atoms, *i.e.* that the weights of equal volumes of different gases were proportional to the weights of their atoms. He rejected this supposition, however, as not being in harmony with the facts. Two measures of nitric oxide give on decomposition one measure of nitrogen and one measure of oxygen, *i.e.* on Dalton's assumption, two atoms of nitric oxide give one atom of nitrogen and one atom of oxygen. But there must be at least two atoms of nitrogen in two atoms of nitric oxide if the elementary atoms are really indivisible, which contradicts the above hypothesis. Avogadro showed how this difficulty might be overcome by distinguishing in the case of the elements between the different senses of indivisibility above referred to. The gist of his reasoning is as follows :—

The particles of a gas may be supposed to be the smallest particles obtainable by mechanical division, whether they are particles of elements or of compounds. But it does not follow, even for the elements, that this limit of mechanical or physical divisibility is also the limit of chemical divisibility. The gaseous particles of a compound can be chemically decomposed into something simpler ; so may the gaseous particles of an element, only in the latter case the products of the decomposition of the gaseous particle must be atoms of the same kind, and not atoms of different kinds as with the compounds. He made the distinction, therefore, between atoms and molecules as these terms are used at the present day. The **molecules** are the mechanically indivisible gaseous particles, which may consist each of more than one elementary atom—of different kinds in the case of compounds, of the same kind in the case of elements.

The hypothesis which Avogadro now made to account for the relations between combining weights and volumes was the following. Equal volumes of different gases under the same physical conditions contain the same number of molecules ; or, the weights of equal volumes of different gases are proportional to the weights of their molecules. There is now no longer any difficulty encountered in the volume relations of nitric oxide and its decomposition products. According to Avogadro, two molecules of nitric oxide give one molecule of nitrogen and one molecule of oxygen. But as two molecules of nitric oxide must contain at least two atoms of nitrogen and two atoms of oxygen, the molecule of nitrogen must contain at least two atoms of nitrogen, and the molecule of oxygen two atoms of oxygen.

The general adoption of this one principle has practically proved sufficient to fix the combining weights of the elements, and provide us with our present system of atomic weights. Although Avogadro published his hypothesis in 1811, the times were not ripe for it; and it was only in the fifties that its application became at all general. In the middle of the century the greatest confusion prevailed, different writers using different systems of combining weights, so that each compound had as many different formulæ as there were competing tables of equivalents. It is only within a few years that the last traces of one of the old systems have disappeared, many chemists, especially in France, having adhered to equivalents which gave HO or H_2O_2 as the formula of water, and C_2H_4 as the formula of marsh gas. So long as weights only were considered, one system was as good as another; but when volume relations, physical properties, and the nature of the substances produced in chemical actions systematically carried out, are taken into account, the present system of atomic weights is the only one which gives a simple and consistent expression of the results.

The hypothesis of Avogadro often goes under the name of Avogadro's Law, but it must be borne in mind that it is a purely hypothetical statement, and not to be confounded with a generalised expression of fact such as the Law of Constant Proportions. This latter is independent of any theory, while the former is entirely theoretical—a fact which of course in no way impairs its usefulness.

In the following pages a sketch is given of the mode employed in fixing our present system of atomic weights with the help of Avogadro's principle. The atoms and molecules having themselves only a hypothetical existence, we are not for our present purpose concerned with their absolute weight—all that we require is to express their weights relatively to each other. To begin with, a **standard** must be chosen to which all chemical weights are to be referred. The standard is purely arbitrary, and in choosing it we only consult our own convenience. Two elements, hydrogen and oxygen, have been selected on practical grounds for this purpose. Dalton chose **hydrogen** because it had the smallest equivalent of the elements; Berzelius chose **oxygen** because it was easy to compare the equivalents of the other elements with that of oxygen directly. Hydrogen does not form many well-defined and easily-analysed compounds with the other elements, so that comparison with the equivalent of hydrogen has usually to be indirect, frequently through the medium of oxygen. Both of these standards are at present in use. Some chemists choose hydrogen, and make its atomic weight equal to 1. Others select oxygen, and fix its atomic weight at 16. The actual number selected as standard magnitude is again arbitrary; Berzelius, for example, made the equivalent of oxygen equal to 100, and referred the other numbers to this. The reason why the number 16 has been chosen to express the atomic weight of oxygen when that element is taken as standard, is that when hydrogen is made to have an atomic weight equal to unity, the number which then expresses the atomic weight of oxygen is very nearly equal to 16. Thus, whichever of the two standards is adopted, we obtain practically the same set of numbers for the atomic weights of the other elements, if round numbers only are required. For purposes requiring a high degree of accuracy it is necessary to distinguish between the two sets. Formerly the ratio between the atomic weights of oxygen and hydrogen was not known with the same degree of accuracy as had been attained in fixing the ratios of the atomic weight of oxygen to that of many other elements. By taking $H=1$ therefore, each new determination of the ratio $H:O$ necessitated the alteration of a great many atomic weights. By taking $O=16$, the new determination only necessitates the alteration of the atomic weight of hydrogen. From recent researches carried out by independent investigators the ratio $H:O$ has been determined with accuracy to be $1:15{\cdot}88$, or $1{\cdot}0075:16$. With $O=16$ then, we have a set of atomic weights all 1·0075 times greater than when $H=1$. For accurate purposes this difference between the two systems must be considered, but for the everyday purposes of chemistry the system is practically one of round numbers based on $O=16$, although we still often look on $H=1$ as the theoretical standard.

In fixing our system of atomic weights on Avogadro's principle, the **weights of equal volumes of gases** are compared.[1] Now the weights of equal volumes of gases are proportional to their relative densities, and for the present purpose these densities are most conveniently referred to that of hydrogen $=2$, or, for accurate purposes, of oxygen $=32$. The reason for choosing the density of hydrogen equal to 2 instead of equal to 1, as is customary, is that on the former assumption the density of a gas is expressed by the same number as its molecular weight, instead of by half that number. The selection of the unit is quite arbitrary, and we may as well choose that which leads to the greatest simplicity. The atomic weight of hydrogen is 1, and on Avogadro's principle we must argue that the molecule of hydrogen contains two atoms, in order to satisfy the volume relations for the formation of hydrochloric acid gas from hydrogen and chlorine. Two volumes of hydrochloric acid gas are formed from one volume of hydrogen and one volume of chlorine, so that by reasoning similar to that employed above in the case of nitric oxide, each hydrogen molecule and each chlorine molecule must contain two atoms. The molecular weight of hydrogen is therefore at least 2 if its atomic weight is 1. It is convenient thus to express molecular weights in the same unit as atomic weights, for then the molecular weight is simply the sum of the atomic weights contained in the molecule.

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[1] The volumes must of course be measured under the same conditions of temperature and pressure.

The determination of the molecular weight of a substance therefore resolves itself into finding the weight of its vapour in grams which will occupy the same volume as 2 g. of hydrogen measured under the same conditions of temperature and pressure. This weight is called the gram-molecular weight of the substance, and the volume which it occupies is called the **gram-molecular volume**. It is practically the same for all gases, and at 0° and 76 cm. may be taken equal to 22·38 litres. Only rough values of the molecular weight are in this way obtained, for the determination of the density of gases and vapours does not under ordinary circumstances admit of any great degree of accuracy; besides which Avogadro's principle can be applied in strictness only to perfect gases, *i.e.* to those which obey the laws for gases with absolute exactness. It is easy, however, to arrive at the true molecular weight from the approximate value obtained from vapour-density determinations by taking account of the results of analysis, which are susceptible of great accuracy.[1] It is evident that the true molecular weight must contain quantities of the elements which are exact multiples or submultiples of the combining proportions of these elements, and the combining proportions are the results of analysis alone. We therefore select as true molecular weight the number fulfilling this condition which is nearest the approximate molecular weight. For example, the molecular weight of sulphuretted hydrogen, as determined from the vapour density, is 34·4, *i.e.* 34·4 g. of sulphuretted hydrogen occupy the same volume as 2 g. of hydrogen under the same external conditions. But we know that for 1 g. of hydrogen in the sulphide there are 16·0 of sulphur. The true molecular weight therefore must contain a multiple of 1·0 g. of hydrogen, and the same multiple of 16·0 of sulphur. The number 34·0 evidently does this, for it is equal to $2(1·0 + 16·0)$. We consequently take 34·0 as the true molecular weight of hydrogen sulphide instead of the number 34·4 obtained from the determination of the vapour density.

The atomic weight of an element is now deduced from the true molecular weights of its gaseous compounds as follows. A list of the molecular weights of the gaseous compounds is prepared, and the quantities of the element in these weights of the compounds are noted alongside. The figures in this second column are the results of analysis alone, and their greatest common measure is in general equal to the atomic weight of the element. Examples are given in the following tables. The first column of numbers contains the gram-molecular weights of the compounds; the second column contains the number of grams of the element in question in the gram-molecular weight; the third column shows the relation of these numbers to their greatest common measure.

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[1] A method for determining accurate molecular weights of gases from their physical properties without considering the results of analysis will be found in Chap. X.

HYDROGEN

Compound.	I.	II.	III.
Hydrochloric acid	36·5	1	1
Hydrobromic acid	81	1	1
Hydriodic acid	128	1	1
Water	18	2	2 × 1
Hydrogen sulphide	34	2	2 × 1
Hydrogen	2	2	2 × 1
Ammonia	17	3	3 × 1
Hydrogen phosphide	34	3	3 × 1
Methane	16	4	4 × 1
Ethane	30	6	6 × 1
		G.C.M.	1

OXYGEN

Water	18	16	1 × 16
Carbon monoxide	28	16	1 × 16
Phosphorus oxychloride	153·5	16	1 × 16
Nitric oxide	30	16	1 × 16
Oxygen	32	32	2 × 16
Carbon dioxide	44	32	2 × 16
Sulphur dioxide	64	32	2 × 16
Chlorine peroxide	67·5	32	2 × 16
Sulphur trioxide	80	48	3 × 16
Methyl nitrate	77	48	3 × 16
Osmium tetroxide	263	64	4 × 16
		G.C.M.	16

CHLORINE

Hydrochloric acid	36·5	35·5	1 × 35·5
Chlorine peroxide	67·5	35·5	1 × 35·5
Nitrosyl chloride	65·5	35·5	1 × 35·5
Cyanogen chloride	61·5	35·5	1 × 35·5
Chlorine	71	71	2 × 35·5
Chlorine monoxide	87	71	2 × 35·5
Thionyl chloride	119	71	2 × 35·5
Sulphuryl chloride	135	71	2 × 35·5
Phosphorus trichloride	137·5	106·5	3 × 35·5
Phosphorus oxychloride	153·5	106·5	3 × 35·5
Chloroform	119·5	106·5	3 × 35·5
Boron trichloride	117·5	106·5	3 × 35·5
Carbon tetrachloride	170	142	4 × 35·5
		G.C.M.	35·5

NITROGEN

Ammonia	17	14	1 × 14
Nitric oxide	30	14	1 × 14
Nitrogen peroxide	46	14	1 × 14
Methyl nitrate	77	14	1 × 14
Cyanogen chloride	61·5	14	1 × 14
Nitrogen	28	28	2 × 14
Nitrous oxide	44	28	2 × 14
Cyanogen	52	28	2 × 14
		G.C.M.	14

CARBON

Compound.	I.	II.	III.
Methane	16	12	1 × 12
Chloroform	119·5	12	1 × 12
Carbon monoxide	28	12	1 × 12
Carbon dioxide	44	12	1 × 12
Cyanogen chloride	61·5	12	1 × 12
Ethylene	28	24	2 × 12
Ethane	30	24	2 × 12
Cyanogen	52	24	2 × 12
Acetylene	26	24	2 × 12
Propane	44	36	3 × 12
Butane	58	48	4 × 12
Pentane	72	60	5 × 12
Hexane	86	72	6 × 12
Benzene	78	72	6 × 12
		G.C.M.	12

SULPHUR

Compound.	I.	II.	III.
Hydrogen sulphide	34	32	1 × 32
Sulphur dioxide	64	32	1 × 32
Sulphur trioxide	80	32	1 × 32
Sulphuryl chloride	135	22	1 × 32
Sulphur	64	64	2 × 32
Carbon disulphide	76	64	2 × 32
		G.C.M.	32

Proceeding on the principle explained above, we should now make the following table of the atomic weights of these elements:—

Hydrogen = 1
Oxygen = 16
Chlorine = 35·5
Nitrogen = 14
Carbon = 12
Sulphur = 32

These numbers are the generally accepted values for the atomic weights of the elements above considered, and indeed if any element has a large number of volatile compounds whose molecular weights can be determined from their vapour densities, the principle we have adopted leads to practically certain conclusions. The weights of any element contained in the molecular weights of its compounds must be equal to the atomic weight or must be multiples of it, so that if we take the greatest common factor of these multiples, it must either be a simple multiple of the atomic weight or the atomic weight itself. From this it appears, then, that the method is one which only gives values which the atomic weights cannot exceed. But if a great many volatile compounds of the element are known, the chance is very slight that the greatest common factor is still a multiple of the atomic weight, *i.e.* that another substance may be discovered which will not contain this greatest common factor in the weight of the element which enters into its molecule; and so the atomic weight fixed in the manner indicated above has a great degree of probability. If, on the other hand, only a few volatile compounds of the element are available for vapour-density determinations, the method may conceivably fail to give the correct result. Nowadays, however, we are in possession of other means of determining molecular weights besides the method of vapour densities, so that for each element a great many compounds of known molecular weight can be tabulated, even though the volatile compounds of some may be few in number. If we make use of these new methods, the atomic weights of the elements as determined from the molecular weights of their compounds are practically fixed with certainty.

The recently-discovered gases, argon, helium, etc., are in all probability elementary; but it has not been found possible to determine their atomic weights with absolute certainty. They enter into no combinations, so that no analysis is possible, and the only method for ascertaining their characteristic weights is the determination of their vapour densities. The atomic weights must in the meantime be assumed equal to their densities compared with hydrogen equal to 2, *i.e.* their molecules must be assumed to consist of one atom until we find reason to the contrary. That this assumption has a considerable degree of probability will be seen in the sequel (Chaps. V. and VI.).

Other methods have been used for fixing the atomic weights of the elements, but these must now be looked on rather as checks on the method from molecular weights than as methods of independent applicability. These are the methods depending on Dulong and Petit's Law (Chap. V.), and on the Periodic Law (Chap. VI.), and will be referred to in the sections treating of these regularities.

From what has been said, the fixing of exact values of the atomic weights consists of two problems—the determination of a set of equivalents from accurate quantitative experiments, and then the selection of one of these according to some definite principle such as that referred to in the preceding pages. The nature of the quantitative experiments performed depends on the character of the element whose equivalent is to be determined, but it usually consists in the exact comparison of the weights of two substances which contain the same quantity of the element. As far as possible, the experiments are chosen of a simple kind, and should involve the smallest possible number of other elements. Berzelius, for example, dissolved 25·000 g. of lead in nitric acid, evaporated the lead nitrate to dryness and ignited the residue carefully, thereby obtaining 26·925 g. of lead oxide. Twenty-five g. of lead combine therefore with 1·925 g. of oxygen, so that if we take $O = 16$, we obtain the value 207·8 as one of the possible equivalents of lead. Taking the mean of four similar experiments, we obtain the value 207·3. These experiments may, however, all be affected by a systematic error, *i.e.* by an error which is the result of this particular method of experiment. The equivalent must therefore be determined by some other method as a check. Berzelius converted lead directly into lead sulphide, and obtained 207·0 as the combining weight of lead if that of sulphur was taken as 32. By converting weighed quantities of lead oxide into lead sulphate, he obtained $Pb = 207·0$, on the assumption $O = 16$ and $S = 32$. Other observers using different methods have all got numbers approximating to 207·0, and Stas, who used every conceivable precaution, and whose number is usually accepted as the most correct value, obtained 206·9.

The error in a well-conducted quantitative transformation under ordinary laboratory conditions is about 0·1 per cent of the amount transformed. To secure an error as low as 0·01 per cent extraordinary precautions have to be taken, and it is only in the hands of skilled operators that this degree of accuracy can be attained. In order, too, that this accurate work may be of value, it is obviously essential that the substances operated on should be of a degree of purity corresponding to the excellence of the quantitative determinations. Now "chemically pure" substances usually contain an amount of impurity greatly exceeding 0·01 per cent of their weight, so that special skill and trouble must be devoted to the purification of the substances employed in the determination of the gravimetric ratio. Even after an experimental accuracy of 0·01 per cent has been secured with pure substances the error in the equivalent is generally much larger than this. Thus, supposing that Berzelius made an error of only this amount in the conversion of lead into lead oxide, 25 g. of lead would give 26·925 g. of oxide, with a possibility of error of 0·0025 g. This means, however, that the quantity of oxygen with which the lead has combined is 1·925, with a possible error of 0·0025 g., *i.e.* an error of 0·12 per cent on the amount of oxygen. Now this amount is required to fix the equivalent of lead, so that the error in the equivalent is not less than 0·12 per cent, and the value 207·8 may therefore be two units out in the first decimal place, even on the assumption of this very great experimental accuracy.

It may be taken for granted that only for very few elements has an accuracy of 0·1 per cent on the atomic weight been attained. The elements whose atomic weights were determined by Stas with every experimental refinement are generally accepted as being the most accurate.[1] As an example of modern work, we may take recent determinations of the ratio in which oxygen and hydrogen combine to form water, a very important ratio, since these substances are the standards of the different systems of atomic weights. Here gases have to be weighed—a fact which greatly enhances the experimental difficulty, so that the highest degree of accuracy can scarcely be expected.

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[1] These are silver, the halogens, potassium, sodium, lead, sulphur, with less accurate determinations for lithium and nitrogen.

Observers.	Atomic Weight of Hydrogen for O = 16.	Atomic Weight of Oxygen for H = 1.
Dittmar and Henderson	1·0085	15·866
Scott and others	1·0082	15·868
Cooke and Richards	1·0082	15·869
Keiser	1·0076	15·879
Morley	1·0076	15·879
Berthelot	1·0074	15·881
Leduc	1·0074	15·881
Rayleigh	1·0069	15·890
Noyes	1·0064	15·897

Here the extreme difference between the values of different observers is 0·2 per cent—an exceedingly good agreement. The value generally accepted at present for the atomic weight of hydrogen is the mean 1·0076, or 1·008 for accurate practical purposes, although in the laboratory the approximation 1·0 is usually sufficient.

The table of atomic weights on p. 21 gives the most probable values for practical use, each figure being significant. Thus, the atomic weight of carbon, C = 12·00, indicates that the atomic weight probably lies between 11·995 and 12·005; whilst the atomic weight of indium, In = 114, indicates that the true atomic weight probably lies between 113·5 and 114·5. It is possible that the atomic weights of some elements have been determined with greater accuracy than that given, but the reverse is probably more often the case.

Occasionally the figure in the first decimal place is printed in small type. This indicates either that the value is the mean of several not very concordant determinations, or that, for some other reason, a considerable amount of uncertainty attaches to the figure.

An inspection of this table shows that there are some forty-eight elements whose atomic weights have been determined with such accuracy that the first figure after the decimal point may be supposed to possess a real significance. Now according to the rules of probability, we might expect three-tenths of these, namely thirteen, to have values of the first decimal figure lying within 0·15 of a whole number. Instead of three-tenths, however, we find that more than one-half of this number of elements, namely twenty-nine, possess atomic weights diverging by 0·15 or less from the whole numbers. If we only consider elements whose atomic weights are less than 100, the chances of accuracy of the first decimal place are increased, since a unit in that place forms a higher proportion of the whole; yet here also the proportion of elements diverging by 0·15 at most from whole numbers is considerably more than half; and if we consider only the elements whose atomic weights were determined by Stas, we find that two-thirds of them have atomic weights diverging by less than 0·1 from whole numbers. It is difficult to believe that this approximation to whole numbers is quite fortuitous. Early in the century Prout suggested that all atomic weights were multiples of that of hydrogen. This is clearly not the case, for well-investigated elements like chlorine and copper have atomic weights which cannot possibly be brought under such a scheme. It is much less easy to show that the atomic weights of the elements are not multiples of the thirty-second part of the atomic weight of oxygen, *i.e.* that all atomic weights do not end in ·0 or ·5. There is a distinct grouping of the values of the first decimal place round these two numbers, and the grouping is more marked the more we exclude elements of doubtful atomic weight. To conclude from this, however, as has sometimes been done, that all the elements are built up of a fundamental element whose "atomic weight" is one-half of that of hydrogen, and that the actual divergencies from whole or half numbers are due to experimental error, is, to say the least, scarcely justifiable in the present state of our knowledge.

An interesting account of the work of Stas, and a general discussion of methods of atomic-weight determination, will be found in the "Stas Memorial Lecture" by J. W. MALLET (*Journal of the Chemical Society*, 1893, **63**, p. 1). Some work by Stas on pure chemicals is reprinted in the *Chemical News*, 1895, **72**. The student may also be referred to the following examples of modern determinations of equivalents:—

T. W. RICHARDS (*American Academy of Arts and Sciences*, **25** to **28**, and *Chemical News*, 1891-93, **63** to **67**): Equivalents of Copper and of Barium.

E. W. MORLEY (*Smithsonian Contributions*, **29**, and *Zeitschrift für physikalische Chemie*, 1896, **20**): Combining Ratio of Oxygen and Hydrogen.

R. J. STRUTT (*Philosophical Magazine*, 1901 [6th series], **1**, 311): Tendency of the Atomic Weights to approximate to Whole Numbers.

For the origin of the conceptions atom and molecule the student should consult—

Alembic Club Reprints, No. 2. Foundations of the Atomic Theory.
Alembic Club Reprints, No. 4. Foundations of the Molecular Theory.

ATOMIC WEIGHTS

Aluminium	Al	27·1	Neon	Ne	20
Antimony	Sb	120·2	Nickel	Ni	58·7
Argon	A	40	Niobium	Nb	94
Arsenic	As	75·0	Nitrogen	N	14·04
Barium	Ba	137·4	Osmium	Os	191
Beryllium	Be	9·1	**Oxygen**	**O**	**16·000**
Bismuth	Bi	208·5	Palladium	Pd	106·5
Boron	B	11·0	Phosphorus	P	31·0
Bromine	Br	79·96	Platinum	Pt	194·8
Cadmium	Cd	112·4	Potassium	K	39·15
Cæsium	Cs	133	Praseodymium	Pr	140·5
Calcium	Ca	40·1	Radium	Ra	225 (?)
Carbon	C	12·00	Rhodium	Rh	103·0
Cerium	Ce	140	Rubidium	Rb	85·4
Chlorine	Cl	35·45	Ruthenium	Ru	101·7
Chromium	Cr	52·1	Samarium	Sm	150
Cobalt	Co	59·0	Scandium	Sc	44·1
Copper	Cu	63·6	Selenium	Se	79·2
Erbium	Er	166	Silicon	Si	28·4
Fluorine	F	19·0	Silver	Ag	107·93
Gadolinium	Gd	156	Sodium	Na	23·05
Gallium	Ga	70	Strontium	Sr	87·6
Germanium	Ge	72·5	Sulphur	S	32·06
Gold	Au	197·2	Tantalum	Ta	183
Helium	He	4	Tellurium	Te	127·6
Hydrogen	H	1·008	Terbium	Tb	160
Indium	In	114	Thallium	Tl	204·1
Iodine	I	126·85	Thorium	Th	232·5
Iridium	Ir	193·0	Thulium	Tm	171
Iron	Fe	55·9	Tin	Sn	119·0
Krypton	Kr	81·8	Titanium	Ti	48·1
Lanthanum	La	138·9	Tungsten	W	184·0
Lead	Pb	206·9	Uranium	U	238·5
Lithium	Li	7·03	Vanadium	V	51·2
Magnesium	Mg	24·36	Xenon	Xe	128
Manganese	Mn	55·0	Ytterbium	Yb	173·0
Mercury	Hg	200·0	Yttrium	Y	89·0
Molybdenum	Mo	96·0	Zinc	Zn	65·4
Neodymium	Nd	143·6	Zirconium	Zr	90·6

CHAPTER III

CHEMICAL EQUATIONS

In general, if we know all the reacting substances in a chemical transformation, and all the products of the reaction, there is one and only one numerical solution of which the equation is susceptible. For example, if we are given the reacting bodies, copper and nitric acid, and the products, copper nitrate, water, and nitric oxide, *i.e.* the incomplete equation

$$?\,Cu + ?\,HNO_3 = ?\,Cu(NO_3)_2 + ?\,H_2O + ?\,NO,$$

there is only one set of numbers (not containing a common factor) by means of which we can complete the equation, viz.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

It is occasionally a matter of some difficulty to find the proper numbers, and the student is not recommended to proceed to the solution by a process of trial and error, for even in a case like the above the work entailed would be considerable. The solution can always be arrived at by splitting the reaction ideally into simpler reactions whose numbers can be easily determined by inspection, and adding together the equations thus obtained. With a little practice the student can soon acquire sufficient skill to enable him to dispense with the cumbrous array of figures which he must otherwise carry in his memory.

Taking the above example, we might conceivably attack the problem in two different ways. The essential feature of the action is reduction of the nitric acid and oxidation of the copper. We begin, then, by writing an equation to express the reduction of the nitric acid to nitric oxide, ascertaining how many atoms of oxygen are available for oxidising purposes:—

$$2HNO_3 = H_2O + 2NO + 3O.$$

It is evident that the numbers must be as they are given here in order that we may have the same numbers of atoms of hydrogen and nitrogen on the right-hand side.

Then the oxidation of the copper by the three atoms of oxygen is expressed thus :—

$$3Cu + 3O = 3CuO,$$

and the conversion of the copper oxide into nitrate by the nitric acid thus :—

$$3CuO + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O.$$

Adding these equations together, right and left, we get

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

We might, instead of considering the copper to be oxidised directly to the oxide, imagine it to be converted into nitrate by the nitric acid, with liberation of hydrogen, the hydrogen then going to reduce nitric acid to nitric oxide; or we might write everything in the old dualistic system, which supposes salts to be made up of an acidic and a basic oxide, and acids to be composed of an acidic oxide and water, thus :—

$$\begin{aligned} 2HNO_3 &= N_2O_5 + H_2O, \\ N_2O_5 &= 2NO + 3O, \\ 3Cu + 3O &= 3CuO, \\ 3CuO + 3(N_2O_5 \,.\, H_2O) &= 3(CuO \,.\, N_2O_5) + 3H_2O. \end{aligned}$$

Adding these equations, and rejecting the terms which appear on both sides, we get the same equation as before.

As another instance, we may take the oxidation of ferrous chloride to ferric chloride by potassium bichromate in presence of hydrochloric acid :—

$$?\,K_2Cr_2O_7 + ?\,FeCl_2 + ?\,HCl = ?\,KCl + ?\,CrCl_3 + ?\,FeCl_3 + ?\,H_2O.$$

One side of the action is

$$FeCl_2 + HCl = FeCl_3 + H.$$

The bichromate is converted into potassium chloride, chromic chloride, and water :—

$$K_2Cr_2O_7 + 8HCl = 2KCl + 2CrCl_3 + 4H_2O + 3O.$$

The surplus oxygen unites with the hydrogen of the first action, which necessitates multiplying its equation by 6, thus :—

$$\begin{aligned} 6FeCl_2 + 6HCl &= 6FeCl_3 + 6H, \\ 6H + 3O &= 3H_2O. \end{aligned}$$

Adding these three equations, we obtain

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O.$$

Sometimes equations appear indeterminate, and permit an indefinite number of numerical solutions. An example may be found in the decomposition of potassium chlorate by heat, with formation of potassium perchlorate, potassium chloride, and oxygen:—

$$?\,KClO_3 = ?\,KClO_4 + ?\,KCl + ?\,O_2.$$

The equation usually given in the text-books is

$$2KClO_3 = KClO_4 + KCl + O_2,$$

and this has the merit of simplicity. But the equation

$$6KClO_3 = KClO_4 + 5KCl + 7O_2$$

is numerically quite as correct as the other, although entirely different from it, and there are besides an infinite number of other solutions. The reason for this divergence from the general rule that there is only one solution to each equation, is that we are here dealing with two apparently independent actions which go on simultaneously, viz.—

$$(a)\quad 2KClO_3 = 2KCl + 3O_2,$$
$$(b)\quad 4KClO_3 = KCl + 3KClO_4.$$

If we add these equations as they stand, we get

$$6KClO_3 = 3KCl + 3KClO_4 + 3O_2,$$

or dividing by 3,

$$2KClO_3 = KCl + KClO_4 + O_2,$$

the usual book equation.

Multiplying the equation (*a*) by 7, thus—

$$14KClO_3 = 14KCl + 21O_2,$$

and adding (*b*), we obtain

$$18KClO_3 = 15KCl + 3KClO_4 + 21O_2.$$

Dividing by 3, we get

$$6KClO_3 = 5KCl + KClO_4 + 7O_2, \text{ as above.}$$

In general, multiplying (*a*) by x, (*b*) by y, and adding, we have the equation

$$2(x + 2y)KClO_3 = (2x + y)KCl + 3xO_2 + 3yKClO_4,$$

where x and y may each independently have any integral value whatever, so that the numerical solutions are infinite in number. That we are here actually dealing with two simultaneous reactions is evident from the fact that the relative proportions of chloride, perchlorate, and oxygen formed depend on the temperature and the conditions employed to effect the decomposition.

Another instance may be found in the action of hydrochloric acid on a chlorate to produce "euchlorine":—

$$?\,KClO_3 + ?\,HCl = ?\,KCl + ?\,H_2O + ?\,ClO_2 + ?\,Cl_2.$$

This equation too admits of an indefinite number of solutions. In reality two reactions progress simultaneously, viz.—

$$\begin{aligned}&(a)\ KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2,\\&(b)\ 5KClO_3 + 6HCl = 5KCl + 3H_2O + 6ClO_2.\end{aligned}$$

If we add these equations, we obtain

$$6KClO_3 + 12HCl = 6KCl + 6H_2O + 3Cl_2 + 6ClO_2,$$

or

$$2KClO_3 + 4HCl = 2KCl + 2H_2O + Cl_2 + 2ClO_2.$$

The equation usually given in the text-books is

$$8KClO_3 + 24HCl = 8KCl + 12H_2O + 6ClO_2 + 9Cl_2,$$

which is more complicated. It may be obtained by multiplying (*a*) by 3 and adding it to (*b*), thus :—

$$\begin{array}{l}3KClO_3 + 18HCl = 3KCl + 9H_2O + 9Cl_2\\ 5KClO_3 + 6HCl = 5KCl + 3H_2O + 6ClO_2\\ \hline 8KClO_3 + 24HCl = 8KCl + 12H_2O + 6ClO_2 + 9Cl_2.\end{array}$$

The general expression is

$$(x + 5y)KClO_3 + 6(x + y)HCl = (x + 5y)KCl + 3(x + y)H_2O + 3xCl_2 + 6yClO_2,$$

where x and y may be given any integral values whatever. The actual proportion of chlorine and chlorine peroxide obtained in any one experiment depends on the temperature and on the concentration of the hydrochloric acid employed. From a consideration of the general equation it is easy to obtain an equation which shall express the relative proportions of Cl_2 and ClO_2 obtained in a given experiment. Thus, to write an equation which will correspond to the case of equal volumes of chlorine and chlorine peroxide being evolved, we have only to make $x = 2$ and $y = 1$, which will give the same number of molecules of chlorine and chlorine peroxide, and therefore equal volumes, thus :—

$$7KClO_3 + 18HCl = 7KCl + 9H_2O + 6Cl_2 + 6ClO_2.$$

The reduction of nitric acid to form more than one of the lower oxides of nitrogen will afford similar instances to the student, who is advised to make himself familiar with them.

To express the formation of phosphonium iodide and hydriodic acid from phosphorus, iodine, and water, we sometimes find in books the following complicated equation :—

$$9I + 13P + 24H_2O = 6H_3PO_4 + 2HI + 7PH_4I.$$

That this is needlessly complex may be seen by simple inspection, for without any difficulty we can arrive at the solution

$$2I + 2P + 4H_2O = H_3PO_4 + HI + PH_4I.$$

Since the equation admits of two numerical solutions it must be indeterminate, and permit of an infinite number. We can get the general solution as usual by splitting up the indeterminate equation into the two independent determinate equations of which it is composed. In the one case we have the production of phosphoric acid and hydriodic acid from the reacting substances; in the other we have the production of phosphoric acid and phosphonium iodide, the determinate equations for these reactions being

$$5I + P + 4H_2O = H_3PO_4 + 5HI,$$
$$5I + 9P + 16H_2O = 4H_3PO_4 + 5PH_4I.$$

The general equation is then

$$5(x + y)I + (x + 9y)P + 4(x + 4y)H_2O = (x + 4y)H_3PO_4 + 5xHI + 5yPH_4I.$$

By making $x = 1$ and $y = 1$ in this equation, we obtain, on simplifying, the solution

$$2I + 2P + 4H_2O = H_3PO_4 + HI + PH_4I,$$

and by making $x = 2$ and $y = 7$, we obtain the solution

$$9I + 13P + 24H_2O = 6H_3PO_4 + 2HI + 7PH_4I.$$

Occasionally it happens that substances having the same composition, *i.e.* isomeric or polymeric substances, are produced by a chemical action. In this case the equations are indeterminate, although the chemical action itself may be quite definite. Thus, for the inversion of cane sugar we have the equation

$$?\,C_{12}H_{22}O_{11} + ?\,H_2O = ?\,\underset{\text{(dextrose)}}{C_6H_{12}O_6} + ?\,\underset{\text{(levulose)}}{C_6H_{12}O_6}.$$

This equation is evidently susceptible of an indefinite number of solutions, if we consider separately the isomeric molecules produced, although the only chemical action that goes on is expressed by the equation giving the same number of molecules of dextrose and levulose, viz.

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{(dextrose)}}{C_6H_{12}O_6} + \underset{\text{(levulose)}}{C_6H_{12}O_6}.$$

Since there is in general only one solution to a chemical equation in integers which contain no common factor, this solution may be sought algebraically; but the student of chemistry is not recommended to make use of the algebraic process, as it is purely mechanical and affords little insight into the nature of the chemical actions considered. Thus if we want to find algebraically the values of a, b, c, d, e, f, g in the equation

$$aK_2Cr_2O_7 + bFeCl_2 + cHCl = dKCl + eCrCl_3 + fFeCl_3 + gH_2O,$$

we may proceed as follows. Taking each element separately we obtain the following equations :—

$$
\begin{array}{ll}
2a = d & \text{for K} \\
2a = e & \text{for Cr} \\
7a = g & \text{for O} \\
b = f & \text{for Fe} \\
2b + c = d + 3e + 3f & \text{for Cl} \\
c = 2g & \text{for H}
\end{array}
$$

Here we have 6 equations between 7 unknown quantities, but the further condition that the values shall be integral and contain no common factor, makes the problem determinate. We may make as a preliminary assumption $a = 1$; then it follows at once that $d = 2$, $e = 2$, $g = 7$, $c = 14$; and also, since $b = f$,

$$2b + 14 = 2 + 6 + 3b,$$

or

$$b = f = 6\,;$$

whence

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O.$$

If we had assumed $b = 1$ the values obtained would not have been integral, but multiplication by 6 would have made them so.

With an equation like

$$a\mathrm{I} + b\mathrm{P} + c\mathrm{H_2O} = d\mathrm{H_3PO_4} + e\mathrm{HI} + f\mathrm{PH_4I}$$

we get the algebraic equations

$$
\begin{array}{ll}
a = e + f & \text{for I} \\
b = d + f & \text{for P} \\
2c = 3d + e + 4f & \text{for H} \\
c = 4d & \text{for O}
\end{array}
$$

i.e. only 4 relations between 6 unknown quantities, so that the problem is indeterminate, as has been already stated.

CHAPTER IV

THE SIMPLE GAS LAWS

THE student is doubtless familiar with the fact that the laws regulating the physical condition of gases are of an extremely simple character and of universal applicability. Pressure and temperature affect the volume of all gases to nearly the same degree, no matter what the chemical or other physical properties of the gases may be, so that we can state for gases the following general laws :—

1. *Boyle's Law.*—The volume of a given mass of any gas varies inversely as the pressure upon it if the temperature of the gas remains constant.

2. *Gay-Lussac's Law.*—The volume of a given mass of any gas varies directly as the absolute temperature of the gas if the pressure upon it remains constant.

3. The pressure of a given mass of any gas varies directly as the absolute temperature if the volume of the gas remains constant.

Any one of these laws may be deduced from the other two, and as an example we may take the deduction of the third law from the laws of Boyle and Gay-Lussac. Let the original pressure, volume, and temperature of the gas be p_0, v_0, and T_0. Let the gas be heated at the constant pressure p_0 to the temperature T_1. Then, according to Gay-Lussac's Law,

$$\frac{v_0}{V}=\frac{T_0}{T_1},$$

if V is the volume assumed at T_1.

Now let the gas be compressed to the original volume v_0 at the constant temperature T_1. According to Boyle's Law, the product of the pressure and volume of a gas always remains the same if the temperature is constant. We have therefore at T_1

$$p_0V=p_1v_0,$$

if p_1 represents the value of the pressure after compression to the volume v_0. But from the first equation we have

$$V=\frac{T_1}{T_0}v_0.$$

Substituting this value in the second equation, we obtain

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

which is an expression of the third law for the variation of pressure with temperature at constant volume.

These three separate laws may be put into the form of a single equation as follows. Let the pressure, volume, and temperature of a mass of gas all change, the original values being p_0, v_0, T_0, and the final values p_1, v_1, T_1. Suppose first the volume to remain constant at v_0, and the temperature to assume its final value T_1. The gas will then have a pressure P, given by the equation

$$\frac{p_0}{P}=\frac{T_0}{T_1},$$

Let the gas now expand from v_0 to v_1, at constant temperature T_1; the new pressure p_1 will then be given by the equation

$$Pv_0=p_1v_1,$$

whence

$$P=\frac{p_1v_1}{v_0}.$$

Substituting this value of P in the pressure-temperature equation, we have finally

$$\frac{p_0v_0}{p_1v_1}=\frac{T_0}{T_1},$$

i.e. the product of the pressure and volume of a gas is proportional to the absolute temperature.

The final result may also be made to assume the form

$$\frac{p_0v_0}{T_0}=\frac{p_1v_1}{T_1};$$

that is, the expression pv/T for a given quantity of gas always remains constant. Since if pressure and temperature are constant the quantity of a gas is proportional to the volume taken, the actual value of the expression pv/T is proportional to the quantity or volume considered. Now, since according to Avogadro's principle the gram-molecular weights of all gases occupy the same volume under the same conditions of temperature and pressure, it follows that for these quantities the expression will have a constant value, no matter what the nature of the gas is, or the conditions under which the volume is measured. We have therefore in general for all gases

$$\frac{pV}{T}=R,$$

where R is a constant, and V the volume occupied by the gram molecule of the gas. At 0° and 76 cm. the gram-molecular volume is 22·4 litres, or, more exactly, 22,380 cc. (cp. p. 14). The pressure p in grams per square centimetre is 1033 (p. 3), and T is 273. To calculate the value of R we have therefore

$$R=\frac{1033\times 22{,}380}{273}=84{,}678.$$

This value of the general gas constant R bears a very simple relation to J, the mechanical equivalent of heat, and advantage may be taken of this circumstance to throw the gas equation into a very convenient form for many calculations.

The product pv is of the dimensions of mechanical energy, and may be expressed in gram centimetres, p being expressed as $\frac{\text{g.}}{\text{cm.}^2}$, and v as cm.^{3}, the product therefore being g. × cm., or gram centimetres. To convert this product into thermal units we divide by $J=42{,}650$, and thus obtain

$$R=\frac{1033\times 22{,}380}{273\times 42{,}650}=\frac{84{,}678}{42{,}650}=2 \text{ nearly.}$$

The general gas equation for molecular quantities may therefore be written in the form

$$pV=2T$$

when the gram-calorie is employed as thermal unit.

This equation is very frequently used in measuring the work done upon or done by a gas when it changes its volume under external pressure. The amount of work is equal to the product of the pressure into the change of volume, and can be easily expressed in thermal units by means of the above equation when molecular quantities are considered. Thus if a gram molecule of a gas is generated by chemical action, say from the interaction of zinc and an acid, an amount of heat will be absorbed in performing the external work of expansion equal to 2 T calories, *i.e.* to 546 calories if the action takes place at 0° C. Other examples of the use of this equation will be found in the chapters dealing with specific heats, the gas laws for solutions, and more especially in the chapter on thermodynamics.

These simple gas laws, and the deductions from them, apply in strictness only to ideal or "perfect" gases, no actually existing gas obeying them exactly. For most purposes of calculation, however, they may be applied to ordinary gases without any very serious error being committed, if care be taken in applying them to vapours near the point of condensation or to gases under very great pressures (cp. Chapters IX. and X.).

CHAPTER V

SPECIFIC HEATS

As early as 1819, Dulong and Petit noticed that the products of the atomic weights of the elements into their specific heats were approximately constant. Of course at that time the atomic weights of the elements had been determined with very little certainty, but taking the atomic weights even as they stood there was an unmistakable appearance of regularity. In cases where there was doubt as to which equivalent of an element ought to receive the preference, the rule given by Dulong and Petit was helpful. It was evidently more rational to choose that equivalent which conformed to the regularity displayed by the other elements than an equivalent which would make the element under discussion appear exceptional. This means of selecting a standard number from amongst the different possible equivalents of an element to represent its atomic weight, proved of great use during the period when Avogadro's principle was not recognised as a safe guide in fixing molecular and atomic quantities; and even after the recognition of this principle, the Law of Dulong and Petit rendered much service in precisely those cases where the application of Avogadro's Law failed from want of data.

It must be borne in mind that the Law of Dulong and Petit is a law on precisely the same footing as Avogadro's Law. According to Avogadro's principle, we take as molecular weights those quantities of gases which occupy a certain volume under given conditions, and from these molecular weights we deduce by a consistent process the atomic weights of the elements. According to Dulong and Petit's rule, we take as the atomic weights of the solid elements those quantities which have a certain capacity for heat. As it happens, the atomic weights deduced by the one method coincide with the atomic weights deduced by the other. Since, then, the two rules are not contradictory but lead to the same result, considerable confidence may be placed in the system of atomic weights arrived at by their aid, and the periodic regularities referred to in Chapter VI. seem further to justify this trust.

The rule of Dulong and Petit may be stated in the form that the capacity of atoms for heat is approximately the same for all solid elements. The **atomic heat**, as it is called, is obtained by multiplying the specific heat of the element into its atomic weight, the product being nearly equal to 6·4 when we measure specific heats and atomic weights in the customary units. The following table gives the atomic weights and the specific heats of the solid elements, and also the corresponding products, the atomic heats :—

Table I

Element.	A Atomic Weight.	S Specific Heat.	$A \times S$ Atomic Heat.
Lithium	7	·94	6·6
Beryllium	9	·41	3·7
Boron (amorphous)	11	·25	2·8
Carbon (diamond)	12	·14	1·7
Sodium	23	·29	6·7
Magnesium	24	·245	5·9
Aluminium	27	·20	5·4
Silicon (crystalline)	28	·16	4·5
Phosphorus (yellow)	31	·19	5·9
Sulphur (rhombic)	32	·18	5·7
Potassium	39	·166	6·5
Calcium	40	·170	6·8
Scandium	44	·153	6·7
Chromium	52	·121	6·3
Manganese	55	·122	6·7
Iron	56	·112	6·3
Cobalt	59	·107	6·3
Nickel	59	·108	6·4
Copper	63	·093	5·9
Zinc	65	·093	6·1
Gallium	70	·079	5·5
Arsenic (crystalline)	75	·082	6·2
Selenium (crystalline)	79	·080	6·3
Bromine (solid)	80	·084	6·7
Zirconium	91	·066	6·0
Molybdenum	96	·072	6·9
Ruthenium	102	·061	6·2
Rhodium	103	·058	6·0
Palladium	106	·059	6·3
Silver	108	·056	6·0
Cadmium	112	·054	6·0
Indium	114	·057	6·5
Tin	119	·054	6·5
Antimony	120	·052	6·2
Tellurium	127	·047	6·0
Iodine	127	·054	6·8
Lanthanum	139	·045	6·2
Cerium	140	·045	6·3
Tungsten	184	·033	6·1
Osmium	191	·031	6·2
Iridium	193	·0324	6·3
Platinum	195	·032	6·3
Gold	197	·032	6·3
Mercury (solid)	200	·032	6·4
Thallium	204	·0335	6·8

Element.	*A* Atomic Weight.	*S* Specific Heat.	*A*×*S* Atomic Heat.
Lead	207	·031	6·4
Bismuth	209	·030	6·3
Thorium	232	·0276	6·4
Uranium	239	·0276	6·6

It will be observed that though the values of the atomic heats fluctuate to some extent, they are generally not far from the mean 6·4. The diagram on p. 40 shows the regularity between atomic weights and specific heats in graphic form, and will be discussed later.

If we consider for a moment the elements whose atomic heats are quite exceptional and give values widely divergent from the mean 6·4, we find that they are all elements with low atomic weights. The chief are beryllium, boron, carbon, silicon, aluminium, and sulphur. Even in these cases the divergence is perhaps only apparent, and that for the following reason. The specific heats of all substances vary with the temperature at which they are measured; and though the variation is often slight, it is occasionally of relatively great dimensions. When this is so in the case of an element, the question arises: At what temperature must the measurement of the specific heat be made in order to get numbers comparable with those for the other elements? No definite answer has been given to this question, but it is found that as the temperature rises, the specific heat seems to approach a limiting value, and this value is not in general far removed from that which would make the atomic heat approximately equal to 6·4. The following table gives the results obtained by Weber for carbon and silicon, and by Nilson and Pettersson for beryllium.

Table II

CARBON

Diamond			Graphite		
Temperature.	Specific Heat.	Atomic Heat.	Temperature.	Specific Heat.	Atomic Heat.
−50	0·0635	0·76	−50	0·1138	1·37
+10	0·1128	1·35	+10	0·1604	1·93
85	0·1765	2·12	61	0·1990	2·39
206	0·2733	3·28	202	0·2966	3·56
607	0·4408	5·3	642	0·4454	5·35
806	0·4489	5·4	822	0·4539	5·45
985	0·4589	5·5	978	0·4670	5·5
BERYLLIUM			SILICON		
23	0·397	3·62	−40	0·136	3·81
73	0·448	4·08	+57	0·183	5·13
157	0·519	4·73	129	0·196	5·50
257	0·582	5·29	232	0·203	5·63

As may be seen in the case of carbon, when an element exists in more than one modification, each modification has its own specific heat. Thus, at the ordinary temperature the specific heats of diamond and graphite are very different. At high temperatures, however, they become identical, reaching the same limiting value.

An approximate rule for compounds, of like nature to Dulong and Petit's principle for elements, was stated by Neumann in 1831. On comparing compounds of similar chemical character, he found that the products of their specific heats and molecular weights were constant. This may be stated in the form that the **molecular heats** of similarly constituted compounds in the solid state are equal. This rule is a special case of a regularity of wider scope. Kopp showed that very frequently the molecular heat of a solid compound was equal to the sum of the atomic heats of its component atoms. The atoms in combining together to form molecules thus retain their heat capacity practically unchanged. By making use of this general principle, the specific heats of elements in the solid form have been calculated even when the elements themselves were not known to exist in the solid state. Thus the specific heat of solid oxygen could not be determined directly, but by taking the molecular heats of a great number of solid oxygen compounds and subtracting from them the heat capacities of the atoms of the other elements present, the remainder (which was supposed to be the heat capacity of the oxygen atoms in the compound) always gave an atomic heat for oxygen in round numbers equal to 4. This value was therefore taken as the atomic heat of oxygen in the solid state, whence on dividing by 16 we get 0·25 as the specific heat of solid oxygen.

The foregoing rules apply only to solids. The **specific heat of liquids** usually varies very much with the temperature, but definite relations have been discovered in certain classes of compounds. Thus Schiff found that all the ethereal salts of the fatty acids examined by him had the same specific heat, no matter what their molecular weight was, provided that the specific heats were all measured at the same temperature. In other groups of liquid substances less simple relations exist, but there is usually an approach to regularity of some sort.

The **specific heat of gases** presents a different aspect from the specific heats of solids or of liquids. If we compress a gas, we warm it, although we supply no heat to it; if we allow a gas to expand under atmospheric (or other) pressure, it cools, although no heat has been abstracted from it. Now specific heat may be defined as the number of heat units which must be supplied to 1 gram of a substance in order that its temperature may be raised 1 degree centigrade at the ordinary temperature. But we can raise the temperature of 1 gram of a gas through 1 degree centigrade, without supplying any heat at all, by simply compressing it. We should therefore have to say that its specific heat under these conditions is zero, as its temperature has been raised without any heat being supplied. On the other hand, if we allow the gas to expand sufficiently against pressure while heat is being supplied to it, its temperature may be kept absolutely constant, the heat supplied merely counterbalancing the cooling due to the expansion. The specific heat of the gas in this case is infinite, for a finite amount of heat has been supplied and has only produced an infinitely small rise of temperature. The specific heat of a gas therefore depends on its volume relations. It may have any positive specific heat between zero and infinity, or even any negative specific heat, according to the manner in which its volume changes during the process of heating. We must always specify, therefore, under what conditions we measure the specific heat of a gas. There are two conditions which are usually looked upon as standard conditions. In the one case the volume of the gas is not allowed to change during the change of temperature. This gives the specific heat at constant volume. In the other case the volume is allowed to change during the change of temperature and the gas is permitted to expand or contract under a constant pressure. This gives the specific heat at constant pressure, which for practical measurements is the most convenient, the gas being allowed to change its volume at the atmospheric pressure.

The relation between these two specific heats is easily determined. Suppose we raise the temperature of 1 g. of gas from 0° to 1°, maintaining the volume constant; the quantity of heat required is the specific heat of the gas at constant volume. Let the temperature of the same gas be raised now from 0° to 1°, the gas being allowed to expand against the atmospheric pressure according to Gay-Lussac's Law; the quantity of heat required is the specific heat at constant pressure. The quantity of heat required in the second is greater than in the first. This is owing to the fact that the gas on expanding against pressure cools by doing work, and heat must be supplied to make up for this cooling. To find the amount of this heat we measure the amount of work the gas does in expanding against the atmospheric pressure. As we have already seen in Chapter IV., the work done is the product of the pressure into the change of volume. It is thus better to consider a certain volume of gas than a certain weight, and for purposes of comparison we take the gram-molecular volume (22·4 litres at 0° and 760 mm.), *i.e.* the volume occupied by the gram molecule of any gas. By Gay-Lussac's Law the expansion between 0° and 1° is $\frac{1}{273}$ of the volume, viz. $\frac{22,400}{273} = 82$ cc. The work is therefore 82×1033, or about 84,700 gram centimetres. Now to supply 1 cal. of heat, *i.e.* to heat 1 g. of water from 0° to 1°, we must do 42,650 gram centimetres of work. The work done, therefore, by the gram-molecular volume of gas on expanding is equal to $\frac{84,700}{42,650} = 2$ cal. To heat the gram molecule of gas from 0° to 1° requires 2 cal. more at constant pressure than at constant volume. It is usual to call the amount of heat required to raise the temperature of the gram molecule one degree, the molecular heat, this being the product of the molecular weight into the specific heat. The molecular heat of a gas at constant pressure is thus 2 cal. greater than the molecular heat at constant volume. The following table contains the molecular heats of some of the simpler gases :—

TABLE III

Name.	Formula.	Mol. Heat at Constant Pressure C_p.	Mol. Heat at Constant Volume C_v.	$\frac{C_p}{C_v}$.
Argon	A	...	...	1·66
Helium	He	...	...	1·66
Mercury	Hg	...	...	1·66
Hydrogen	H_2	6·82	4·82	1·41
Nitrogen	N_2	6·83	4·83	1·41
Oxygen	O_2	6·96	4·96	1·40
Chlorine	Cl_2	8·58	6·58	1·30
Bromine	Br_2	8·88	6·88	1·29
Nitric oxide . . .	NO	6·95	4·95	1·40
Nitrous oxide . . .	N_2O	9·94	7·94	1·25
Carbon monoxide . .	CO	6·86	4·86	1·41
Carbon dioxide . . .	CO_2	9·55	7·55	1·26
Sulphur dioxide . .	SO_2	9·88	7·88	1·25
Hydrochloric acid . .	HCl	6·68	4·68	1·43
Sulphuretted hydrogen .	H_2S	8·27	6·27	1·31
Ammonia	H_3N	8·64	6·64	1·30
Methane	H_4C	9·49	7·49	1·27

It is a matter of great difficulty to determine the specific heat of a gas at constant volume, owing to a comparatively small amount of the heat supplied going to heat the gas, the greater part being absorbed by the vessel which contains the gas. It is much easier to determine the specific heat at constant pressure, for then we can pass large quantities of the gas through a worm contained in a calorimeter, and measure the amount of heat it gives or takes. The molecular heats at constant volume in the above table have been obtained merely by subtracting 2 cal. (the value of the work of expansion per gram molecule) from the molecular heat at constant pressure.

The **ratio of the specific heats** at constant pressure and constant volume can be ascertained with great accuracy from a determination of the velocity of sound in the gas under consideration. The values of the ratios thus obtained by Kundt's method agree closely with those of the above table. In the case of mercury vapour, argon, and helium, Kundt's method has alone been used in determining the ratios of the specific heats.

From the kinetic theory of gases it follows that if the molecules of a gas are monatomic, so that all the heat they receive from without goes only to increase their rectilinear velocity, and not to perform any kind of change within the molecule, the molecular heat at constant pressure will be 5, and at constant volume 3, *i.e.* the ratio $\frac{C_p}{C_v}$ will be 1·66. If a molecule consists of more atoms than one, we should expect that a larger quantity of heat would be absorbed for the same rise of temperature, a portion of the heat being employed within the molecule in changing the relations of the constituent atoms to each other. The molecular heat at constant volume would therefore be greater than 3, say $3 + m$. But the molecular heat at constant pressure is obtained by adding 2 to that at constant volume; it is therefore $5 + m$, and the ratio $\frac{5 + m}{3 + m}$ is consequently less than the theoretical ratio $\frac{5}{3}$.

Accordingly, when the molecule of a gas consists of a single atom, we should expect the ratio of the specific heats to be 1·66; for here no heat can be expended in rearrangements of atoms within the molecule. Where the molecule of a gas consists of a number of atoms, we should expect on the other hand that a portion of the heat would be expended in effecting new relations between the constituent atoms, and would not go entirely towards increasing the rectilineal velocity of the molecule as a whole, and therefore that the ratio of the specific heats would be less than 1·66. Until recently one elementary gas only was known for which the vapour-density results led to the conclusion that there was only one atom in the molecule. This gas was mercury vapour, and its density corresponded to the molecular weight 200, which is identical with the atomic weight. Now Kundt and Warburg, from determination of the speed of sound in mercury vapour, found that the ratio of its specific heats is 1·66, a figure in accordance with the theoretical value deduced for monatomic gases.

The recently-discovered gases, argon, helium, etc., resemble mercury in this respect. The ratio of their specific heats is 1·66, and we are therefore obliged to conclude, provisionally, at least, that they are elementary substances having only one atom in the molecule. If they were compound substances they would necessarily contain more than one atom in the molecule, and one would expect the ratio to have a lower value. It has been held that argon is an allotropic modification of nitrogen, differing from ordinary nitrogen as ozone differs from oxygen. On this assumption the molecular weight of argon would be 42, and its formula would be N_3. But if this were so, we should expect the ratio of the specific heats to be less than the ratio for ordinary nitrogen, viz. 1·410, instead of being equal to the theoretical value for monatomic gases. Until we have direct evidence to the contrary, we must look upon argon, helium, etc., as being monatomic, and therefore elementary gases; for the ratio of the specific heats is the best evidence we have of the character of their molecules, and that pronounces the molecule to be monatomic.

It should be noted by the student that the specific heat at constant volume of a "perfect" gas is independent of the volume which the gas occupies. No known gas is in this sense "perfect,"—indeed the deviation from perfection of existing gases has important practical applications, *e.g.* in machines for producing liquid air (Chap. IX.),—but the conception is of value as simplifying many thermo-dynamical calculations.

CHAPTER VI

THE PERIODIC LAW

We have learned in what has preceded that there are about eighty distinct chemical substances which have resisted all our attempts to decompose them into anything simpler. The question now arises: Are our elements in truth undecomposable, or are they merely compounds which we are unable to decompose? It is impossible at present to give any definite answer to this question, and it may be left open without affecting our views on practical chemical problems at all. We may be tolerably certain, however, that if our well-known elements are really compounds, they are all compounds of the same type, that type being different from the compounds of the elements among themselves. The reason for this statement is not far to seek. We have seen that the product of the atomic weight and specific heat of solid elements is nearly constant, and equal to 6·4 if the ordinary units for atomic weight and specific heat are adopted. We may express this relation in the form of a curve (Fig. 1). On the horizontal axis are plotted atomic weights, on the vertical axis specific heats. If the product were exactly equal to 6·4, the curve would be the smooth rectangular hyperbola shown in the figure. The actual values are indicated near the symbols, and it will be seen that they never fall very far away from the curve. Here, then, we have a regularity amongst the elements—a regularity, moreover, which is not shared by the compounds (cp. Neumann's Law, p. 34). It is evident, then, from this alone, that whatever the ultimate nature of our elements may be they form a class of substances apart from all others.

The same conclusion is reached when we tabulate properties of the elements other than the specific heat. Let us take, for example, the **specific gravity** of the elements, and as before tabulate the values on the vertical axis, atomic weights being tabulated on the horizontal axis. The points thus obtained do not lie, as with the specific heat, approximately on a continuous curve, but, as the lines in Fig. 2 indicate, on a series of somewhat irregular curves, which resemble each other closely in general appearance. If the whole series is looked upon as a single curve, that curve is what is termed a **periodic curve**, *i.e.* one which after a certain interval repeats itself. Each repetition is called a period, and the periods have been marked in the figure by Roman numerals. The elements alone fall naturally into their places on this curve; compounds, if we take their formula weight as representing the atomic weight, fall far away from it, so that we are again justified in assuming that our elements, if they are composite, are not compounds in the ordinary sense.

The periodic character of the curve shows the existence of many relations which do not appear in the curve of specific heats. There

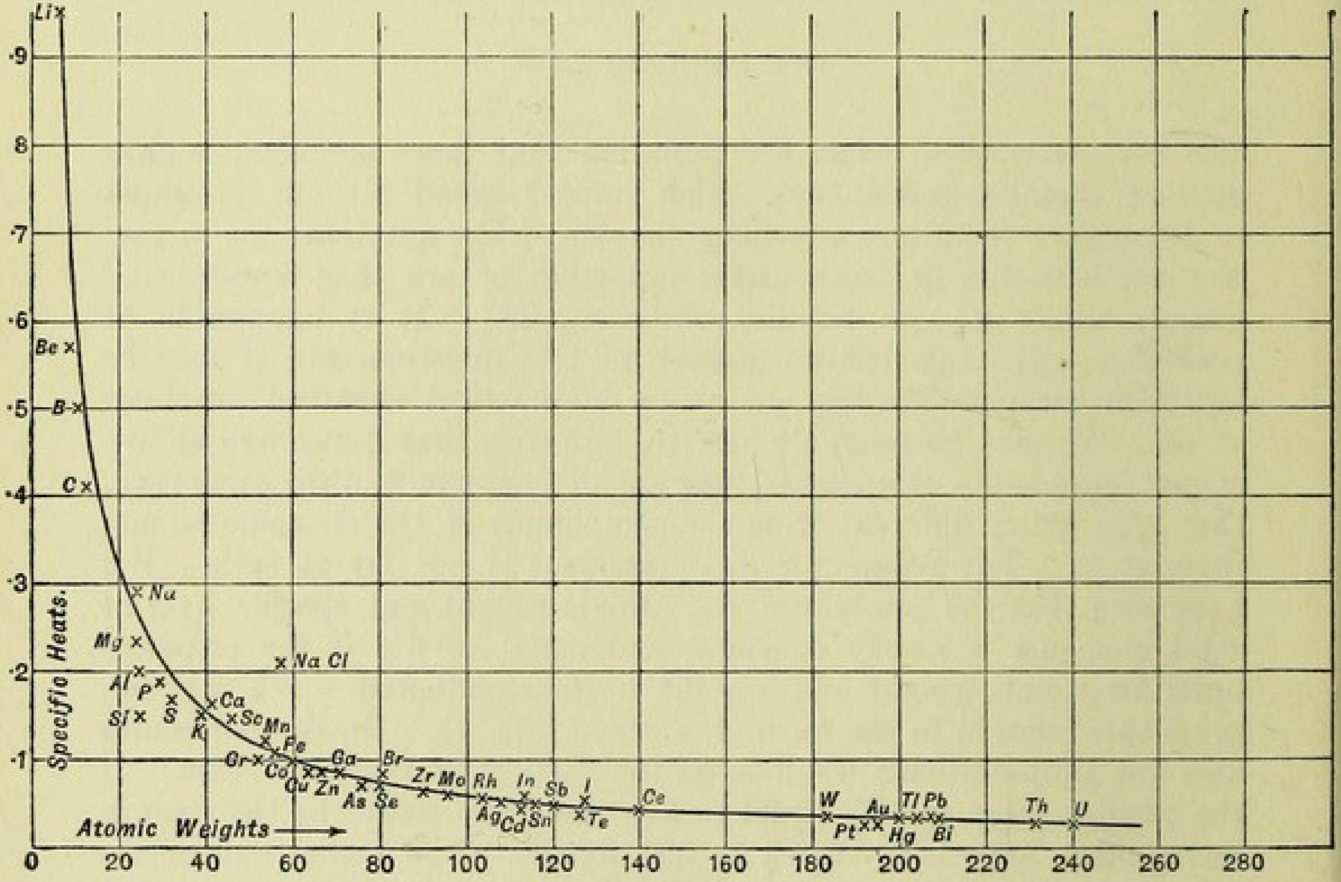

Fig. 1.

are evidently two sorts of periods in the figure, the first two being very much smaller than the others. These are called the *short* periods; the others are *long* periods. We see at once from the curve that elements which occupy similar positions in the separate periods are similar in their chemical character. Thus the first element in each complete period, long or short, is an alkali metal, the second is a metal of the alkaline earths, and the last element a halogen.

It will be noticed, too, that similar elements very often in this diagram lie on or near straight lines. Thus if we join the points for lithium and cæsium, the first and the last alkali metals, we find that the straight line passes close by the points for sodium, potassium, and rubidium, the three intermediate alkali metals. Similarly, the points

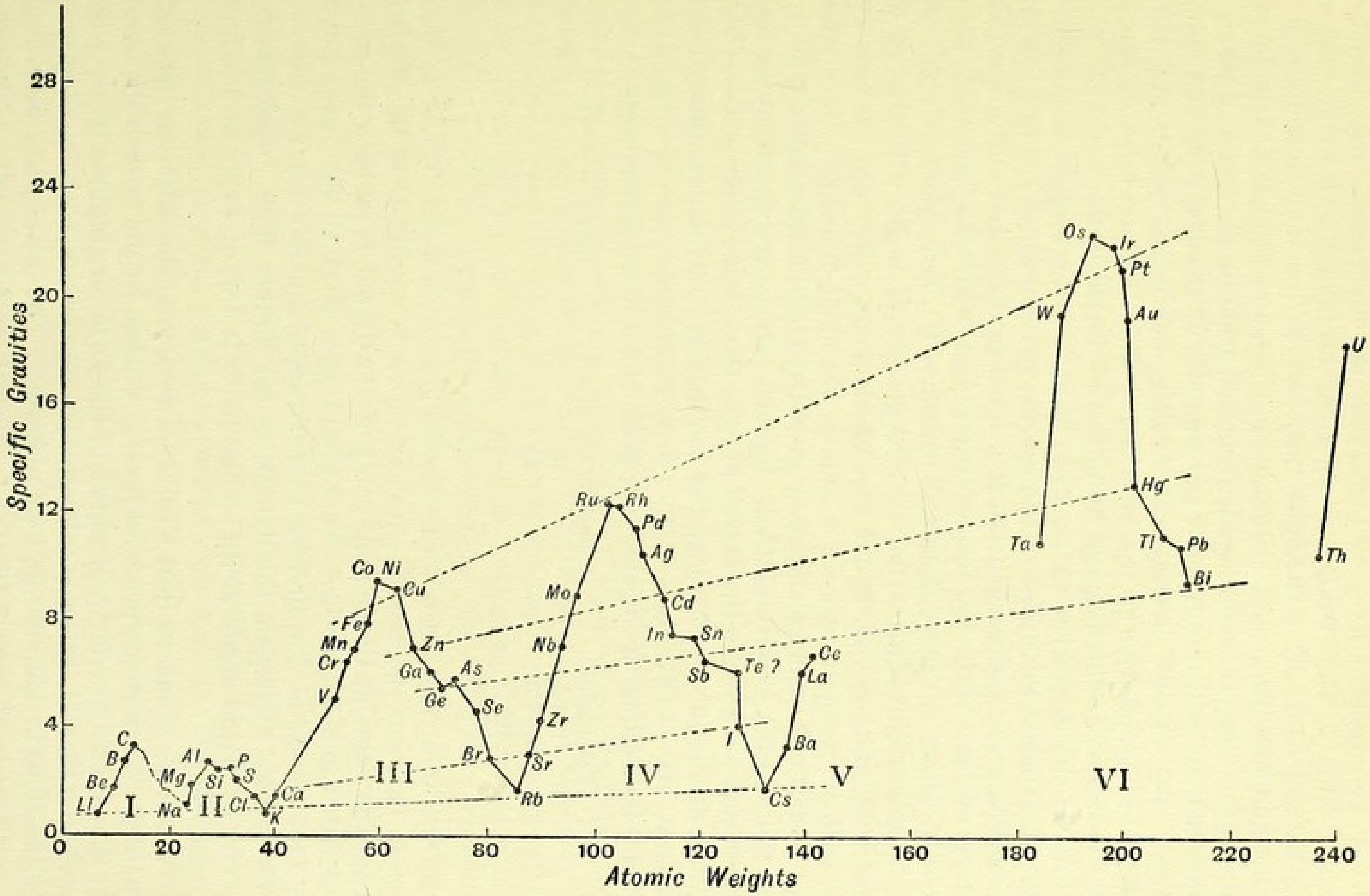
Specific Gravities
28
24
20
16
12
8
4
0
0
20
40
60
80
100
120
140
160
180
200
220
240
Atomic Weights
Li
Be
B
C
Na
Mg
Al
Si
P
S
Cl
K
Ca
V
Cr
Mn
Fe
Co Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te ?
I
Cs
Ba
La
Ce
Ta
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
I
II
III
IV
V
VI

Fig. 2.

for the metals of the alkaline earths, together with those of the closely related metals beryllium and magnesium, lie very nearly in one straight line. The halogens, chlorine, bromine, and iodine may also be connected by a straight line, and so too may arsenic, antimony, and bismuth; zinc, cadmium, and mercury; sulphur, selenium, tellurium. The platinum metals (osmium, iridium, platinum; ruthenium, rhodium, palladium) lie at the summits of the last complete long periods, the related metals iron, nickel, and cobalt occupying the corresponding position in the first long period. These relations have been indicated in the diagram by means of dotted lines.

As is the case with the specific heat, it is here again somewhat difficult to select the values of the specific gravity which are to be used for comparative purposes in such a table as the above. The specific gravity varies with the temperature and with the chemical and physical states of the substances considered. It is obviously out of the question to compare the specific gravity of a gas with that of a solid or liquid, so that in the case of elements which are gaseous at the ordinary temperature we encounter the chief difficulty. It is true that all the well-known elementary gases have been condensed to liquids, but the specific gravity of these liquids varies very greatly with the temperature. Thus in the case of oxygen the specific gravity at – 130° is 0·76, at – 140° it is 0·88, and at the boiling point under atmospheric pressure, viz. – 181°, it is 1·12. A decision in the case of nitrogen is equally impossible, as Wroblewski gives the following numbers:—

Temperature.	Pressure in Atmospheres.	Specific Gravity.
– 146·0	38·5	0·455
– 153·7	30·7	0·584
– 193·0	1·0	0·830
– 202·0	0·1	0·866

Here within a range of 60° the specific gravity is doubled. If a comparison between the specific gravities of such liquids is to be effected at all, the value at the boiling point of the liquid is perhaps the most reasonable one to choose. This would give us 1·12 for oxygen and 0·83 for nitrogen. For fluorine we have approximately 1·2, for chlorine 1·35, and for hydrogen, the lightest of all liquids, 0·07. The specific gravity of liquid argon at its boiling point is 1·2, of krypton 2·2, and of xenon 3·5.

When we come to deal with solid elements, the selection between different modifications presents itself. Carbon in the form of diamond has the specific gravity 3·3, whilst in the form of graphite it has only the value 2·15. Similar differences are found with the various modifications of sulphur and phosphorus. The metals, too, according to their mode of preparation and physical treatment, have often very different specific gravities—that of cobalt, for instance, varying between 8·2 and 9·5. In the diagram the highest value has been entered in such cases as probably being the most appropriate for comparative purposes.

There is a function of the specific gravity which is very frequently tabulated for the purpose of exhibiting the periodic character of the properties of the elements, namely the **atomic volume.** The atomic volume is the product of the atomic weight into the specific volume, or, what is the same thing, the quotient of the atomic weight by the specific gravity. The curve, first drawn by Lothar Meyer, is shown in Fig. 3 (p. 44). The periodic chararcter of the curve is again well marked, only now the shape of the periods is different, the maxima corresponding to the mimima of the specific-gravity curve, and *vice versa.* The difference between the short and long periods is once more evident, and similar elements once more occupy corresponding positions on the curve. In general, we may say that elements on steep portions of the curve have very pronounced chemical characters: as we proceed from left to right, the elements on descending portions of the curve are base-forming, and those on ascending portions acid-forming. Elements at or before the minima cannot be said to be decidedly acid-forming or decidedly base-forming; in different stages of oxidation they may be either.

Most well-defined properties of the elements are periodic, *e.g.* melting point and magnetic power. When the numerical values are tabulated against the atomic weights, the curve obtained is broken up into periods, the shape of the period varying according to the property tabulated. The regular non-periodic curve obtained for the specific heat is quite exceptional. Not only are the properties of the elements themselves periodic, but the properties of their corresponding compounds are also frequently periodic. Thus if we tabulate the heat of formation of the chlorides of the elements against the atomic weights of the elements which combine with the chlorine, a periodic curve results. The same periodicity is observed in the molecular volumes of the oxides, and in the melting and boiling points of various corresponding compounds.

We may tabulate the elements in another way without reference to any particular property such as the specific gravity, but in a manner which brings out the general periodic character of the properties of the elements with reference to the atomic weights. Newlands observed in 1864 that if the elements were arranged in the order of their atomic weights, similar elements occurred in the series at approximately equal intervals. He stated this regularity in the form of a "Law of Octaves," according to which every eighth element in the series belonged to a natural group, all the members of which resembled each other more than they did the other elements. Thus the alkali metals fell into one of these groups, the metals of the alkaline earths into another, etc. This rule, however, is not very accurate, and had to be relinquished when better data for the atomic weights accumulated. It is to Mendeléeff and to Lothar Meyer that we owe the periodic arrangement of the elements in its present form.

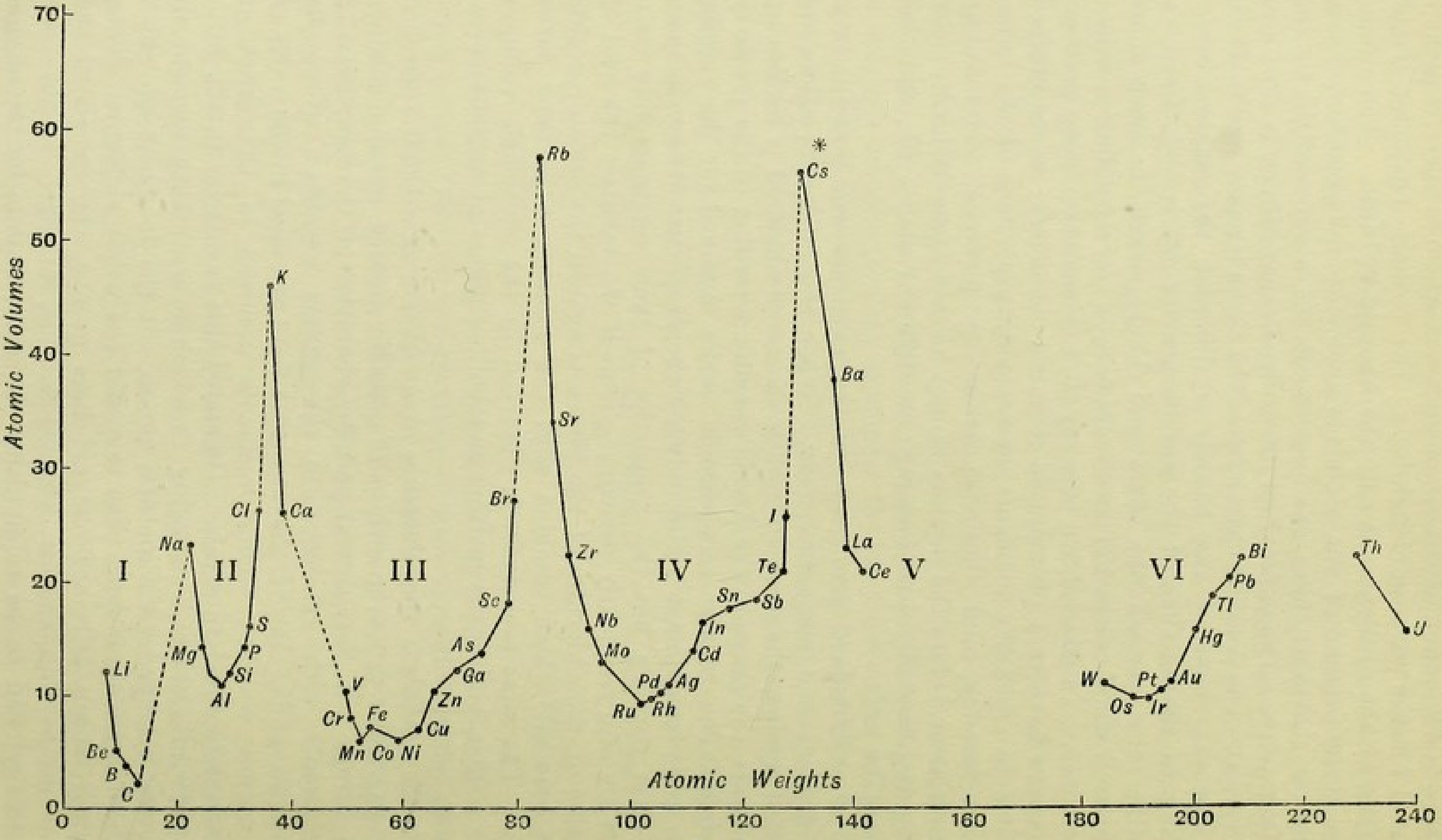

FIG. 3.

* This value for the atomic volume of cæsium is the mean of the concordant observations of Menke and Beketoff. A more recent determination by Eckhardt and Graefe gives the value 70.

In the following table the elements are ordered according to their atomic weights, beginning at the top of the left-hand column, proceeding downwards to the bottom, then passing to the top of the next column on the right, and so on. The position of the new helium-argon group of elements has been indicated within brackets. In the following general discussion of the table they are not referred to, but are treated in a separate section at the end of the chapter.

TABLE I

		I.	II.	III.	IV.	V.	VI.	VII.	
1.		Li	Na	K	Rb	Cs	...	...	
2.				Ca	Sr	Ba	...	Ra?	
3.				Sc	Y	La	Yb	...	
4.				Ti	Zr	Ce	...	Th	Even Series.
5.				V	Nb	...	Ta	...	
6.				Cr	Mo	...	W	U	
7.				Mn	...	...	...	...	
				Fe	Ru	...	Os		
8.				Co	Rh	...	Ir		Transition Elements.
				Ni	Pd	...	Pt		
1.				Cu	Ag	...	Au		
2.		Be	Mg	Zn	Cd	...	Hg		
3.		B	Al	Ga	In	...	Tl		
4.		C	Si	Ge	Sn	...	Pb		
5.		N	P	As	Sb	...	Bi		Odd Series.
6.		O	S	Se	Te	...	...		
7.	(H)	F	Cl	Br	I	...	...		
[8.	*He*	*Ne*	*A*	*Kr*	*Xe*]	...	...		
	i.	I.	II.	III.	IV.	V.	VI.		

The vertical columns represent periods, which are denoted by the same Roman numerals as in Figs. 2 and 3. A complete short period contains seven elements—a complete long period seventeen, which are made up of two series of seven elements each and a transition group of three elements. Within any one period, whether short or long, there is no sudden change in general chemical properties as we pass from one element to the next in order. Descending any series, we proceed from base-forming elements, through elements whose oxides are neither strongly acidic nor strongly basic, to acid-forming elements. In the short periods, which consist of only one series, we start from elements which form powerful bases, and end with elements which form powerful acids. In the long periods the uppermost or even series start with strong base-forming elements, and end with elements which form both acidic and basic oxides. The lower or odd[1] series, on the other hand, begin with only moderately strong base-forming elements, and end with elements which are very markedly acid-forming. The elements connecting the odd and even series in the long periods are intermediate in their behaviour between the elements they connect; those of the first row (iron, ruthenium, osmium) forming acids as well as bases, the others forming only bases.

When we pass from one period to the next, there is a sudden change in the properties of consecutive elements. Thus the last element of Period I., F = 19, is in complete contrast in its chemical nature to the next element, Na = 23, which belongs to Period II. The same thing occurs in the long periods. Iodine, the last member of Period IV., forms powerful acids; while cæsium, the first member of Period V., is one of the most powerful base-forming elements we know. These sudden changes in the chemical properties correspond in Figs. 2 and 3 to sudden changes in the direction of the curves.

If we consider the elements in a horizontal row, denoted by an Arabic numeral in the table, we find that they are on the whole such as would naturally fall together in a classification of the elements according to their general chemical characters. Thus in the first row we have lithium, sodium, potassium, rubidium, and cæsium, metals of the alkalies; in the second row, calcium, strontium, and barium, metals of the alkaline earths; and so on. It will be observed that the numbers of the rows in the table are repeated, running in order from 1 to 8, and then beginning again at 1. There are therefore two rows, one in the even and one in the odd series, which are represented by the same number. Between the members of these two rows there is a general similarity of properties, although it is not so great as that between members of the same row. Thus the compounds of vanadium, niobium, etc., in the even series, bear considerable resemblance to those of phosphorus, arsenic, bismuth, etc., in the odd series. The most striking property which exemplifies this is the combining capacity or valency of the elements. All the elements of two rows indicated by the same number, form, in general, compounds with precisely similar formulæ. Take, for example, the "highest" oxides, *i.e.* the oxides containing most oxygen, of the rows

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[1] The terms "odd" and "even" refer to the numbers of the series in the original arrangement of Mendeléeff.

marked 5, which form the two subdivisions of one natural family. We find their formulæ to be :—

Group 5 . .	Even series			V_2O_5	Nb_2O_5 – Ta_2O_5
	Odd series	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5 – Bi_2O_5.

Two atoms of all the elements of Group 5, then, combine with five atoms of oxygen. The same thing holds good for other groups, each group having its own combining capacity, which increases regularly from Group 1 to Group 8, as may be seen in Table II., where instead of the elements of Table I. the oxides of these elements have been tabulated. In the case of elements forming more than one oxide, the highest base-forming or acid-forming oxide is usually taken. The oxides enclosed in brackets are not known, but are the anhydrides of well-characterised series of salts.

TABLE II

GROUP	I.	II.	III.	IV.	V.	VI.	VII.
1.	[Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O]*	...	...
2.			Ca_2O_2	Sr_2O_2	Ba_2O_2	...	...
3.			Sc_2O_3	Y_2O_3	La_2O_3	Yb_2O_3	...
4.			Ti_2O_4	Zr_2O_4	Ce_2O_4	...	Th_2O_4
5.			V_2O_5	Nb_2O_6	...	Ta_2O_5	...
6.			Cr_2O_6	Mo_2O_6	...	W_2O_6	U_2O_6
7.			Mn_2O_7	...	...	...	...
8.			(Fe_2O_6)	Ru_2O_8	...	Os_2O_8	
			Co_2O_3	Rh_2O_4	...	Ir_2O_4	
			Ni_2O_3	Pd_2O_4	...	Pt_2O_4	
1.			Cu_2O	Ag_2O	...	Au_2O	
2.	Be_2O_2	Mg_2O_2	Zn_2O_2	Cd_2O_2	...	Hg_2O_2	
3.	B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	...	Tl_2O_3	
4.	C_2O_4	Si_2O_4	Ge_2O_4	Sn_2O_4	...	Pb_2O_4	
5.	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	...	Bi_2O_5	
6.	...	S_2O_6	(Se_2O_6)	Te_2O_6	...	...	
7.	...	Cl_2O_7	...	I_2O_7	...	...	
	I.	II.	III.	IV.	V.	VI.	VII.

* The hydroxides corresponding to the monoxides of the alkali metals are well known. The existence of many of the oxides themselves is doubtful.

In order that the amounts of oxygen in the various oxides may be readily compared, the formulæ have been written throughout so as to contain two atoms of the element combined with oxygen, and are consequently not in every case the usual formulæ. The number of the group, with few exceptions, corresponds to the number of oxygen atoms united to two atoms of the elements of the group. It must be conceded, however, that in order to get this regularity the oxides tabulated have been selected somewhat arbitrarily. Thus for copper we have selected the lower oxide Cu_2O instead of the equally characteristic higher oxide CuO. The selection in the case of sulphur, too, is quite arbitrary. Sulphuric anhydride, SO_3, is not the highest acid-forming oxide, as we have the oxide S_2O_7 corresponding to the well-characterised persulphates. Ni_2O_3, PbO_2, and Bi_2O_5 have no stable acids or salts corresponding to them, and behave in general like peroxides. Thus, while there is undoubted periodic regularity in the formulæ of the oxides of the elements, the regularity is not so definite as at first sight appears from a study of a table such as that given above.

The same sort of regularity appears when we tabulate the highest chlorides, bromides, etc., instead of the oxides; only in these cases there are still more exceptions. The highest chlorides of the elements of the even series are given in the following table as examples:—

Table III.

Group	I.	II.	III.	IV.	V.	VI.	VII.
1.	LiCl	NaCl	KCl	RbCl	CsCl	...	...
2.			$CaCl_2$	$SrCl_2$	$BaCl_2$	...	...
3.			$ScCl_3$	YCl_3	$LaCl_3$	$YbCl_3$	...
4.			$TiCl_4$	$ZrCl_4$	$CeCl_3$	...	$ThCl_4$
5.			VCl_4	$NbCl_5$	...	$TaCl_5$	...
6.			$CrCl_3$	$MoCl_5$	...	WCl_6	UCl_4
7.			$MnCl_4$?	...	...	...	...

We here perceive that there is a general correspondence between the group number and the number of chlorine atoms with which one atom of the elements can combine, but that there is a tendency of the elements in the higher groups to unite with fewer atoms than are given by the group number.

When we study the compounds of the elements with hydrogen or the alcohol radicals, we find that the combining capacity of the different groups is somewhat different from before. In the first place, it is chiefly elements of the odd series that unite with hydrogen or the alcohol radicals to form definite compounds. As we proceed downwards in the periods, we find that the combining capacity does not now steadily increase, but reaches a maximum at Group 4, thereafter to decrease regularly.

Thus in the first period we have:—

Group.	Methyl Compound.	Hydrogen Compound.
1.	$Li(CH_3)$	LiH
2.	$Be(CH_3)_2$	...
3.	$B(CH_3)_3$	BH_3
4.	$C(CH_3)_4$	CH_4
5.	$N(CH_3)_3$	NH_3
6.	$O(CH_3)_2$	OH_2
7.	$F(CH_3)$	FH

The power of combining with hydroxyl groups seems to be determined by the number of hydrogen atoms with which the element can unite. This may be seen from the following table, which gives for the elements of the second period those compounds which contain most hydroxyl groups:—

Group.	Compound.	Formula.
1.	Sodium hydroxide	$Na(OH)$
2.	Magnesium hydroxide	$Mg(OH)_2$
3.	Aluminium hydroxide	$Al(OH)_3$
4.	Silicic acid	$Si(OH)_4$
5.	Orthophosphoric acid	$PO(OH)_3$
6.	Sulphuric acid	$SO_2(OH)_2$
7.	Perchloric acid	$ClO_3(OH)$

Corresponding to the oxide P_2O_5 there should be the hydroxide $P(OH)_5$, if for all the oxygen the equivalent amount of hydroxyl were introduced. But this compound does not exist, the acid $PO(OH)_3$, orthophosphoric acid, being the compound with the greatest number of hydroxyl groups in the molecule, apparently in connection with the fact that there is a hydrogen compound PH_3, but no hydrogen compound PH_5.

It has been pointed out that not only are elements in the same horizontal row similar, but that there is no sudden change in the properties of consecutive elements in the vertical series. We should therefore expect to find a general resemblance amongst the elements gathered together in one part of the table, and this resemblance does in fact appear. The upper rectangle formed by the dotted lines in Table I. contains the metals of the rare earths, which occur in groups in a few minerals found only in certain localities, and which, from their similarity of chemical properties, are extremely difficult to separate from one another. The lower rectangle contains all the "metallurgical" elements, *i.e.* the heavy metals which are prepared on the large scale from their ores, although all the elements enclosed within this rectangle are not of technical importance. Bordering on the rectangle are the light metal aluminium and the half-metals arsenic, antimony, and bismuth, all of which are commercially important.

When we look at the position of the elements composing these groups on the curve of specific gravities, we find that the metals of the rare earths occupy the middle of the ascending portions of the curve in the long periods, and that the "metallurgical" metals lie at or close after the maxima. On the curve of atomic volumes, the metals of the rare earths are found at the middle of the descending portions of the curve, and the metallurgical metals at, or immediately after, the minima.

The distinction between metals and non-metals is not a very sharp one, for the properties of the one class gradually merge into those of the other. There is, however, a classification which is generally adopted in practice, and this classification is in conformity with the periodic table. The elements enclosed in the dotted triangle at the lower left-hand corner of Table I. are the non-metals as usually understood. All the other elements tabulated are metals.

As to the blanks in Table I., we may reasonably expect that some of them at least will be filled up by elements hitherto undiscovered, and that the new elements will be of the same kind as those we already know. When the table was first constructed, the number of blanks in it was greater than now, and Mendeléeff was bold enough to predict the existence of elements to fill the gaps. His predictions have been more than once fulfilled. The three well-defined elements, gallium, germanium, and scandium, have all been discovered since his formulation of the Periodic Law, and have fallen naturally into their places in the third period. Mendeléeff not only predicted the existence of these elements, but also their chief chemical and physical properties from a consideration of the properties of their nearest neighbours in the table. By consulting the specific-gravity curve (p. 41), it is easy to see, for instance, that an element of atomic weight 70 will probably have a specific gravity intermediate between the specific gravities of zinc and arsenic, the nearest well-known elements on either side. The value will therefore lie between 5·7 and 7·2, say about 6·4. The actual specific gravity of gallium, at. wt. 70, is 5·93. Similarly the melting point and general chemical properties might be roughly predicted. It should be said that experiments on the newly-discovered elements entirely justified Mendeléeff's prediction of their properties.

Another use to which the periodic table has been put is the correction of supposed erroneous atomic weights. For instance, the atomic weights of the transition elements of Group 8 presented in some cases exceptions to the Periodic Law (the elements when arranged in order of their atomic weights being out of harmony with the natural grouping), and were therefore subjected to a revision, the result of which has been to show that the requirements of the Periodic Law are in reality fulfilled. Again, the atomic weight of tellurium was found to be greater than that of iodine, which caused iodine to come before tellurium in the periodic classification, so as to fall into the sulphur group, while tellurium fell into the halogen group. But this contradicts the whole chemical behaviour of these elements; iodine from its properties must be classed along with chlorine and bromine, and tellurium naturally belongs to the sulphur and selenium group. It was therefore thought probable that one or other of the atomic weights had been incorrectly determined, doubtless that of tellurium, as iodine has been the subject of repeated concordant determinations. Fresh investigations at first seemed to show that tellurium had an atomic weight of about 125, in accordance with the Periodic Law, but the most recent researches have agreed in giving the value 127·6, which is distinctly above the atomic weight of iodine. We have here then a well-marked exception to the periodic regularity.

Considerable interest attaches to the position of the atmospheric gases discovered by Ramsay—helium, neon, argon, krypton, and xenon—in the periodic system. Since these gases do not enter into any compounds in the ordinary sense, we are entirely dependent on their gas-densities for fixing their characteristic weights. As we have seen, the evidence of their specific heat ratio points to their atomic weights being identical with their molecular weights, so that we have provisionally

	He	Ne	A	Kr	Xe
Atomic Weight . .	4	20	40	82	128

if we make use of the latest density determinations. Should there be any place at all for these elements in the periodic table, it must be between the last (halogen) member of one series and the first (alkali) member of the succeeding series, for it is only there that a group of vacant spaces occurs. It is only reasonable, too, that these chemically neutral elements should fall between the *negative* halogen elements and the diametrically opposed *positive* alkali metals. Proceeding on this basis we obtain the following table for the transition between the successive series:—

	O	S	Se	Te
	16	32	79	127·6
H	F	Cl	Br	I
1	19	35·5	80	127
He	*Ne*	*A*	*Kr*	*Xe*
4	*20*	*40*	*82*	*128*
Li	Na	K	Rb	Cs
7	23	39	85·5	133
Be	Mg	Ca	Sr	Ba
9	24	40	87·5	137·5

As far as the atomic weights are concerned, the non-valent elements here fall naturally into their places between the negative univalent elements and the positive univalent elements, argon being exceptional with an atomic weight somewhat greater than that of potassium. Too much stress, however, need not be laid on this divergence from uniformity, for we have a similar case in tellurium, its atomic weight being somewhat greater than that of iodine, which it precedes in the periodic arrangement.

The atomic volumes, refractive indices, and other properties of the new elements find a natural place in periodic diagrams if we adopt the atomic weights given above, so that the position of the new elements may now be considered as fairly well established.

The place of hydrogen in the periodic system has been the subject of some discussion. As it is an univalent element, it must be placed either at the head of the alkali metals, or of the halogens. In physical properties it certainly must be ranked with fluorine, chlorine, etc., and not with lithium, sodium, etc. In chemical properties it is very different from the members of either group; although in acids it is easily replaced by the alkali metals, and in organic compounds by the halogens. In the periodic table as usually given, fluorine and manganese are placed as consecutive members in the same sub-group. Proceeding in a similar way hydrogen and chlorine would be placed together if we reckon hydrogen with the halogens. There is certainly as much to be said in favour of the one arrangement as of the other. Manganese and fluorine differ more from each other in their chemical and physical characters than do hydrogen and chlorine. However unaccustomed, then, we may be to regard hydrogen as in any way related to the halogens, it must be conceded that it finds its place as naturally with them as do some of the other elements with their neighbours in the original periodic grouping (cp. Masson, *Chemical News*, **73**, p. 283).

Within the past few years much attention has been devoted to the study of radioactive substances, which constantly emit radiations of various qualities, called Becquerel rays after their discoverer. These radiations can penetrate opaque substances, confer electrical conductivity on the air, and affect a photographic plate.

The substances which possess the property in the most marked degree are compounds of the new element radium, the atomic weight of which has been provisionally determined as 225. It apparently belongs to the same natural family as barium, and it is interesting to note that it falls into the same vertical column in the table on p. 45 as the two other markedly radioactive elements, thorium and uranium.

CHAPTER VII

SOLUBILITY

THE solutions we most frequently meet with in inorganic chemistry are solutions in which water is the solvent. The substances dissolved may be gaseous (*e.g.* ammonia, hydrochloric acid) or liquid (*e.g.* bromine), but in the vast majority of cases they are solid.

When excess of a solid, such as common salt, is brought into contact with water at a given temperature, it dissolves until the solution reaches a certain concentration, after which the solution may be left for an indefinite time in contact with the solid without either undergoing any change, provided the temperature is kept constant, and that evaporation is prevented. Such a solution is said to be **saturated** with respect to the salt at the given temperature, and the solubility of salt in water under these conditions is merely an expression for the strength of the saturated solution. The strength may be given in various ways, *e.g.* 100 parts of water are said to dissolve at the given temperature so many parts of salt, or the saturated solution contains so much per cent of the solid, or so many grams of salt are contained in 100 cc. of the solution. All these methods of expressing the strength of solutions are in common use, the last especially for volumetric work, and it is a matter of convenience which to choose in any particular case. When a solution is capable of dissolving more salt at the given temperature than it already contains, it is said to be **unsaturated**; when it is made by some device to contain more salt than it would be capable of taking up directly under the given circumstances, it is said to be **supersaturated.** The one and only test to find whether a solution is saturated, unsaturated, or supersaturated, with respect to a given solid, is to bring it in contact with that solid. If it is saturated, it will remain unchanged; if unsaturated, it will dissolve more solid; if supersaturated, it will deposit the excess of dissolved substance till the strength diminishes to that of the saturated solution.

The solubility of all substances varies with the temperature. With most solids it increases as the temperature rises. Thus 100 g. of water will dissolve 35·6 g. of sodium chloride at 0°, and

40 g. at 100°; 47 g. of sodium thiosulphate[1] at 0°, and 102 g. at 60°; 13 g. of potassium nitrate at 0°, and 247 g. at 100°. In some cases, however, the solubility diminishes as the temperature rises. For example, calcium citrate is more soluble in cold water than in boiling water, and many other calcium salts of organic acids exhibit a similar behaviour. The change of solubility with change of temperature may be seen in the accompanying diagram, the solubilities being given as parts of anhydrous salt dissolved in 100 parts of water. The curves in general are continuous, but the curve representing the solubility of sodium sulphate is not continuous, having a sudden break at 33°. The explanation is that we are not here dealing with one solubility curve but with two solubility curves. The curve below 33° is the solubility curve of the hydrate $Na_2SO_4 . 10H_2O$; the curve above 33° is the solubility curve of the anhydrous salt Na_2SO_4. When the hydrate is heated to 33° it splits up into water and the anhydrous salt. The hydrate, therefore, has no stable existence above 33°, and the only solid with which the solution can be in contact above that temperature is the anhydrous salt, and the curve therefore represents its solubility and not that of the hydrate. That we are here actually dealing with two curves may be proved by bringing the anhydrous salt in contact with water below 33°. It

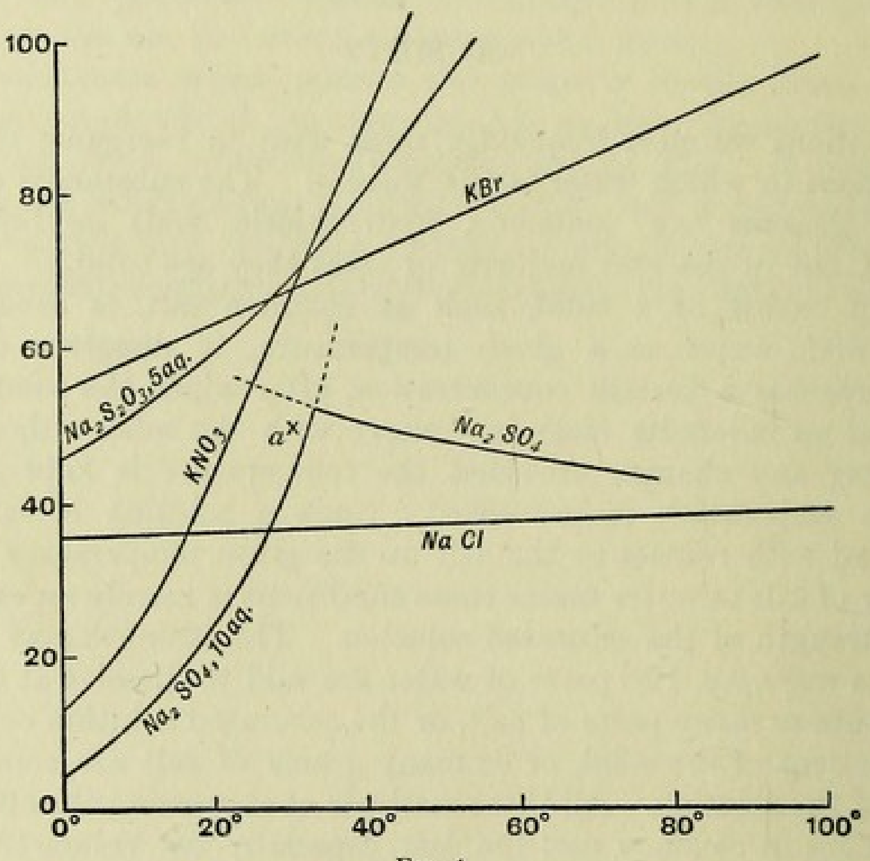

FIG. 4.

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[1] Calculated as anhydrous salt.

does not at once unite with water to form the solid hydrate, so that we may measure its solubility at such temperatures and represent it by means of the dotted line in the figure. It will be seen that the dotted line is a continuation of the upper curve, and is quite independent of the curve of the hydrate, except in so far as it cuts it at the temperature of the transformation of the hydrate into the anhydrous salt. If we take a point in the diagram lying between the dotted line and the lower curve, that marked *a*, for example, we find that it represents the strength of a solution which is unsaturated with respect to the anhydrous salt, and supersaturated with respect to the hydrate $Na_2SO_4 . 10H_2O$. We can prove that this is so in reality, for if we bring the solution into contact with the anhydrous sulphate it will dissolve some of the salt; whilst if we bring it into contact with the hydrated salt it will deposit a fresh quantity of the hydrate. It is very necessary, then, to specify exactly the solid with respect to which a solution is said to be saturated or not. To speak of a solution being a saturated solution of sodium sulphate is ambiguous, for while the solution may be saturated with regard to one form of the solid salt, it may be unsaturated or supersaturated with regard to another.

When a saturated solution of hydrated sodium sulphate, $Na_2SO_4 . 10H_2O$, is made in warm water so that none of the solid remains, and is then cooled to the ordinary temperature, care being taken that there is no separation of the salt, the solution may be kept unaltered in the supersaturated state for a great length of time. It frequently happens that the solution on standing deposits crystals of another hydrate, $Na_2SO_4 . 7H_2O$, which at low temperatures is more soluble than the decahydrate. The solution then becomes saturated with respect to this heptahydrate, but is still supersaturated with respect to the decahydrate, as may be seen by dropping in a crystal of the latter, when further crystallisation at once commences. It is mostly in the case of salts which crystallise with water of crystallisation that we can easily form supersaturated solutions. Salts which separate only in the anhydrous state do not often form aqueous supersaturated solutions, the excess being usually deposited as the cooling progresses. Sodium chlorate, however, is a good example of an anhydrous salt which does form supersaturated solutions.

The question of the transformation of different hydrates into each other will be discussed in the chapter on the Phase Rule.

It has been recently observed that the state of division of a solid has a considerable influence on its solubility when the fineness of the powder is such that a comparatively great diminution of surface results from the dissolution of a small quantity of solid. Thus, whilst the saturated solution of $CaSO_4 . 2H_2O$ at 25° is 0·0153 normal with ordinary particles, the solubility increases to 0·0182 normal with particles averaging 0·3 micromillimetres in diameter. By reducing the size of the particles of barium sulphate from 1·8 micromillimetres to 0·1 micromillimetres, the solubility is almost doubled.

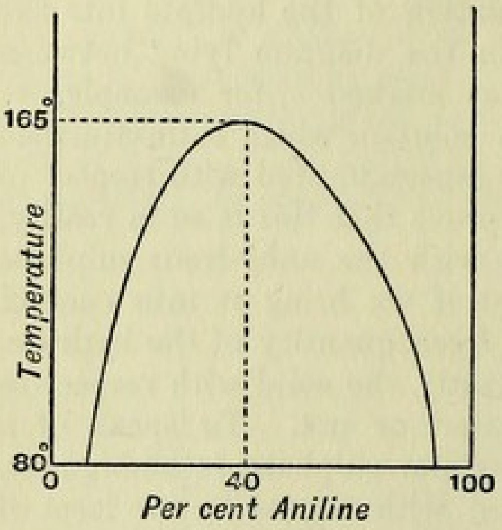

Fig. 5.

Liquids sometimes mix with each other in all proportions, *e.g.* water and alcohol; sometimes not at all, *e.g.* water and mercury. In some instances there is **partial miscibility**. When we shake up water and ether together in about equal proportions, the water dissolves a little of the ether, and the ether a little of the water, the two saturated solutions then separating. The lower layer is a saturated aqueous solution of ether, the upper layer is a saturated ethereal solution of water.[1] Suppose that with two partially miscible liquids, *A* and *B* (say aniline and water), the solubility of each liquid in the other increases with rise of temperature. On raising the temperature we should find that the composition of the two saturated layers, or phases, as they are called, would tend to approximate to the same value. We may represent this diagrammatically, as in Fig. 5. Temperatures are plotted on the vertical axis, and points on the horizontal axis represent the percentage composition of the liquids.

As the temperature rises, the solubility of *B* in *A* and of *A* in *B* increases, so that the corresponding points on the two curves approximate. At a certain temperature the two curves will meet. This means that at that particular temperature the solution of *A* in *B* and the solution of *B* in *A* have the same composition, *i.e.* are identical. At this temperature the liquids are miscible in all proportions. There is therefore no fundamental distinction between wholly miscible and partially miscible liquids; for liquids which only mix partially at one temperature may mix in any proportion at another. We have here, likewise, an illustration of the arbitrary manner in which we

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[1] The following table gives the mutual solubility at 22° of water and some common organic solvents:—

	Vols. Substance in 100 Vols. Water.	Vols. Water in 100 Vols. Substance.
Chloroform	0·42	0·15
Ligroïn	0·34	0·33
Carbon bisulphide	0·17	0·96
Ether	8·11	2·93
Benzene	0·08	0·22
Amyl alcohol	3·28	2·21
Aniline	3·48	5·22

It has been pointed out that, as far at least as water and organic liquids are concerned, partial miscibility involves the presence of an "associated" liquid (cp. Chapter XIX.), "non-associated" liquids being completely miscible.

employ the terms "solvent" and "dissolved substance." We have spoken of the solubility of *A* in the solvent *B* for one part of the curve, and the solubility of *B* in *A* for the other. At the temperature where the saturated solutions become identical it is obviously impossible to make any distinction between solvent and dissolved substance; and in general, it may be said that, though for the sake of convenience we often thus discriminate between the two constituents of the solution, there is in the solution itself no actual distinction of this kind. If it suits our purpose we may call dissolved substance what is usually termed solvent, and *vice versa*, without fear of committing any theoretical error.

The solubility of some pairs of miscible liquids in each other increases with rise of temperature, *e.g.* aniline and water (Fig. 5); the mutual solubility of other pairs diminishes, *e.g.* dimethylamine and water (Fig. 6). The diminution of solubility by rise of temperature is very easily seen in the case of water and paraldehyde. If these liquids are shaken up together in a test-tube at the ordinary temperature, they separate on standing into two clear layers. If now the test-tube is plunged into warm water, the aqueous layer at once becomes turbid from separation of the excess of paraldehyde.

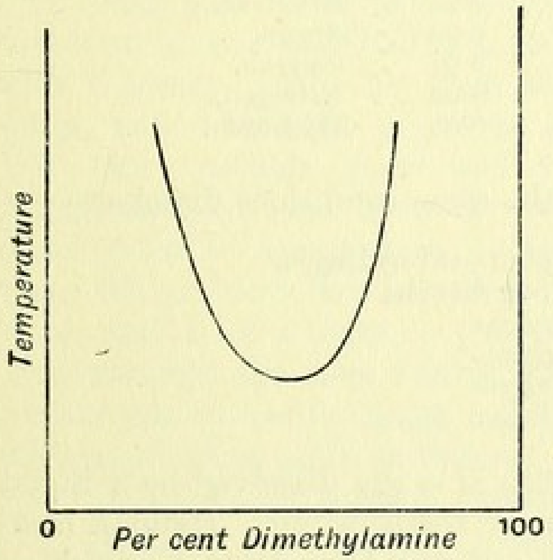

FIG. 6.

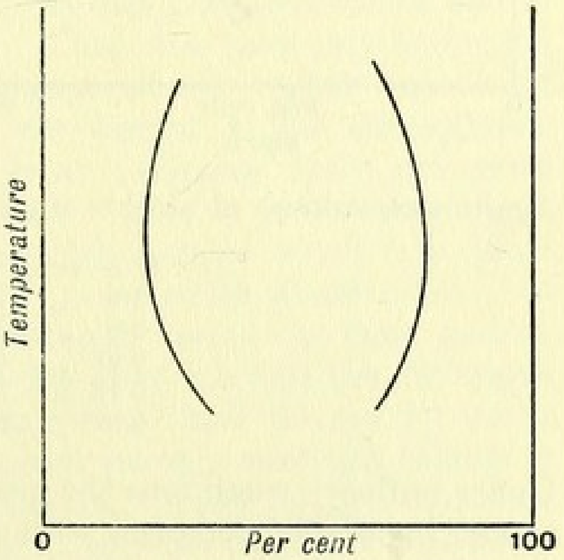

FIG. 7.

Many lactones exhibit a peculiar behaviour with water, indicated diagrammatically in Fig. 7. The aqueous solution prepared by shaking up the two substances at the ordinary temperature becomes turbid at about 40° owing to the lessened mutual solubility, but at 80° again becomes clear. Here there is first diminution of the solubility of the lactone in water by rise of temperature to a minimum value, after which we have increasing solubility with further rise of temperature. The figure shows the non-aqueous layer to present similar phenomena to the aqueous layer. This does not generally hold good for lactones, but has been observed, for example, in the case of secondary butyl alcohol. It is conceivable that the solubility curve of some particular substance might be a closed curve, as in Fig. 8, there being complete miscibility at high and at low temperatures, whilst at intermediate temperatures there would be only partial miscibility.

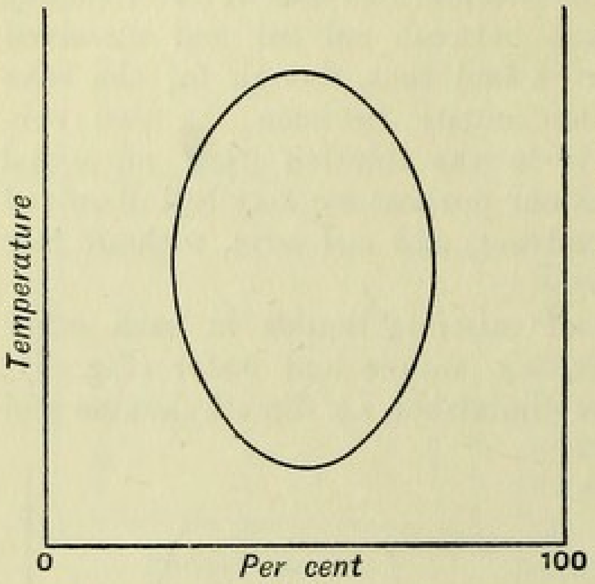

FIG. 8.

Gases vary very much with respect to their solubility in liquids. For example, one volume of water at 0° and 760 mm. dissolves—

1050	vols.	Ammonia.
505	,,	Hydrochloric acid.
80	,,	Sulphur dioxide.
4·4	,,	Sulphuretted hydrogen.
1·8	,,	Carbon dioxide.
0·25	,,	Ethylene.
0·06	,,	Argon.
0·04	,,	Oxygen.
0·02	,,	Nitrogen.
0·02	,,	Hydrogen.

Again, one volume of alcohol under the same conditions dissolves—

17·9	vols.	Sulphuretted hydrogen.
4·3	,,	Carbon dioxide.
3·6	,,	Ethylene.
0·28	,,	Oxygen.
0·13	,,	Nitrogen.
0·07	,,	Hydrogen.

Under ordinary conditions the quantity of a gas dissolved by a liquid almost invariably decreases with rise of temperature. Helium, however, is an exception, its absorption-coefficient[1] in water diminishing from 0° to 25°, thereafter to increase as the temperature is raised.

The following table of absorption-coefficients of argon and helium shows the influence of temperature on the solubility of these gases in water:—

Temp.	Argon.	Helium.
0	0·0578	0·0150
10	0·0453	0·0144
20	0·0379	0·0139
25	0·0347	0·0137
30	0·0326	0·0138
40	0·0286	0·0139
50	0·0257	0·0140

When the gases are only moderately soluble in the solvent chosen, they obey a simple law with regard to pressure known as **Henry's Law**. One mode of stating this law is: A given quantity of

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[1] The absorption-coefficient of a gas in a liquid is not the actual solubility, *i.e.* the volume of the gas dissolved by 1 vol. of liquid at the experimental temperature, but this volume reduced to 0°.

the liquid solvent will always dissolve the same volume of a given gas, no matter what the pressure may be, so long as the temperature is constant. Another equivalent form is: A given quantity of the liquid will dissolve at constant temperature quantities (by weight) of the gas which are proportional to the pressure of the gas. Thus, if a quantity of water will dissolve 1 g. of oxygen at the atmospheric pressure, it will dissolve 2 g. of oxygen at a pressure of 2 atm. The equivalence of the two forms of the law may of course at once be seen by considering that doubling the pressure of a gas halves its volume, so that the 2 g. of oxygen at a pressure of 2 atm. occupy the same volume as 1 g. of oxygen at a pressure of 1 atm.

When a mixture of two or more gases is dealt with, each dissolves in the liquid as if all the others were absent. This rule may be also stated in the form, that when a mixture of gases dissolves in a liquid, each component dissolves according to its own partial pressure, and in this form it is called **Dalton's Law**. These two laws only hold good with accuracy when the gases are comparatively slightly soluble in water, and when the pressures do not exceed a few atmospheres. With very soluble gases and at great pressures there are great divergencies, at least from Henry's Law. This is probably owing in many cases to chemical or quasi-chemical changes which take place when the gas dissolves in water. The gases which dissolve freely in water are all of a more or less pronouncedly acidic or basic nature. Thus amongst the most soluble gases are ammonia and the hydrogen compounds of the halogens. Neutral gases, which do not by union with water form acidic or basic substances, are only sparingly soluble in water, *e.g.* the chief gases of the atmosphere, the gaseous hydrocarbons, etc. There is also a general connection between easy compressibility to the liquid state at atmospheric temperatures and easy solubility in water. The so-called "permanent gases," nitrogen, oxygen, argon, helium, carbon monoxide, nitric oxide, methane, are all very slightly soluble. The simple gases which are easily condensed to liquids are much more soluble.

In general, we may state that when a substance exhibits chemical relationship with a liquid it is more or less soluble in that liquid. Organic compounds containing hydroxyl are very frequently soluble in water, and the more hydroxyl they contain proportionally in the molecule the more soluble they are. Thus the higher monohydric alcohols of the series $C_nH_{2n+1}OH$, say $C_6H_{13}OH$, are scarcely soluble, whilst the polyhydric alcohols, such as mannitol, $C_6H_8(OH_6)$, are freely soluble. Hydrocarbons are, as a rule, very sparingly soluble in simple compounds containing hydroxyl, *e.g.* water, alcohol; and substances with proportionately much hydroxyl are very slightly soluble in hydrocarbons. The solid hydrocarbons are, however, freely soluble in the liquid hydrocarbons, and that the more as the solvent and dissolved substances approach each other more nearly in character. Sulphur and the metals are insoluble in water; the former, however, dissolves freely in liquid sulphur compounds, *e.g.* carbon disulphide and sulphur chloride, whilst the latter are often soluble in the liquid metal mercury, or in other metals in the fused state, whence the possibility of forming alloys and amalgams.

The solubility of salts, acids, and bases in water is very variable; but the following rules for ordinary compounds may be of use to the student:—

Salts of potassium, sodium, and ammonium are soluble.

Normal nitrates, chlorates, and acetates are soluble.

Normal chlorides are soluble (except those of silver, mercurosum, and lead).

Normal sulphates are soluble (except those of calcium, strontium, lead, and barium).

Hydroxides are insoluble[1] (except those of potassium, sodium, and ammonium, which are freely soluble, and those of calcium, strontium, and barium, which are sparingly soluble).

Normal carbonates, phosphates, and sulphides are insoluble (except those of potassium, sodium, and ammonium).

Basic salts are, as a rule, insoluble.

Acid salts are, as a rule, soluble if the acid is soluble, which is mostly the case with inorganic acids.

A process of purification very frequently made use of is that of **recrystallisation**. This consists in dissolving the impure substance and allowing a portion of it to separate out of the solution, either by a change of temperature that will lower the solubility, or by evaporation of the solvent. Suppose the substance to contain 90 per cent of pure material and 10 per cent of an equally soluble impurity. The mixture is treated with as much solvent as will dissolve the whole. If we make the temporary assumption that the substances have no influence on each other's solubility, the solution is now saturated with respect to the pure material, but far below the saturation point of the impurity. By removing part of the solvent, say by evaporation, we make the solution supersaturated with regard to the pure material, so that a portion of the latter is deposited. The solution still remains unsaturated, however, with regard to the impurity, so that none of this component falls out. We can therefore go on removing the solvent, and so obtain crystals of the pure material, until we reach the saturation point of the impurity, when the operation must be stopped, for then pure substance and impurity would deposit in equal proportions. In this way $\frac{8}{9}$ths of the original substance would be obtained in the pure state by the sacrifice of $\frac{1}{9}$th, which would be more highly contaminated with the original impurity. Purification by crystallising is always attended by loss of material, but if the

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[1] By "insoluble" we generelly mean "very sparingly soluble." The relative solubilities of some common "insoluble" substances are given in Chapter XXVI.

process of recrystallisation is carried out systematically, this loss in the majority of cases need only be slight. In no case is the process so simple as in the scheme given above, and it is almost always necessary to repeat the crystallisation several times, the separation being even then by no means perfect. In organic chemistry the success of purification by crystallisation largely depends on the choice of solvent, a proper choice leading to a rapid and perfect separation with a good yield of pure substance, where an unsuitable selection would give a small yield of still impure material. Where, as in the case of the Stassfurt salts, complex recrystallisations of aqueous solutions are carried out, the temperatures of crystallisation are carefully chosen, and the nature of the solvent for any particular salt is varied by using solutions of other salts of varying concentration. In this way, and in successive operations, it is found possible to obtain pure potassium chloride from the very complex salt deposits.

A method of separation often practised in organic chemistry is **extraction from aqueous solution** by means of ether. The principle of the process is as follows. If a substance is soluble in two liquids which are not themselves miscible, it will distribute itself between the two solvents, when shaken up with them in the same vessel, in a manner depending on its solubility in each of the solvents separately. The simplest case is when the solvents are perfectly immiscible, and when the dissolved substance has the same molecular weight in both. The rule for this case is that the substance on shaking up distributes itself between the two solvents in such a proportion that the ratio of the concentrations of the two solutions is equal to the ratio of the concentrations of solutions saturated separately with the substance at the temperature of experiment, *i.e.* the ratio of the concentrations is the ratio of the solubilities in the separate solvents. Suppose, for example, that the immiscible substances are water and benzene, that the molecular weight of the substance in these two liquids is the same, and that the substance is twice as soluble in benzene as in an equal volume of water. On shaking up the substance with benzene and water in quantity insufficient to saturate both these solvents, we shall find that the substance distributes itself so that the concentration of the benzene solution is twice that of the aqueous solution. It will be seen that nothing is here said as to the absolute or relative volumes of the solvents—it is entirely a question of final concentrations. Using the above rule, we might consider the practical question: Whether is it more economical in the above instance to extract the aqueous solution with an equal volume of benzene in one operation, or to apply the same quantity of benzene in several portions, shaking up and separating each time? If the amount of substance in one volume of the aqueous solution is A, then on shaking up with one volume of benzene, we shall have one-third of A remaining in the aqueous solution, and two-thirds of A in the benzene. We thus with one volume of benzene extract $0{\cdot}67A$ if we perform the extraction in one operation. Let us now suppose the extraction to be performed in two stages, using the same total quantity of benzene as before. To one volume of the aqueous solution we add half a volume of benzene. Let x be the amount extracted by the benzene. $A-x$ will be the amount left in one volume of water; x is the amount in $0{\cdot}5$ volume of benzene. The concentrations are therefore as $A-x$ to $\frac{x}{0{\cdot}5}=2x$. But by the above rule the concentration in the benzene is twice that in the water, so we have

$$2x=2(A-x)$$
$$x=0{\cdot}5A.$$

We have therefore by using half a volume of benzene extracted $0{\cdot}5A$, leaving $0{\cdot}5A$ behind in the water. Extracting this aqueous solution again with half its volume of benzene, we shall again remove half of what it contains, viz. $0{\cdot}25A$; so that by extracting in two successive operations we obtain $0{\cdot}5A+0{\cdot}25A=0{\cdot}75A$ instead of $0{\cdot}67A$, the result obtained by using the same quantity of benzene in one operation. If we are therefore desirous of getting the maximum amount extracted with a given quantity of the extracting solvent, and time is not in consideration, it is better to apply the extracting liquid in successive small portions than to use all in one operation.

In the actual extraction with ether economy of time has more frequently to be considered than economy of ether, and larger quantities in fewer operations are as a rule employed. This may the more readily be done as the easy volatility enables one portion to be distilled off and made ready for a second operation while extraction with another portion is in progress. The case of ether and water is not the ideal case for which the solubility rule applies accurately. Ether and water are partially miscible, and the partition coefficient of a substance between them is on account of this not the ratio of the solubilities of the substance in pure ether and pure water separately. It very frequently happens, too, that the molecular weight of the substance in water is not the same as the molecular weight of the substance dissolved in ether (see Chap. XIX.). There is then no constant "partition coefficient" at all, and the ratio of the concentrations of the two solutions depends on the relative proportion of dissolved substance and solvents present. The effect of a difference in molecular weight being exhibited in the two solvents will be discussed in the chapter on Molecular Complexity.

The resemblance between the above problem and that of shaking a gas and liquid up together in a closed vessel is evident. If we regard "vacuum" as a solvent, we may state Henry's Law in the form that there is always a definite "partition coefficient" between the vacuum and the liquid solvent, this partition coefficient being the solubility of the gas in the liquid. Let equal volumes of water and nitrogen be shaken up in a stoppered bottle. The solubility of nitrogen is n, *i.e.* one volume of water dissolves n volumes of nitrogen. The final concentration of the gas in the water is thus n times the final concentration of the gas in the vacuum; or the partition coefficient between water and vacuum is $n:1=n$. The original amount of nitrogen is, say, N. Let xN be the amount dissolved. We have $N-xN$ for the amount remaining, and as the volumes of vacuum and water are equal, the final concentrations are $N-xN$ and xN respectively; but these are in the ratio of 1 to n, so that we have

$$\frac{N-xN}{xN}=\frac{1-x}{x}=\frac{1}{n}.$$

whence

$$x=\frac{n}{1+n}.$$

Since according to Dalton's Law the presence of one gas does not affect the solubility of another, we can easily solve problems concerning the solubility of mixtures of gases in the same solvent. The student will find it a useful exercise to calculate from the tables of solubilities given above, the pressure and composition of the residual gaseous mixture of oxygen, nitrogen, and argon obtained by shaking up 1 vol. of purified air with 1 vol. water at 0° and 760 mm. in a closed vessel.

If a gas has not the same molecular weight in a given solvent as it has in the gaseous state, then Henry's Law is not followed (cp. Chap. XIX.).

CHAPTER VIII

FUSION AND SOLIDIFICATION

WHEN a solid such as glass is heated, it gradually loses its rigidity, and by degrees, as the temperature is raised, assumes the fluid form, passing through the stages of a tough, inelastic solid and of a viscid, pasty liquid. It cannot be said, therefore, to have a definite melting point. A crystalline substance such as sulphur, on the other hand, when heated remains solid up to a certain temperature, after which the further application of heat liquefies it, the temperature remaining constant during liquefaction. This constant temperature is the **melting point** of the solid, and is a characteristic property of each particular crystalline substance. Not only is the melting point used as a means of identification, but sharpness of melting point, *i.e.* constancy of temperature during liquefaction, is often employed as a test of purity of crystalline substances, especially in organic chemistry. Should a substance crystallise in more than one form, each crystalline variety has its own melting point. The melting point of rhombic sulphur, for example, is 114·5°, while the melting point of monoclinic sulphur is 120°.

When a fused substance is cooled below the point at which the solid melted, it may or may not solidify according to circumstances. Once the solidification does begin, however, the temperature adjusts itself to the melting point of the solid, for that is the only temperature at which the solid and the liquid can permanently exist in contact. Of course we may put a piece of ice into water of 15°, and the two may coexist for a time though the temperature of the ice is 0°. But here there is no permanent coexistence, for the ice is constantly melting, and the temperature of the water is being lowered. If we wish to ascertain the exact temperature at which the solid and liquid coexist, we must ensure their intimate mixture, otherwise the solid might be at one temperature and the bulk of the liquid at another.

When a crystallised solid is heated, it is apparently impossible to warm it above its melting point without its assuming the liquid state. It is easy, however, in the case of most liquids to lower their temperature below the melting point of the solid without actual solidification taking place. The freezing point of a liquid, therefore, if defined as the temperature at which the liquid begins to freeze, is not a definite temperature, and as a matter of practice only *melting* points of pure substances are determined. Although ice when heated melts at 0°, water may be cooled to − 4° or lower without any separation of ice taking place. The liquid is then said to be **superfused.** The introduction of a crystal of the solid into the superfused liquid at once determines crystallisation, so that a superfused liquid in this respect resembles a supersaturated solution (p. 53).

Fusion is always attended by absorption of heat, and solidification by evolution of heat. When a superfused liquid begins to solidify, therefore, heat is disengaged and the temperature of the liquid rises. This rise of temperature accompanying the separation of the solid goes on until the melting point of the solid is reached, when no further change occurs, for at this temperature the solid and liquid are in equilibrium, *i.e.* can exist together in any proportion without affecting each other. If there is no heat exchange with the exterior, the solid and liquid remain in contact at their melting point without alteration. If heat is added from an external source, part of the solid liquefies, thereby absorbing the heat supplied. If heat is withdrawn from the mixture, part of the liquid solidifies, thereby producing sufficient heat to allow the temperature to remain constant at the melting point.

It has been said above that the introduction of a crystal of the substance into a superfused liquid is in all cases sufficient to determine its crystallisation. This would appear to be true even when the crystalline particle is so minute as to be unrecognisable by ordinary means, for experiments have shown that as small a quantity as one-hundred-thousandth part of a milligram is effective in producing solidification. Experimental researches have also been made to investigate the tendency of a superfused liquid to crystallise by itself, the possibility of the introduction of any crystallised particle from without being excluded. In most superfused liquids **crystalline nuclei** soon make their appearance at different parts of the liquid, and then begin to grow until all the liquid has solidified, or until the heat disengaged on solidification has raised the temperature of the whole to the freezing point. It is obvious that the chance of such a nucleus appearing increases with the quantity of liquid taken, and we might therefore expect to keep a small portion of a superfused liquid for a longer time uncrystallised than we should a larger quantity. This is found to be in accordance with fact, and it is a comparatively easy matter to count the number of nuclei formed in a given time if the superfused liquid is enclosed in a capillary tube, and to determine by measurement the rate at which these nuclei grow. It has been ascertained that the rate of growth is approximately proportional to the degree of superfusion when that degree is not very great, and that the number of nuclei formed in a given volume in a given time at first increases with the degree of superfusion, but afterwards reaches a maximum, and begins to diminish as the liquid becomes highly superfused. It is possible, therefore, by suddenly cooling a fused liquid far below the proper freezing point, to diminish the tendency to nucleus formation so greatly that the substance may be kept for days, weeks, or even months, without crystallisation taking place. Such a highly superfused substance is no longer a liquid but a solid of the same nature as glass. It has no definite melting point, but would, if crystallisation were prevented, like glass become gradually softer and less viscous until it might be said to have assumed the ordinary liquid form, there being at no time a sudden passage from the solid to the liquid state. If such a glassy solid is brought into contact with the corresponding crystalline substance, it crystallises, but the velocity of the crystallisation is extremely small, the rate being measurable in millimetres per hour.

We have then no sharp line of demarcation between amorphous solids and liquids, but a gradual passage from the one state to the other. The line of demarcation is rather between crystalline substances and non-crystalline substances, *i.e.* between substances which have their particles arranged in a regular manner, and those in which the arrangement is confused and irregular. It was for long supposed that no regular arrangement of particles could subsist in liquids, the particles of which have a certain freedom of motion not possessed by solids, but of late **crystalline liquids** have been discovered which possess properties hitherto only encountered in solid crystals. Thus when para-azoxyanisole is heated, it melts at 114°, but the liquid obtained exhibits a somewhat turbid appearance and strong double refraction. This double refraction points to a regular arrangement of particles in the substance, which is yet undoubtedly a liquid so far as its mechanical properties are concerned. It flows easily, and rises in a capillary tube, and from the capillary rise its molecular weight may be calculated by the method of Ramsay and Shields (Chap. XVIII.). At 134·1° it suddenly loses its turbidity and double refraction, and becomes in all respects similar to an ordinary liquid. The transition from the state of "crystalline" liquid to ordinary liquid is accompanied by a diminution in density, but by no change in the molecular weight. On cooling, the reverse changes occur: the ordinary liquid passes into the crystalline liquid at 134·1°, and this into the crystalline solid at 114°.

The phenomena of nucleus formation, nuclear growth, and extreme superfusion can be very easily shown with hippuric acid, a substance melting at 188°. A small quantity of it is melted at a temperature not exceeding 195°, in order to avoid decomposition, and a portion of the liquid is sucked up into a thin-walled capillary (melting-point tube) about 6 inches long and 1 mm. or less in diameter, the lower end of which is drawn out to a fine jet but not sealed. The liquid is manipulated above a flame until it settles in the middle of the tube, and the narrow end of the capillary is then carefully sealed off. The tube is held horizontally by the open end, and moved above the flame until every crystalline particle has disappeared, after which it is suddenly chilled by dipping into a beaker of cold water. The contents have then assumed the state of a transparent glass. If the tube is broken, it is found that the acid is undoubtedly solid in the ordinary sense, though not crystalline. When left to itself it remains unchanged for days, but if it is dipped into water at 100°, nuclei will appear and grow along the tube at a moderate rate. The growth may be interrupted at any time by chilling the tube in cold water. If a small flame be passed rapidly across the tube, nuclei will be found to form at the heated portions and not elsewhere.

When a foreign substance is dissolved in a liquid, the freezing point of the solution is lower than that of the pure solvent. It is, strictly speaking, necessary here to specify what substance separates out, but unless it is otherwise expressly indicated we shall always assume that it is the solidified solvent. A solution of a substance in water must be cooled below the freezing point of water before ice separates out, and for small concentrations the lowering of the freezing point is proportional to the amount of the substance in solution (Blagden's Law). The **freezing point of a solution** is best defined as the temperature at which the solution is in equilibrium with the solid solvent. At this temperature it may be mixed with the solid solvent in any proportion without undergoing change; it neither melts the solid nor deposits any solvent in the solid form. Practical everyday applications of the lowering of the freezing point by substances in solution are to be found in the melting of snow or ice by salt, and in the addition of alcohol or glycerine to wet gas-meters to prevent freezing in cold weather. In the latter case the alcohol or glycerine added to the water lowers its freezing point greatly; a mixture containing, for instance, 25 per cent of alcohol freezes at −13°, so that the external temperature must fall far below the freezing point before the gas-meter ceases to act. Glycerine has a certain advantage over alcohol for this purpose, inasmuch as it is non-volatile. When alcohol is used it slowly evaporates, and the solution, owing to this cause, becomes both smaller in bulk and weaker. Glycerine not only does not evaporate itself, but also greatly reduces the vapour pressure of the water (Chap. IX.), so that it both diminishes the chances of freezing and prevents rapid evaporation.

The action of salt in melting snow or ice may be seen from the following consideration. A solution containing a little salt is in equilibrium with ice at a temperature somewhat below 0°. If we cool the solution below this particular temperature, ice will separate, and the remaining solution will therefore become more concentrated. Its freezing point will consequently be lower than that of the original solution. If we continue the cooling process, more and more ice will fall out and the solution will become still more concentrated and have a still lower freezing point. This process might be conceived to go on without limit if salt were infinitely soluble in water. But we know that there is a limit to the solubility of salt in water, *i.e.* at a given temperature a certain quantity of water will only take up a definite amount of salt and no more. This finite solubility of salt in water accordingly sets a limit to the lowering of the freezing point. We may best understand this by making use of a combined solubility and freezing-point diagram. The horizontal axis gives the composition, *i.e.* percentage of salt in the mixture. Temperatures are plotted on the vertical axis. If we lower the temperature of a solution containing a little salt, ice will begin to separate out and the freezing point will fall as the concentration of the remaining solution increases. The relation between the concentration of the solution and its freezing temperature (*i.e.* the temperature at which it is in equilibrium with ice) is represented by the curve on the left, which we shall call the freezing-point curve. If on the other hand we begin with a saturated solution of salt above 0° and cool it, salt will separate out and the solution will become less concentrated, for the solubility of the salt diminishes with falling temperature. The relation between the concentration and temperature at which the solution is in equilibrium with the solid salt is given by the curve on the right, which is therefore an ordinary solubility curve. The two curves evidently tend to approximate with fall of temperature, the concentration of the solution which is in equilibrium with ice increasing, and the concentration of the solution which is in equilibrium with salt diminishing; and at a certain temperature they meet.

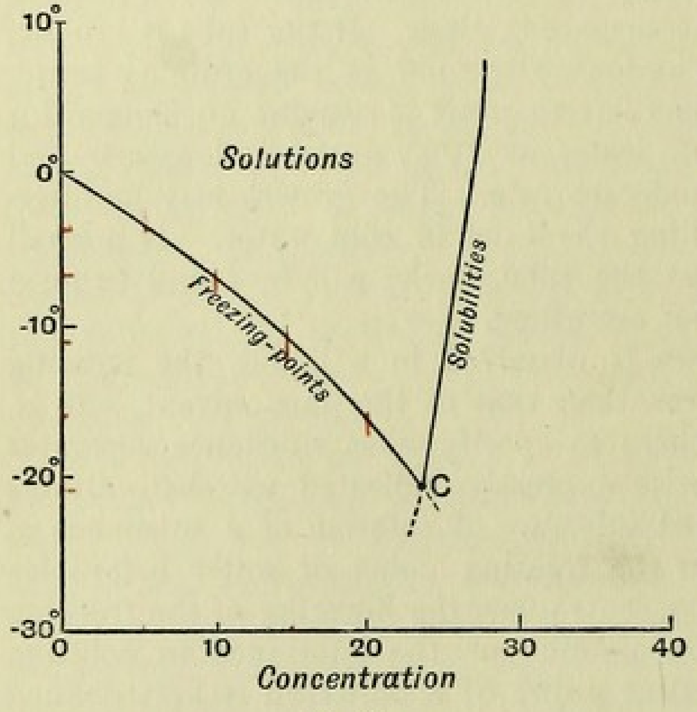

FIG. 9.

We shall now consider what occurs when we follow a salt solution down either of the curves to the point C where the curves intersect. Starting with a weak solution, we find that as the temperature falls, ice separates and the solution becomes more concentrated. This goes on until the freezing-point curve cuts the solubility curve, at which point the solution remaining behind becomes saturated. If we attempt to lower the temperature still farther, ice separates out; but the solution remaining is now supersaturated, and therefore deposits salt until the saturation point is again reached. But the solution which was cooled was a saturated solution, so that the ice and salt must have separated out in the proportions in which they existed in this saturated solution, *i.e.* the solution solidifies like a single substance.

The same result is arrived at if we follow the curve for the cooling of a strong solution of salt instead of a weak one. When the solution is cooled a point is at last reached at which the solution is saturated. The result of further cooling is that some of the salt separates out, the solution being now saturated for the lower temperature. As we cool the solution, therefore, it becomes less and less concentrated, the concentrations following the solubility or saturation curve on the right-hand side of the diagram. At last a point is reached where the saturation curve cuts the freezing-point curve. If we could follow the solubility curve below this point, further cooling would cause more salt to separate, but the weaker solution resulting would now be below its freezing point, and consequently ice would begin to separate out, and this would continue until the concentration of the solution was restored to the original value it possessed where the two curves intersect. If we take a solution of the particular concentration given by the point of intersection of the freezing-point and saturation curves, we may cool it without the separation of either salt or ice until we come to the temperature corresponding to the intersection. If we continue to abstract heat, the solution solidifies as a whole, both ice and salt separating in the proportions in which they exist in the solution, without any change of temperature taking place until all is solid. The solution then behaves like a pure liquid, and has a definite freezing point. For this reason the separated substance was supposed to be a definite compound of salt and water, and was called a **cryohydrate**. It is now known, however, that the salt and ice separate out independently of each other and not in the form of a compound. Cryohydric solutions, in fact, are quite analogous to the constant-boiling mixtures referred to in Chapter IX.; they are constant-freezing mixtures.

It can be easily seen from a study of the diagram that no solution of salt in water can exist in a stable state below the cryohydric temperature, and that this temperature is the lowest that can be produced by mixing ice and salt, or snow and salt together. If we consider a horizontal line cutting the diagram at the temperature 0°, we see that there is only a certain range of concentrations, viz. from 0 per cent to 26·3 per cent, possible for salt solutions, for above the latter concentration we should have supersaturated solutions, and salt would separate. A similar line at – 10° cuts both curves, and it is only the part between the two curves, viz. from 14 per cent to 25 per cent, that represents possible concentrations for salt solutions. If we had a stronger solution than 25 per cent, it would be supersaturated at that temperature, and salt would fall out; if we had a weaker solution at that temperature than 14 per cent, it would be below its freezing point, and ice would separate. Taking horizontal lines at still lower temperatures, the parts enclosed between the two curves, *i.e.* the range of possible concentrations, become smaller and smaller, until at the cryohydric temperature it has shrunk to a point. At that temperature, therefore, there is only one salt solution possible, and below that temperature none is possible at all, unless indeed it be an unstable supersaturated or superfused solution, which when brought into contact with the corresponding solid will immediately assume the temperature and concentration of the cryohydric solution.

At and below the cryohydric temperature, ice and salt can exist together without affecting each other; and at the cryohydric temperature they can also exist together with the cryohydric solution. Above the cryohydric point, ice can only exist in contact with a solution having one definite concentration, and salt with a solution having another definite concentration. If we mix, therefore, ice, salt, and water at a temperature above the cryohydric point, and keep them well mixed, there can be no real equilibrium. The water will tend to dissolve salt until it becomes saturated, but this saturated solution will not be in equilibrium with ice, being too concentrated (compare the diagram at -10° say). Ice will therefore melt and the solution will become more dilute, and again dissolve more salt, with the result that more ice will melt. Now a certain amount of heat must be supplied in order to melt ice. If this heat is not supplied from an external source it must be derived from the mixture itself. The temperature of the mixture will therefore fall, and if we continue to mix, the same causes will effect a further lowering of temperature until the cryohydric point is reached, at which one and the same solution can be in equilibrium with both ice and salt. The solution adjusts itself to this concentration, and ice and salt now melt (if heat from external sources reaches the mixture) in the proportions of the cryohydric solution, and the temperature will remain constant at the cryohydric point until all the ice or all the salt has disappeared. It may happen, of course, that the original proportions of ice, salt, and water may have been such that one of the solids will disappear before the cryohydric point is reached. No further cooling can occur after this disappearance takes place, and the mixture is not then a satisfactory freezing mixture. In order that a freezing mixture may be effective and reach the cryohydric point, thorough mixing of the ingredients is also necessary, for on this depends the attainment of the final equilibrium. For this reason snow and salt form a better freezing mixture than pounded ice and salt, for in the latter case the mixing can scarcely be so thorough.

When ice and salt are brought into contact at a constant temperature below the freezing point of water but above the cryohydric point, they form a liquid solution at the points at which they come in contact, and this solution strives to adjust itself so as to be in equilibrium with both solids, with the result that one of the solids entirely disappears. If, as is the case in salting snow or ice-covered streets, the solution assumes the general ground temperature, both solids disappear when enough salt has been added. The quantity of salt necessary to melt a given quantity of ice depends on the temperature of the ice, which is practically the temperature of the ground immediately below it. This quantity can easily be calculated from the above diagram. Let the temperature of the ice be -2° C. From the diagram we find that the solution which freezes at this temperature contains about 3 per cent of salt. If we add less salt than amounts to 3 per cent of the weight of ice to be removed, the whole of the ice will not be melted, but only enough for the formation of a solution of the above strength, this solution then being in equilibrium with the remaining ice. If we add 3 per cent of the weight of the ice, all the latter will melt. If we add more than 3 per cent of salt, the ice will all melt and the solution will dissolve the excess of salt, unless the excess is so great that the solution becomes saturated before the whole excess is dissolved. If the temperature of the ground (and the ice) is below the cryohydric point, no amount of salt, however great, will melt the ice. It should be noted that the circumstances of the case are here somewhat different from those under which a freezing mixture is usually formed. In the latter case conduction is avoided as far as possible, as the object is to keep the temperature down. If, on the other hand, excess of salt is thrown on the streets, although the temperature may for a short time sink below the temperature of the street, conduction from below restores it to its original value.

In the above discussion it will be observed that there is no practical difference between the behaviour of the solutions towards the ice and towards the salt. The solution which can remain unchanged in contact with ice may be said to be saturated with regard to ice, just as the solution which can remain unchanged in contact with common salt is said to be saturated with regard to the salt. This serves to illustrate the conventional nature of the distinction between solvent and dissolved body. As soon as we reach a temperature at which both substances are solid, the solution bears for all practical purposes the same relation to both.

What has been said with regard to salt and water holds equally well for other substances, where we have two concentration curves meeting. The **hydrates** of many inorganic salts afford excellent instances in point. As an example we may take the hydrates of ferric chloride. In the diagram temperatures are tabulated as before on the vertical axis and concentrations on the horizontal axis.

The concentrations, however, in this case are expressed not in parts of salt dissolved in 100 parts of water, but as the number of molecules of ferric chloride (Fe_2Cl_6) to 100 molecules of water. Ferric chloride is usually met with as the yellow hydrate $Fe_2Cl_6 . 12$ aq. or as the black metallic-looking scales of the anhydrous salt. It also exists, however, in the form of hydrates, having the formulæ $Fe_2Cl_6 . 7$aq., $Fe_2Cl_6 . 5$ aq., and $Fe_2Cl_6 . 4$ aq. The diagram shows the solubility of all these hydrates. Each hydrate has its own solubility curve, and these curves cut each other at various points. Towards the left of the diagram is given the freezing-point curve of dilute ferric chloride solutions, water being considered the solvent. The curve cutting this is the solubility curve of the hydrate $Fe_2Cl_6 . 12$ aq. On the left of this curve we have precisely the kind of diagram already given on p. 68, with the difference that the solid salt is now a hydrate of ferric chloride instead of anhydrous sodium chloride. The point where the curves cut is the cryohydric point, and gives the lowest temperature that can be got by mixing ice and $Fe_2Cl_6 . 12$ aq.

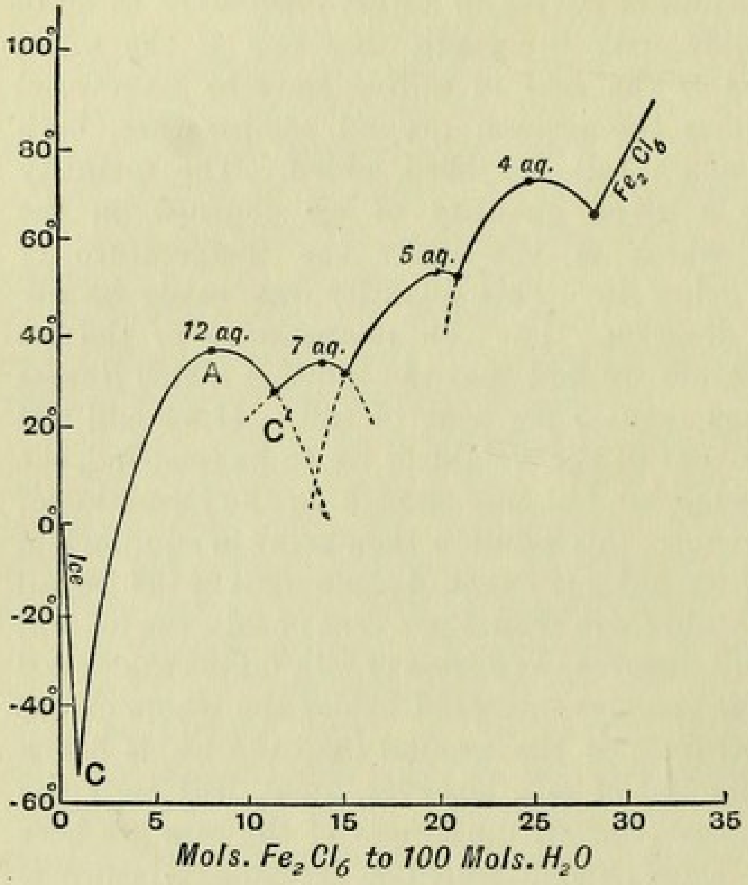

FIG. 10.

To the right of the cryohydric point it will be observed that the curve of the dodecahydrate culminates at a point A, declining from this maximum as the concentration increases. If we draw a horizontal line at a temperature a little below 40°, it will cut the curve of the dodecahydrate in two places, *i.e.* at one and the same temperature this hydrate has apparently two solubilities, or can be in equilibrium with two ferric chloride solutions of different concentrations. This is not an uncommon occurrence with hydrates, and may be most easily understood by a reference to the maximum point. The concentration here is the same as the composition of the solid hydrate, *i.e.* 1 molecule Fe_2Cl_6 to 12 molecules of water. The solution then may be looked upon as the melted hydrate, and the maximum temperature as the melting point of the hydrate. Now we have seen that ice is in equilibrium in contact with water plus a foreign substance at a lower temperature than when in contact with water (*i.e.* melted ice) alone. The melting point of ice therefore is highest when it is in contact with a liquid of its own composition: it melts at a lower temperature when the liquid with which it is in contact contains a foreign substance. This holds true generally—a substance always melts at the highest temperature when in contact with the liquid produced by its own complete fusion. Now in the above case the maximum melting point of the hydrate $Fe_2Cl_6 . 12$ aq. occurs when the concentration of the solution corresponds to this formula. If the solution contains either ferric chloride or water in excess of this ratio, the dodecahydrate will melt at a lower temperature. The curve therefore falls both to the right and the left of the concentration given by the ratio of Fe_2Cl_6 to water in the dodecahydrate, with the result that there are two different solutions with which the hydrate can be in equilibrium at one and the same temperature. One of these solutions contains more water than the solid with which it is in equilibrium—the other contains more ferric chloride. The branch of the curve to the left of the maximum may evidently either be looked on as a solubility curve of the dodecahydrate in water, or as a melting-point curve of the dodecahydrate in contact with solutions of varying concentration. The branch to the right we usually regard as a melting-point curve; but it also may be looked on as a solubility curve.

If we follow now the right descending branch of the curve of the dodecahydrate, we find that we reach a point where it cuts the curve of another hydrate, the heptahydrate $Fe_2Cl_6 . 7$ aq. From inspection of the diagram, the point of intersection is evidently of the same nature as the cryohydric point, where the curve for the melting point of ice intersects the curve for the melting point of the dodecahydrate. At the cryohydric point proper, ice and the solid dodecahydrate can exist together with each other and with a solution of a certain concentration: at the other point of intersection, the dodecahydrate and the heptahydrate can exist together and in contact with another solution of definite concentration. If a solution of this particular concentration is cooled, it solidifies as a whole, and the freezing point remains constant. As before, however, the solid which separates out is not a pure substance, but a mixture of solids—the two hydrates. Proceeding farther to the right, we again reach a maximum and again dip to a "cryohydric" point, viz. the point where the curves of the heptahydrate and the pentahydrate intersect. In still more concentrated solutions the same phenomena are repeated, until we finally come to a cryohydric point where the curve of the tetrahydrate cuts the solubility curve of the anhydrous salt, after which we have a solubility curve of the ordinary type. Every maximum corresponds in composition to a definite hydrate, and in temperature to the melting point of that hydrate, the solid melting at a definite and constant temperature. At every intersection we again have a composition corresponding to a constant melting point and freezing point; here, however, it is not a definite solid that melts or separates out, but a mixture of two solids.

It should be noted that whenever we have a constant freezing point, the composition of the liquid and of the solid is the same. If the composition of the solid which separates is not the same as that of the liquid from which it separates, the temperature will fall as the freezing goes on.

It is often possible to follow the curves of hydrates below their points of intersection, as the dotted continuations in the figure indicate.

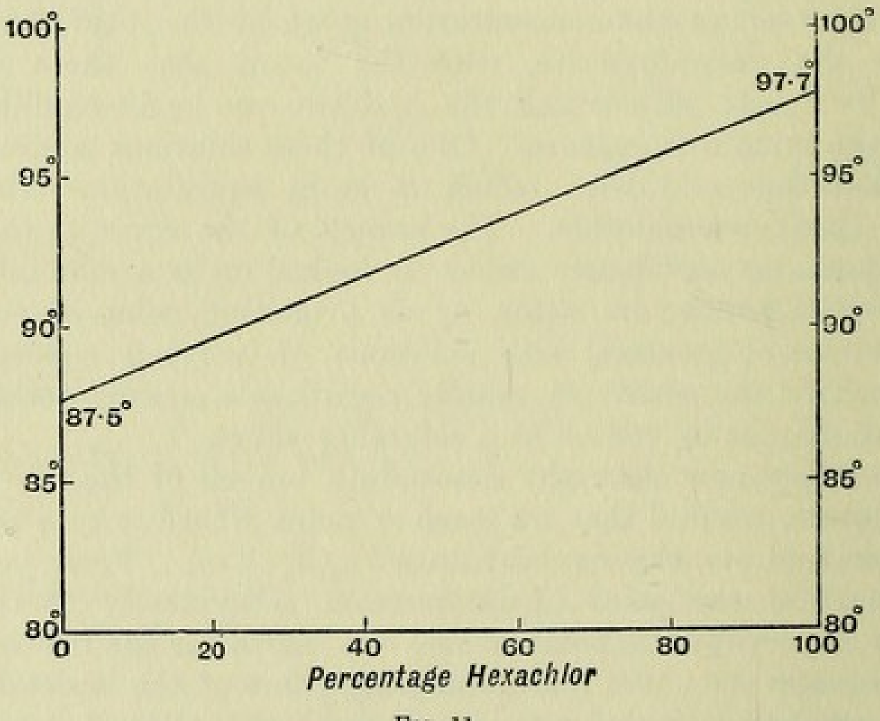

FIG. 11.

The phenomena here are of the same nature as those already referred to on page 69. The solution which is saturated with respect to the dotted hydrate is unstable, or rather "metastable" (cp. Chap. XI.), and may suddenly deposit another hydrate.

It occasionally happens that when two substances are melted together, the liquid when cooled does not deposit one of the substances only, but both at once. This we have seen to be the case with salt solutions having the cryohydric composition, but it is only when the liquid has this peculiar concentration that the deposition of both solids occurs. With other substances, however, both solids may be deposited simultaneously, no matter what the composition of the liquid is. This generally occurs when the two solids crystallise in the same form and are capable of forming isomorphous mixtures. Such homogeneous solid mixtures are often called "solid solutions," as they present many points of analogy to liquid solutions. If the solids are always deposited in the proportions in which they exist in the liquid, the liquid will have a constant freezing point. An instance of this kind apparently exists in the case of two substances recently investigated. These are closely related chemically, one being the hexachlor-derivative of a cyclopentenone, and the other the corresponding pentachlor-monobrom-derivative. The diagram Fig. 11 gives temperatures (melting points) on the vertical axis and compositions (molecular percentages) on the horizontal axis. The curve is practically a straight line joining the melting points of the two substances. No matter what the composition of the liquid may be, it freezes as a whole and the solid has a constant melting point.

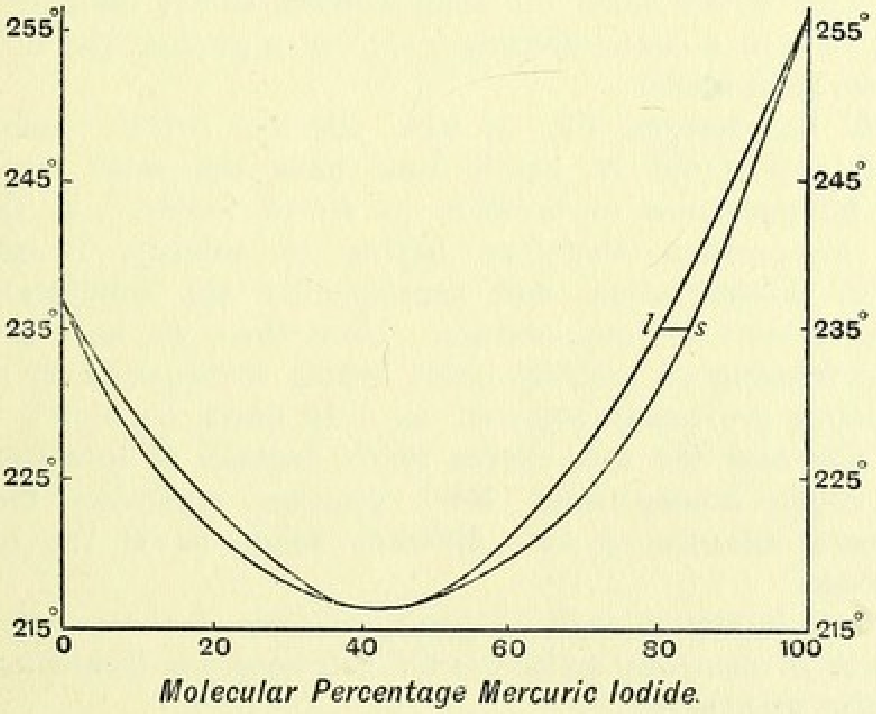

Fig. 12.

If the solid mixture which separates out has not the same composition as the liquid, but a different one, which varies with the varying composition of the residual liquid, the temperature will fall as solidification progresses. Should a point be reached where the composition of the solid separating is the same as that of the residual liquid, the liquid will then freeze as a whole.

An instance of this kind is afforded by mercuric bromide and mercuric iodide, which are capable of forming isomorphous mixtures in all proportions. These substances melt at 236·5° and 255·4° respectively, but, as will be seen from the diagram (Fig. 12), the melting points of the isomorphous mixtures by no means lie on the straight line joining the melting points of the pure substances. The lower curve is the curve of "melting points" of solid solutions of different compositions; the higher curve is the curve of "freezing points" of liquid solutions of different compositions. The compositions of the solid and liquid which are in equilibrium at any one temperature are given by the points on the adjacent curves which are at the same horizontal level; thus the points *l* and *s* represent the compositions of the liquid and solid which are in equilibrium with each other at 235°. If we consider what occurs when a liquid having the composition *l* begins to solidify, we see that as the solid which separates out contains a larger proportion of iodide, the concentration of the liquid with respect to iodide falls off, and, as the curve shows, the freezing point falls. There is thus no constant freezing point, but, just as in the case of salt solution, a gradual lowering of the temperature of equilibrium as the solidification progresses. Conversely, if we consider what occurs when the solid solution slowly liquefies we shall find that there is no fixed melting point, but a gradual rise in temperature as the solid melts.

It will be observed that at 216° the two curves touch. Here the solid and liquid in equilibrium have the same composition, namely, 60 molecules of bromide to 40 of iodide. If the liquid of this composition therefore begins to solidify, it suffers no change in concentration, and consequently the solidification progresses at a constant temperature. Here, then, we have a constant minimum freezing or melting point, which corresponds to the cryohydric points previously referred to. It must be noted, however, that in this case the two curves touch, instead of intersecting, and that a single homogeneous solid solution separates, instead of an intimate mixture of two different solids as is the case with cryohydrates.

Solids of minimum melting point, whether of the nature of cryohydrates or of constant melting solid solutions, are frequently known as **eutectic mixtures.**

In the ordinary method of melting-point determination practised by organic chemists, it is well known that pure substances give sharp melting points, whilst impure substances begin to soften and melt at a temperature several degrees lower than the temperature at which they are completely liquefied. This corresponds with the general rule that the presence of a foreign substance lowers the freezing point, the melting point being similarly lowered. In many cases when solids are brought into contact with each other the melting point of one of them will be depressed. Thus it is possible to liquefy a mixture of filings of cadmium, zinc, lead, and bismuth by merely leaving them in contact at 100°, although all of them have melting points much above 100°. If a solid, therefore, is mixed with another solid as an impurity, its melting point will very likely be lowered, especially when, as usually happens, the impurity is a chemically similar substance. In this case the two will probably be mutually soluble, when liquid, and mutual solubility is a necessary condition for lowering of the melting point.

If the substances are not mutually soluble, *e.g.* sand and sulphur, the melting point will not be affected.

With reference to the fusion and solidification of alloys the student should read a paper by W. C. ROBERTS-AUSTEN (*Proc. Roy. Soc.* 1898, **63**, p. 447); also C. T. HEYCOCK and F. H. NEVILLE, "On the Constitution of the Copper-Tin Series of Alloys," Bakerian Lecture, 1903.

CHAPTER IX

VAPORISATION AND CONDENSATION

When a gas is subjected to great pressures it occupies a small volume compared to that which it occupies at the ordinary pressure, although perhaps a larger volume than it would occupy if it contracted exactly according to Boyle's Law (cp. Chap. X.). Every gas, above a certain temperature which is characteristic for it, exhibits this behaviour, but if the gas be below the characteristic temperature, constantly increased pressure will at length convert it into a liquid. The temperature below which the substance can be condensed into a liquid, and above which it undergoes compression without liquefaction, is called the **critical temperature** of the substance, and the pressure which at the critical temperature just suffices to condense the gas to the liquid form, is called the **critical pressure.** Under these conditions the substance has a certain definite **critical density,** the reciprocal of which is the **critical volume.** The following table gives the critical temperature and pressure of various substances, the temperatures being in degrees centigrade and the pressures in atmospheres.

	Critical Temperature.	Critical Pressure.
Hydrogen . . .	−234·5	20
Nitrogen . . .	−146	35
Argon	−121	50·6
Oxygen	−118·8	50·8
Methane	− 81·8	54·9
Carbon dioxide . .	+ 31·35	73·0
Nitrous oxide . . .	36·0	71·9
Sulphur dioxide . .	157·0	78·9
Ethyl ether . . .	194·4	35·6
Ethyl alcohol . . .	243·0	63

It will be observed that the critical pressure, which is the pressure necessary to liquefy the gas at the highest temperature at which the liquefaction of the gas by pressure is possible, in no case in the above table exceeds 100 atmospheres, being in general very much less than this. At lower temperatures than the critical temperature, a smaller pressure than the critical pressure effects the liquefaction. We may indeed say, as a general rule, that if a gas under any given conditions is not liquefied by a pressure of 100 atmospheres, it will not under these conditions be liquefied by any pressure, however great. Needlessly high pressures were employed when the liquefaction of the so-called permanent gases (oxygen, nitrogen, and the like) was first successfully attempted, 500 atmospheres being not uncommon.

For the liquefaction of a gas a **low temperature** is the necessary condition, not a great pressure. If the gas is not cooled to its critical point, no pressure which can be applied is capable of liquefying it, while at temperatures not far below this point the gas may be liquefied at the atmospheric pressure. All known gases, with the single exception of helium, have now been obtained in the liquid state, and the liquefaction in all cases can be effected by cooling alone.

One of the methods by which oxygen and similar gases were first successfully liquefied was to cool the gas to as low a temperature as possible while it was subjected to great pressure, and then suddenly to release the pressure. The gas expanded, and in doing so performed work. An amount of heat equivalent to this work must therefore have been supplied. This heat was partially abstracted from the gas itself, with the result that a portion of it liquefied owing to the fall of temperature.

A method which has of late been worked with conspicuous success to liquefy the least condensible gases also depends on the expansion of the gases by diminution of pressure, but the principle involved is entirely different from that just referred to. When any actually existing gas is made to pass, at a suitable temperature, through a porous plug or valve from a high pressure to a low pressure, its temperature is slightly diminished; and if the process is repeated, the gas gets colder and colder, until finally its point of liquefaction is reached. Now while this is true for existing gases, it is not true for an ideally perfect gas. For such a gas there would be no cooling (Joule-Thomson effect), and liquefaction in this way would be impossible. The cooling here observed is due to deviations from the simple gas laws, and must therefore never be confused with the cooling produced by the expansion of a gas under suddenly released pressure, which depends chiefly on the external work done, and holds good for perfect and imperfect gases alike. A diagram illustrating the principle of Linde's apparatus is given in Fig. 13. The gas enters on the left of the diagram and passes through a pump from the pressure P (say 40 atm.) to the pressure P′ (say 200 atm.), then, following the direction of the arrows, it passes down the central tube of the double-walled coil to the throttle valve T, where the pressure falls again to the original pressure P. In passing through this valve the gas becomes colder, and circulating backwards through the annular space between the tubes of the coil, it cools the next portion of gas coming downwards through the centre tube to the throttle valve. This next portion of gas, after it has passed through the valve, is cooled to a lower temperature than the first portion, and serves in its turn to cool the fresh gas arriving at T. The temperature in the neighbourhood of the throttle valve thus constantly sinks, and finally the point of liquefaction of the gas is reached. Liquid appears at the nozzle N and collects at L, the place of the liquefied gas being supplied by fresh quantities admitted to the pump.

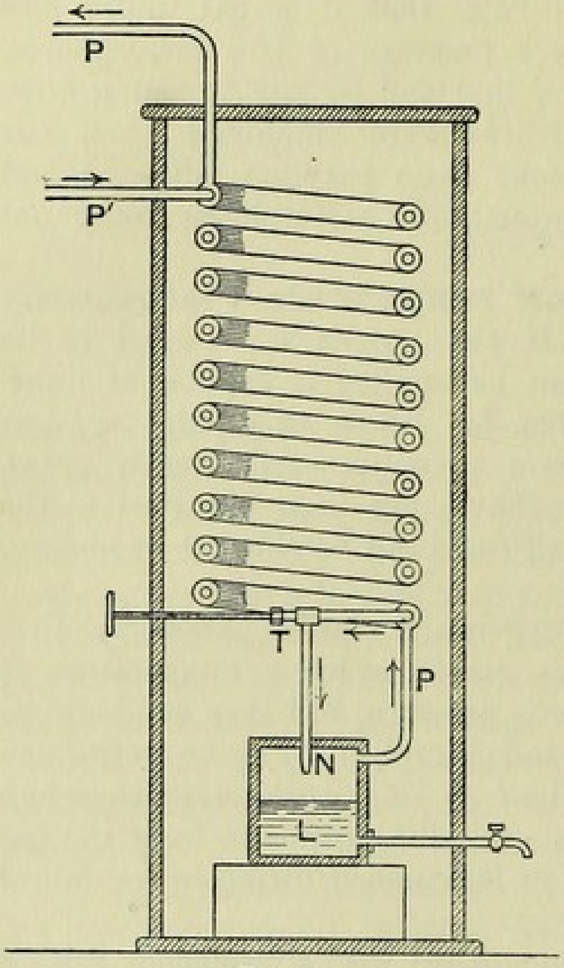

Fig. 13.

All liquids tend to assume the gaseous state, and the measure of this tendency is what we call the **vapour tension** of the liquid. The tendency is exhibited in very different degree by different liquids. Water if left in an open vessel evaporates slowly; alcohol under the same conditions evaporates much more rapidly, and ether more rapidly still. Mercury, on the other hand, scarcely evaporates at all at the ordinary temperature. That it does so slowly, however, may be proved by suspending a piece of gold leaf a little distance above a mercury surface. After some time the gold leaf will be found to be amalgamated, indicating that the mercury has reached the gold in a state of vapour and combined with it to form a gold amalgam.

For a given liquid there corresponds to each temperature a certain definite pressure of its vapour, at which the two will remain in contact unchanged. At that pressure and temperature none of the liquid will pass into vapour; nor will any of the vapour condense to form liquid. The gas pressure of the vapour balances the vapour tension of the liquid, and this gas pressure is said to be the **vapour pressure** of the liquid at that temperature, and the vapour itself is said to be **saturated**. For all liquids the vapour pressure increases with rise of temperature, and consequently all liquids evaporate more readily as the temperature is raised. When the vapour tension of the liquid just exceeds the external pressure (usually the atmospheric pressure) on the liquid surface, the liquid passes freely into vapour, and is said to boil. If we heat a liquid in a closed space of appropriate dimensions, the pressure within the space rises, owing to the increase of the vapour pressure of the liquid, and the properties of the liquid and its saturated vapour gradually approximate to each other, until at last, when the critical temperature is reached, the liquid and the vapour become identical, and all distinction between them disappears.[1] The pressure registered is then the critical pressure of the substance.

Having considered above the effect of raising the temperature of a substance at constant volume, we may now pass to the consideration of the effect of varying pressure at constant temperature. Let us imagine the vapour of a liquid enclosed in a cylinder with a movable piston, and let the pressure on the piston be less than the vapour pressure of the liquid at the constant temperature considered. If the pressure on the piston is gradually increased, the gas will be compressed into smaller bulk at a rate greater than would accord with Boyle's Law, till the moment at which the vapour pressure is reached, when the liquid will begin to make its appearance. If the piston is still pressed home the gas will now pass into the liquid state without any further increase of pressure being necessary. The pressure necessary to liquefy a gas at any given temperature needs therefore to be only slightly greater than the vapour pressure of the liquid at that temperature, which must be always less than the critical pressure, for this is the upper limit of the series of vapour pressures (cp. p. 106).

If on two axes at right angles to each other we plot the corresponding pressures and volumes of a quantity of gas which obeys Boyle's Law, we should get a rectangular hyperbola as **isothermal curve**, or curve of constant temperature. Now all gases diverge more or less from this law, and the isothermal curves obtained only approximate to rectangular hyperbolas when the gas is not near the critical condition. A consideration of Andrews' pv diagram for carbonic acid will be instructive (Fig. 14). The critical temperature of carbon dioxide is about 31·1°. At a temperature of 48° the pv curve runs without any flexure, and though it is not a rectangular hyperbola the volume diminishes regularly with increase of pressure. At temperatures nearer the critical temperature the curves show less regularity, exhibiting at a certain pressure (about 80 atmospheres) contrary flexure, although at lower and higher pressures they are quite regular. At the critical temperature the curve runs for a very short

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[1] The student may compare this behaviour with what happens when aniline and water are heated together in a closed space (p. 56). At first there are two layers, but as the temperature is raised, these layers approximate to each other in composition (Fig. 5), density, etc., until at 165° they become identical, the whole being then homogeneous. The lowest temperature of complete miscibility has been called the "critical solution temperature" for the pair of liquids.

distance parallel to the *v* axis, when the pressure is 73 atmospheres. At a still lower temperature, when the pressure is increased slowly, the volume diminishes somewhat rapidly, until at a certain pressure the curve suddenly breaks and runs horizontally, so that no further rise of pressure is required to effect a diminution of volume. This takes place when the liquid and gas coexist, and the pressure is then the vapour pressure of the liquid. When that pressure is reached, the liquid appears and goes on increasing in quantity by the liquefaction of the gas without further rise of pressure until the gas has entirely disappeared, when the curve suddenly bends upwards from the horizontal. In the liquid a very small change of volume now follows from a considerable rise of pressure.

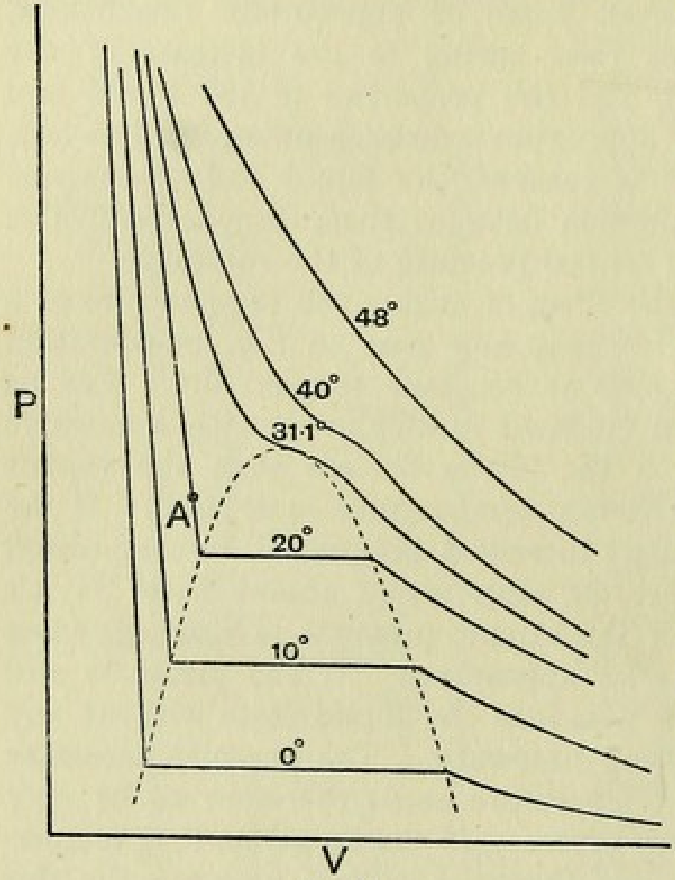

Fig. 14.

At a lower temperature still, the same phenomena are observable: the formation of liquid taking place at lower pressures, for, as we have already seen, the vapour pressures of all liquids diminish with fall of temperature. In each curve there are two breaks: first when the curve becomes horizontal, and second when it ceases to be horizontal. The value of the pressure at the horizontal portion is the vapour pressure at the particular temperature for which the curve is constructed. If all the points where the breaks occur are connected, we get a "border curve" which is shown by the dotted line in the figure. The region within this border curve gives the pressures and volumes at which the gas and liquid can coexist. On the right of the border curve and above it the substance is a gas: on the left it is a liquid. If we so change the temperature, pressure, and volume, that the corresponding points in the diagram keep entirely outside the border curve, liquid and gas never exist together, and there is no discontinuity in the passage from the liquid to the gaseous state, or *vice versa*. Let us, for example, take liquid carbon dioxide at the temperature 20°, and at the pressure and volume indicated by the point A. Let us raise the pressure of this liquid at constant temperature until it passes the critical pressure, and then, keeping the pressure constant, let us increase the temperature until it is greater than the critical temperature, say 48°. At no point during the rise of temperature does the liquid change its state suddenly; it passes with perfect continuity into the state of gas. By expanding now at constant temperature along the isothermal of 48°, and then cooling at constant volume, we finally come to the same temperature curve as that on which we started, viz. 20°, and so have converted the liquid into gas at the same temperature without sudden change of state.

This gradual passage from the gaseous to the liquid state, and *vice versa*, shows us that these states are not so sharply defined from each other as we are in general disposed to imagine, but are rather united by a continuous series of intermediate states. The sharp definition that we are accustomed to perceive is a consequence of the ordinary conditions of temperature and pressure at which we work, rather than of any inherent properties of the substance operated on. In Chapter X. reference will be made to the theory of van der Waals, which deals with the continuity of the liquid and gaseous states in a systematic manner.

When a liquid is made to evaporate rapidly, enough heat may be absorbed by the evaporation to cool a portion of the liquid below its freezing point. Thus in the Carré freezing machine ice is made by the rapid evaporation of water under diminished pressure. Again, when liquid carbon dioxide escapes into the air from a cylinder in which it has been kept compressed, the sudden reduction of pressure brings about such rapid evaporation that a snow of solid carbon dioxide is produced. Even hydrogen has been solidified by Dewar by the rapid vaporisation of liquid hydrogen under reduced pressure.

Solids have often, like liquids, a measurable vapour pressure. On a windy day, snow and ice may be seen to disappear by evaporation, although the temperature may be far below the freezing point. The solid here passes into vapour directly without first assuming the liquid state, and the vapour is removed by the wind as it is formed. A piece of camphor when left in the open air gradually diminishes in bulk and finally disappears, owing to evaporation without melting. Since the vapour pressure of the solid is always less than the vapour pressure of the liquid, the vaporisation in the former case takes place more slowly.

Solids are said to **sublime** when on heating they pass directly into vapour, which on being cooled does not condense to a liquid but directly to a solid. Sublimation takes place with ease under ordinary conditions when the solid has at its melting point a vapour pressure not far removed from the external pressure, or, what practically comes to the same thing, when the melting and boiling points of the substance are comparatively close together. Arsenic trioxide, when heated gradually at the ordinary pressure, passes directly into vapour without assuming the liquid state, and can only be made to melt if heated under increased external pressure. On cooling, the vapours pass at once into the solid form. By sufficiently reducing the external pressure, the boiling point of any substance can always be lowered to the neighbourhood of its melting point, and sublimation can take place. Ice, for instance, can be easily but slowly sublimed at a temperature below the freezing point from one part of an exhausted vessel to another, the ice passing directly into water vapour and the water vapour into ice. In the formation of snow the water vapour assumes the crystalline state directly. Sublimation can in any case be made to occur if the substance is brought to a temperature just below the melting point of the solid, and the vapours derived from it are rapidly cooled.

It has been observed that substances volatilise to a greater extent in a gas than they do in a perfectly exhausted space. It is usually assumed for rough purposes that gases exert no influence on each other, the sum of the values of a physical property for two separate gases remaining the same when the gases are mixed. This cannot be accurately the case, since we are obliged to conclude that the molecules even of the same gas influence each other (see Chap. X.). The reciprocal influence of the gas molecules will evidently be greatest when the molecules are closely packed together, *i.e.* at great pressures, but it may be noticeable even at ordinary pressures with sufficiently refined means of measurement.[1] If we consider that a substance like water must at temperatures just below the critical temperature exert a solvent action on many other substances as long as it remains a liquid, and if we further consider that saturated water vapour at such temperature does not sensibly differ in its properties from liquid water, seeing that the properties of the saturated vapour and the liquid become identical at the critical point itself, we shall not find it surprising that water vapour under these conditions exerts a solvent action even on solids. It is a well-ascertained fact that gases under high pressure exert a solvent action on solids, and the solvent action of gases under ordinary pressure can only differ from this in degree. It is quite in accordance with our theoretical knowledge, then, that a substance such as iodine should be more volatile in air than in a very perfect vacuum, as Dewar has recently ascertained. The air here acts as "solvent," and indeed we can always look on a mixture of two gases as a solution of one in the other, although the influence of the "solvent" is not marked as it is in liquid solutions.

When a substance is dissolved in a liquid, the vapour pressure of

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[1] According to Dalton's law of partial pressures, the total pressure of a mixture of gases is equal to the sum of the pressures which the different gases would exert if each separately occupied the whole space afforded to the mixture. Even for moderate pressures this law is not absolutely exact. A better approximation to the experimental data is given by the following rule :—If we measure the volumes of the separate gases and of the mixture at the same pressure, the sum of the volumes of the component gases is equal to the volume of the mixture.

the latter is lowered at all temperatures, and the lowering for small amounts is approximately proportional to the quantity of substance dissolved in a given amount of the liquid (Wüllner's Law). If we take, for example, a fairly dilute aqueous solution of a very soluble substance such as sugar or calcium chloride (which are not themselves volatile), and evaporate it on a water bath at 100°, the evaporation will at first proceed rapidly, for the vapour pressure of the dilute solution is not much less than that of pure water, being therefore at the beginning nearly equal to one atmosphere. As the evaporation proceeds, however, the solution becomes more concentrated, and the vapour pressure for 100° becomes continually less. The evaporation therefore progresses more slowly, and towards the end the vapour pressure of the water in the solution is so low that practically no vapour comes off at all and the solution cannot be further concentrated. If the solid, on the other hand, is not very soluble and begins to separate out on evaporation, the solution soon reaches its maximum concentration, and the vapour pressure no longer diminishes, so that the evaporation proceeds at a uniform rate until all the water has been driven off.

To get a given vapour pressure of solvent from a solution, the solution must be heated to a higher temperature than would be required for the pure solvent, since at a given temperature the vapour pressure of the solution is lower than that of the solvent. A consequence of the diminution of the vapour pressure of a liquid by the dissolution in it of some foreign substance is therefore that the boiling point of the solution is higher than that of the pure solvent. We may thus obtain an aqueous liquid of higher boiling point than 100° by dissolving some fairly soluble non-volatile substance in water. By employing common salt we obtain a brine bath, which is sometimes used instead of a water bath for heating substances to temperatures slightly above 100°. It should be noted that in this case the vessel to be heated must be immersed in the brine, for the steam from the boiling solution will only heat it to 100°, although the temperature of the salt solution may be as high as 110°. As the boiling point of a saturated solution of calcium chloride is 180°, this substance may be used when still higher temperatures are required.

Distillation of Mixtures.—We supposed in the preceding paragraph that the dissolved substance was non-volatile. When the dissolved body is volatile as well as the solvent, each substance lowers the vapour pressure of the other, and the boiling point of the mixture may be higher or lower than the boiling point of either, depending on the sum of the vapour-pressure values of the two substances. If, for example, we take a mixture of methyl alcohol and water, the vapour given off consists of a mixture of the vapours of these liquids, and the mixture boils when the temperature is such that the sum of the two partial vapour pressures is equal to the atmospheric pressure. In general, the composition of the remaining mixture will not be the same as the composition of the vapour evolved, so that as the evaporation or distillation goes on, the temperature of ebullition changes, since for each mixture a different temperature is required in order that the sum of the vapour pressures may reach the constant atmospheric pressure. It is evident that in the process of distillation as ordinarily conducted the boiling point of the mixture must gradually rise, since the more volatile portions evaporate first. If the original mixture contains much water and little alcohol, the boiling point will gradually rise as the more volatile alcohol (boiling point 66°) distils off, and finally pure water will remain behind when the boiling point reaches 100°. We can therefore, as a rule, free an aqueous liquid from alcohol by heating on a steam bath. If, on the other hand, the solution contains much methyl alcohol and little water, it is practically impossible to get rid of all the water by distillation. At the boiling point of the alcohol, pure water has, it is true, a considerable vapour pressure, but when the mixture consists nearly wholly of alcohol, the vapour pressure is lowered very much, and it is increasingly difficult to get perfect separation of the two constituents as the quantity of water in the liquid gets less and less.

The mixtures of some liquids differ from the example given above inasmuch as they tend to separate on distillation, not into the two components, but into one of the components and a **constant boiling mixture** of both, which can be distilled unchanged, the composition of the distillate being the same as the composition of the residual mixture. The constant boiling mixture is that which has either a greater vapour pressure than that of any other mixture, or a less vapour pressure than that of any other mixture. Thus a mixture of propyl alcohol and water containing 70 per cent of the former has, under ordinary conditions, a greater vapour pressure than any other mixture of the two substances. It is therefore the mixture of minimum boiling point at atmospheric pressure, and if we distil any mixture whatever of the two substances, the distillate will always approximate more closely in composition to this mixture than will the residue in the distilling flask. In the same way the mixture of ethyl alcohol and water containing 96 per cent of alcohol has a minimum boiling point at atmospheric pressure, so that it is impossible by distillation alone to concentrate alcohol beyond this strength. On the other hand, a mixture of formic acid and water containing 75 per cent of the acid has a lower vapour pressure than any other mixture, *i.e.* it is the mixture with the highest boiling point. If, then, we distil any given mixture of formic acid and water, the composition of the residue will always approximate more closely to this mixture of maximum boiling point than will the composition of the distillate.

Certain constant boiling mixtures (mixtures of maximum boiling point) were for long looked upon as true chemical compounds, for their composition was not affected by distillation. Nitric acid, for example (boiling point 86°), forms with water a constant boiling mixture which contains 68 per cent of acid and boils at 126°. If a weaker acid than this is distilled, water comes over in excess, and the residue eventually attains the above composition and boiling point. If a stronger acid than this is distilled, the distillate contains excess of nitric acid, whilst the residue grows weaker and the boiling point rises until the values for the constant boiling mixture are attained. The dilution of the residue is assisted in the case of strong nitric acid by the partial decomposition of the acid into oxygen, nitrogen peroxide, and water, the water remaining for the most part in the distilling apparatus. Hydrochloric acid forms with water a similar mixture of constant boiling point. This mixture contains 20·2 per cent of acid, and distils unchanged at 110° under atmospheric pressure. That such constant boiling liquids are mixtures and not chemical compounds is proved by the composition of the liquid which distils unchanged at any one pressure, varying with the pressure at which the distillation is conducted. Thus the mixture which distils unchanged at 2 atm. contains 19·0 per cent of hydrochloric acid, differing therefore in composition from the constant boiling mixture under ordinary pressure. The same error of assigning definite chemical union to mixtures which pass unchanged through some physical process has often been committed, and instances of this nature have already been referred to (cp. p. 69).

When liquids that are only **partially miscible** are distilled together, a distillate of definite composition is obtained as long as two separate layers are present, for, as can be easily shown, the same vapour is given off by each of the two layers, and the only result of distillation is to change the relative quantities of the two layers, the boiling point remaining constant until one of the layers vanishes, after which the distillation proceeds as in the case of two completely miscible liquids.

When two liquids that are **completely immiscible** are subjected to distillation from the same vessel, neither influences the vapour pressure of the other; and when the sum of their vapour pressures is equal to the external pressure, distillation goes on without change in the composition of the distillate until one of the liquids disappears. Nitrobenzene and water may serve as an instance of a pair of nearly immiscible liquids. The mixture boils at 99° under a pressure of 760 mm. Now water at this temperature has a vapour pressure of 733 mm.; the remaining 27 mm. is therefore due to the vapour pressure of the nitrobenzene. Although the pressure exerted by the nitrobenzene is thus relatively small, the weight of nitrobenzene which distils over with the water is considerable; and it is this circumstance which renders **distillation with steam**, an operation so often employed in organic chemistry, a practical success. The weights may be calculated from the vapour pressure by means of Avogadro's Law. The molecular weight of water is 18; the molecular weight of nitrobenzene is 123. If we consider the weight of the gram-molecular volume at 99°, viz. $\frac{22{\cdot}4\,(273 + 99)}{273}$ litres, the mixed vapour will be found to consist of $\frac{18 \times 733}{760}$ g. of water vapour and $\frac{123 \times 27}{760}$ g. of nitrobenzene vapour. The ratio of the weight of water to nitrobenzene in the vapour is then 18×733 to 123×27, or roughly 4 to 1; and this is the ratio of the weights in the distillate. Thus, although nitrobenzene has only 1/27 of the vapour pressure of water at the boiling point of the mixture, one-fifth of the liquid collected is nitrobenzene. This, of course, is due to the molecular weight of the water being so much smaller than that of the nitrobenzene. If an organic substance is unaffected by water and has a vapour pressure of even 10 mm. at 100°, distillation with steam for purposes of purification will in general be repaid. For although its vapour pressure may be only an insignificant fraction of that of water, the higher molecular weight makes up for this, and appreciable quantities come over and condense with the steam. It is thus the low molecular weight of water which renders it so specially suited for vapour distillation.

CHAPTER X

THE KINETIC THEORY AND VAN DER WAALS'S EQUATION

In the preceding chapters we have seen that a consideration of the composition and properties of substances, and the changes which they undergo, has led to the conception of atoms and molecules; but as yet we have not dealt with the mechanical constitution of these substances; in other words, we have not considered how the molecules go to build up the whole—whether they are at rest or in motion, or whether in the different states of matter there is a difference in the state of the molecules.

It is plain that the kind of matter most suitable for study from this point of view is matter in the gaseous state, for in this form substances obey laws which in point of simplicity and extensive application are not approached by substances in either of the other states of aggregation. We have the simple laws of Boyle, Gay-Lussac, and Avogadro, which connect in a perfectly definite manner the pressure, temperature, volume, and number of molecules in all gaseous substances, whatever their chemical nature or other physical properties may be. These laws point to great simplicity in the mechanical structure of gases, and to the sameness of this structure for all gases. Various hypotheses have from time to time been put forward to explain the behaviour of gases, but only one has been found to be at all satisfactory, and to some extent applicable to the other states of matter.

This hypothesis is called the kinetic theory of gases, and is, in its present form, chiefly due to the labours of Clausius and Maxwell. According to this theory, the particles of a gas—which are identical with the chemical molecules—are practically independent of each other, and are briskly moving in all directions in straight lines. It frequently happens that the particles encounter each other, and also the walls of the vessel containing them; but as both they and the walls are supposed to behave like perfectly elastic bodies, there is no loss of their energy of motion in such encounters, merely their directions and relative velocities being changed by the collision.

The total pressure exerted by a gas on the walls of the vessel containing it is due to the impacts of the gas molecules on these walls, and is measured by the change of momentum experienced by the particles on striking the walls. Suppose a particle of mass m to be moving with the velocity c, and let it impinge on the wall at right angles. The particle will rebound in its line of approach with a velocity equal to its original velocity, but of course with the opposite sign. The original momentum was mc, the momentum after collision is $-mc$, so that the change of momentum is $2mc$. If we calculate now the change of momentum suffered by all the particles of a quantity of gas in a given time by collision with the walls, we are in a position to give the total effect on the walls, and thus the pressure. For the sake of simplicity, we imagine that the vessel is a cube, the length of whose side is s, and that all the molecules have the same mass m, and the same velocity c. Let the total number of molecules in the gas be n. The molecules, according to the original assumption, are moving in all directions, but the velocity of each may be resolved into three components parallel to the edges of the cube, the components being related to the actual velocity by means of the equation $x^2+y^2+z^2=c^2$. Consider a single molecule with respect to its motion between two opposite sides of the cube. Its velocity component in this direction is x, and the number of impacts on the sides in unit time will be $\frac{x}{s}$. The change of momentum on each impact is $2mx$, so that in unit time the total change of momentum of the molecule caused by impacts on the walls considered is $2mx\frac{x}{s}$. The action of the molecule on these walls, therefore, is $\frac{2mx^2}{s}$, and on the other two pairs of walls it will be $\frac{2my^2}{s}$, and $\frac{2mz^2}{s}$. Thus the action of the molecule on all the walls is

$$\frac{2m(x^2+y^2+z^2)}{s}=\frac{2mc^2}{s}.$$

Now in the whole quantity of gas there are n molecules, so that the total action of the gas on the walls of the cube is $\frac{2nmc^2}{s}$. The surface of the six sides of the cube is $6s^2$, and the quotient $\frac{nmc^2}{3s^3}$ therefore gives the action per unit surface. But s^3 is equal to v, the volume of the cube, so that we have finally $p=\frac{nmc^2}{3v}$ or $pv=\frac{1}{3}nmc^2$. All the magnitudes on the right of this equation are constant at constant temperature, hence the product of the pressure and volume of the gas is constant, and thus from the assumptions of the kinetic theory we deduce

Boyle's Law. In the above deduction the vessel was supposed to have the cubical form; but any space may be considered as made up of a large number of small cubes, and as the impacts on the opposite sides of all faces common to two cubes would exactly neutralise each other, the presence of these internal partitions does not affect the impacts on the outer faces of the external cubes, which in the limit constitute the walls of the containing vessel.

Since $\frac{1}{2}mc^2$ is the kinetic energy of a single molecule, the expression $\frac{1}{3}nmc^2$ or $\frac{2}{3} \cdot \frac{1}{2}nmc^2$ may be read as two-thirds of the total kinetic energy of the gas, and we may say that the product of the pressure and volume of a gas is equal to two-thirds of the total kinetic energy of its molecules. We learn that systems of moving particles, such as gases are imagined to be on the assumptions of the kinetic theory, are in equilibrium with each other when the mean kinetic energies of their particles are equal; and we know that gases are actually in physical equilibrium when their pressures and temperatures are equal, *i.e.* they may then be mixed without the pressure or temperature undergoing alteration. Let us consider a number of gases at the same pressure and at the same temperature. If the temperature of the gases is in every case altered in the same degree, the pressure remaining constant, the gases are still in physical equilibrium, and consequently the kinetic energies of their particles must have altered in an equal degree. But the product of pressure and volume of a gas is proportional to the kinetic energy of its particles, and this product has therefore been altered to the same extent for each gas. Since, however, the pressure remained constant throughout, the volume of each gas has thus undergone the same relative change. Thus the kinetic theory enables us to deduce that the volume of different gases is affected equally by the same change of temperature if the pressure remains constant, *i.e.* that all gases have the same coefficient of expansion.

Avogadro's Law may also be deduced from the kinetic theory by making use of considerations similar to the above. Take equal volumes of two gases at the same temperature and pressure. Since $p = p'$, and $v = v'$, $pv = p'v'$, and consequently

$$\tfrac{2}{3}n \cdot \tfrac{1}{2}mc^2 = \tfrac{2}{3}n' \cdot \tfrac{1}{2}m'c'^2.$$

But the mean kinetic energies of the particles of the two gases must also be equal, since they are in mechanical equilibrium, *i.e.*

$$\tfrac{1}{2}mc^2 = \tfrac{1}{2}m'c'^2,$$

whence, dividing the first equation by the second, $n = n'$. Equal volumes of different gases, therefore, at the same temperature and pressure contain the same number of molecules.

We may write the equation $pv = \frac{1}{3}nmc^2$ in the form $c = \sqrt{\frac{3pv}{nm}}$, or since $\frac{nm}{v}$ is the density of the gas, being its weight divided by its volume, $c=\sqrt{\frac{3p}{d}}$. It appears, then, that the speed of the molecules of a gas is inversely proportional to the square root of the density of the gas, a result which is in harmony with the experimental result that the velocity of diffusion (and the velocity of transpiration) of a gas is inversely proportional to the square root of its density.

It is possible to obtain a value for the **speed of the molecules** of a gas by substituting the known values in the equation for the velocity given above. Thus for 32 g. of oxygen under standard conditions we have $p=1,013,000$ dynes[1] per square centimetre, $mn=32$ g., and $v=22,380$ cc., so that $c_0=\sqrt{\frac{3 \times 1,013,000 \times 22,380}{32}}=46,100$ centimetres per second. The molecule of oxygen therefore at 0° C. moves at the rate of 46,100 cm. per second, or nearly 18 miles per minute. The speed of the molecules of any other gas at any temperature may be got from the formula $c_1=c_0\sqrt{\frac{d_0 T}{d_1 . 273}}$, in which d_1 is the density of the gas, d_0 the density of oxygen, and T the temperature in the absolute scale.

In the foregoing we have spoken of the velocity of the particles of a gas as if all the particles had the same velocity. This, however, cannot be the case, for even though the particles had the same velocity at the beginning of any time considered, the velocities of the individual particles would speedily assume different values owing to their encounters. It must be understood, therefore, that the velocity in the above formulæ means a certain average velocity, some of the particles having a greater and some a smaller speed than corresponds to this value. The bulk of the particles have velocities in the neighbourhood of this mean velocity, and the farther we diverge from the mean, the fewer particles we find possessing the divergent values.

If two different gases are brought together, their particles in virtue of their rapid motion in straight lines will soon leave their fellows and mix with the particles of the other gas. This process of intermixture we are acquainted with practically as **gaseous diffusion**. Two gases, no matter how different their densities may be, will mix uniformly if brought into the same space, but the rate of intermixture is very much slower than what we should expect from the rate at which the particles move. This discrepancy, however, may be easily explained. The particles in a gas at ordinary pressure are comparatively close together, and consequently encounter each other frequently; so that, though their rate of motion between individual encounters is very great, their path between points any distance apart is, owing to these encounters, a very long and irregular one, and the rate of mixing is therefore comparatively small. The relative rates at which gases diffuse in like circumstances are inversely proportional to the square roots of their

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[1] One gram weight is equal to 981 dynes.

densities—a result in accordance with the formula deduced above for the actual speeds of their molecules.

After the mixture of two gases has attained the same composition in every part, there is no further apparent change; but the motion of the particles, and thus the mixing process, is supposed to go on as before, only now the further mixing does not alter the composition.

The kinetic theory may be applied in a general way to the study of the processes of **evaporation and condensation.** In a liquid the particles have not the same independence and free path as gas particles, although they are in general identical with the gaseous molecules and have equal velocities. A gaseous substance, in virtue of the freedom of its molecules, can expand so as to fill any space offered to it. A liquid does not do so at low pressures, but retains its own proper volume, although its molecules still possess sufficient independence to move easily between collisions, and thus enable the liquid under the influence of gravitation to accommodate itself to the shape of the vessel containing it. In spite of the clinging together of the liquid molecules, it happens that some of them near the surface have sufficient motion to free themselves from their neighbours, and leaving the liquid altogether, to become free gas molecules. If these gas molecules move away unhindered, other molecules from the liquid will take their place; and so the liquid will go on giving off gas molecules until all has evaporated. If, however, the liquid is kept in a closed space, the gas molecules which leave its surface will be able to proceed no farther than the walls of this space, and must eventually return in the direction of the liquid. It will consequently happen that some of them will strike the surface of the liquid again and be retained by it. But the liquid molecules still continue as before to become gas molecules and leave the surface of the liquid, so that at one and the same time there are molecules entering and molecules leaving this surface. When in a given time as many molecules leave the liquid as are reabsorbed by it, no further apparent change takes place—the relative quantities of the liquid and the vapour remain the same. A stationary state of balance or equilibrium has thus set in, and we may now look at what determines this state.

The number of molecules leaving the liquid depends on the temperature, for it is only those molecules which attain a certain velocity that will succeed in freeing themselves; and the motion of the molecules of a liquid, like those of a gas, depends directly on the temperature. The number of the molecules reabsorbed by the liquid depends on the number of gas molecules striking the surface in a given time, *i.e.* on the number of molecules contained in a given space, and on their speed. As we have seen, this number and the speed together determine the pressure exerted by a gas, so the number of molecules reabsorbed depends on the pressure. Temperature thus regulates the number of molecules freed, and gaseous pressure the number of molecules bound in a given time; consequently for each state of equilibrium when these two numbers are equal, a definite temperature will correspond to a definite gaseous pressure of the vapour in contact with the liquid—or vapour pressure of the liquid, as it is shortly termed. Every liquid, therefore, has at each temperature a definite vapour pressure; and this vapour pressure increases as the temperature rises, for more molecules at the high temperature will have the speed necessary to free them. It may be noted that as it is the molecules with the greatest speed, *i.e.* with the highest temperature, that first leave the liquid, the average temperature of the liquid must sink as evaporation goes on, unless heat is supplied from an external source.

The kinetic theory not only gives us the ordinary gas laws, which are, strictly speaking, obeyed only by ideal gases and not by any actual gas, but also when properly applied affords us a probable explanation of the **deviations from the gas laws** which are experimentally found. So far, we have considered the gas molecules as mere physical points occupying no volume whatever; but certainly if gaseous particles are supposed to exist at all, they must be supposed to possess finite though small dimensions. It is evident that the volume in which these particles have to move is not the volume occupied by the whole gas, but this volume minus at least the volume of the particles. So long as the volume occupied by the gas is great and the pressure small, the volume of the particles vanishes in comparison with the total volume, and the gas laws are closely followed; but when the pressure is great and the total volume small, the volume of the particles themselves bears a considerable proportion to this whole, with the consequence that the divergence from the gas laws is great. Owing to this cause, the pressure would increase in a greater ratio than the volume would diminish, as the following reasoning will serve to show.

Suppose a molecule to be oscillating between two parallel walls in a direction at right angles to them, and suppose the distance between the walls to be equal to 100 times the diameter of the molecule. It is evident that the molecule from its contact with one wall has to travel, not 100 diameters before it comes in contact with the other, as it would have to do if it were a point without sensible dimensions, but only 99. It will therefore hit the walls oftener in a given time than if it were without sensible dimensions, and that in the ratio of 100 to 99. Now suppose the distance between the walls to be reduced to 10 molecular diameters. The particle has now only to travel 9 times its own diameter in order to pass from contact with the one wall to contact with the other. It will therefore in a given time hit the walls oftener in the ratio of 10 to 9, or 100 to 90, than if it were a mere point. By diminishing the distance of the walls to one-tenth, therefore, we have increased the pressure not to ten times the original value, but to this value multiplied by 99 : 90, *i.e.* the pressure has increased to eleven times its former magnitude.

We might now write the gas equation $pv = RT$ in the form

$$p(v - b) = RT,$$

where b is a constant for each gas depending on the magnitude of the molecules of the gas. But there is still another influence at work which interferes with simple obedience to the ideal gas laws. The particles of a liquid undoubtedly exercise a certain attraction on each other, and this attraction must still persist when the liquid particles have become particles of vapour, only in the latter case the particles are in general so far apart that the effect of the attraction is inconsiderable. If the gas is compressed into a smaller volume, however, the influence becomes felt more decidedly owing to the comparative proximity of the particles. Van der Waals has assumed that this attraction is proportional to the square of the density of the gas, or reciprocally proportional to the square of the volume. The effect of the mutual attraction of the particles is the same as if an additional pressure were put upon the gas, so that the correction is applied by adding it to the value of the external pressure. If a denotes the coefficient of attraction, *i.e.* the value of the attraction when the gas occupies unit volume, then the correction for any other volume is $\frac{a}{v^2}$. The equation for the behaviour of a gas under all conditions is, therefore, according to van der Waals,

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

This equation not only gives the behaviour of the so-called permanent gases very accurately up to high pressures, but even that of a comparatively compressible gas like ethylene. The following table gives the values of pv for ethylene at 20° actually found by Amagat, and those calculated from the equation

$$\left(p + \frac{0{\cdot}00786}{v^2}\right)(v - 0{\cdot}0024) = 1{\cdot}005441,$$

p being expressed in atmospheres, and v being made equal to 1 when $p = 1$.

p	1000 pv (observed).	1000 pv (calculated).
1	1000	1000
45·8	781	782
84·2	399	392
110·5	454	446
176·0	643	642
282·2	941	940
398·7	1248	1254

The agreement between the observed and calculated values is very satisfactory. If the gas were an ideal gas the values of *pv* would remain the same for all pressures. We see, however, that this constancy is far from being attained. The gas is at first more compressible than corresponds to Boyle's Law, and then at higher pressures less compressible, the minimum value of the product occurring when the pressure is about 80 atmospheres. From the form of the equation it may be seen that the two corrections act in opposite ways, the value of the product *pv* being diminished by the attraction, and increased by the finite dimensions of the molecules. At low pressures the effect of the attraction greatly overweighs the volume correction which in its turn becomes preponderant when the pressure reaches a high value and the total volume becomes small. With ethylene at the temperature considered, the two corrections balance each other at about 80 atmospheres, and here the gas within narrow limits of pressure obeys Boyle's Law, for the product *pv* then remains sensibly constant.

All gases hitherto investigated, with the exception of hydrogen and helium, give similar deviations from Boyle's Law: the product of pressure and volume at first diminishes, afterwards to increase as the pressure rises. At higher temperatures the deviations are of the same kind, but not so marked. This may be seen directly from the formula, the constants *a* and *b* being independent of the temperature, and the value of the expression on the right-hand side increasing in direct proportionality with the absolute temperature. In the case of hydrogen and helium there is no preliminary diminution of the value of *pv*, on account of the constant of attraction *a* being so small that its effect is counterbalanced from the first by the effect of the constant *b*.

Daniel Berthelot has developed a method whereby accurate molecular weights of gases may be ascertained from their densities without recourse being had to the results of analysis (cp. p. 14). He assumes that for *perfect* gases Avogadro's rule is *strictly* accurate, *i.e.* that the molecular weights of perfect gases would be exactly proportional to their densities, instead of being only approximately proportional as is the case for ordinary gases under ordinary conditions. Now, as we know, there are no perfect gases, but if the gases which actually exist are expanded so as to occupy a very large volume under a correspondingly small pressure, their deviation from "perfection" practically disappears, and the simple gas laws are strictly obeyed. If we could then compare the densities which existing gases possess under these circumstances, we should obtain numbers exactly proportional to their molecular weights, if Berthelot's assumption is correct. This, of course, we cannot do directly, but by means of the constants *a* and *b* of van der Waals's equation we can calculate the limiting density (at infinite expansion) of any gas whose density and compressibility have been investigated with sufficient accuracy under ordinary conditions, *i.e.* make allowance for its deviation from "perfection." Thus at the pressure of 1 atmosphere carbon dioxide is 1·38324 times as dense as oxygen—that is, if the molecular weight of oxygen is 32·000, the approximate molecular weight of carbon dioxide is 44·264. Now making use of the following data—

	a	b
Oxygen . .	0·001588	0·000828
Carbon dioxide .	0·009131	0·002427

Berthelot calculates that at infinite expansion carbon dioxide would be 1·3750 times as dense as oxygen, *i.e.* that its "true" molecular weight is 1·3750 × 32 = 44·000, which is in agreement with the best analytical data.

Proceeding in a similar way Berthelot has calculated the "true" molecular weights of a number of well-investigated gases, and has derived from them atomic weights which agree remarkably well with those determined by the analytical method. In particular he obtains for the atomic weight of hydrogen the number 1·0074 (cp. p. 19).

The equation of van der Waals is especially interesting in its application to the **continuous passage from the gaseous to the liquid state**, as it holds good not only for gases, but also in many ways for liquids. If we rearrange the equation so as to give coefficients of the powers of v, we obtain

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

This cubic equation has in general three solutions, so that for each value of p we have in general three corresponding values of v. The graph of the equation for constant values of a and b, and for various values of T, is given in Fig. 15. The isothermal curves thus obtained would represent the behaviour of a substance at various temperatures. The curves for the lower temperatures are wavy in form, and are cut by horizontal lines of constant pressure, sometimes in three points and sometimes in one. When the curve is cut by the horizontal line only once, the point of intersection gives the real solution of the equation, the other two solutions being imaginary. The resemblance of these curves to the curves on p. 82, which roughly express the result of actual experiment, is at once evident. In the case of the theoretical curves we have no sudden breaks such as we have in the actual discontinuous passage of vapour into liquid by increasing pressure. Van der Waals's equation assumes a continuous passage from the liquid to the vaporous state, and *vice versa*, such as we find when we take the temperature and pressure above their critical values for the substance under consideration. When the passage between the two states is discontinuous, as it usually is, we proceed along a horizontal line from one part of the theoretical curve to another, this line of constant pressure cutting the curve in three points. The volume of the substance as liquid is the least of the volumes corresponding to the constant pressure; another volume, the greatest, is the volume of the vapour derived from the liquid; the substance in a homogeneous state occupying the third intermediate volume is unknown. By studying supersaturated vapours and superheated liquids, we can advance along the theoretical curve for short distances beyond *B* and *C* without discontinuity, but the substance in these states is comparatively unstable. In the neighbourhood of the third volume the state of the substance is essentially unstable, increase of pressure being followed by increase of volume, and so we cannot hope to realise it. Van der Waals has pointed out, however, that in the surface layer of a liquid, where we have the peculiar phenomena of surface tension, it is possible that such unstable states exist, and that the passage from liquid to vapour may after all in the surface layer be really a continuous one.

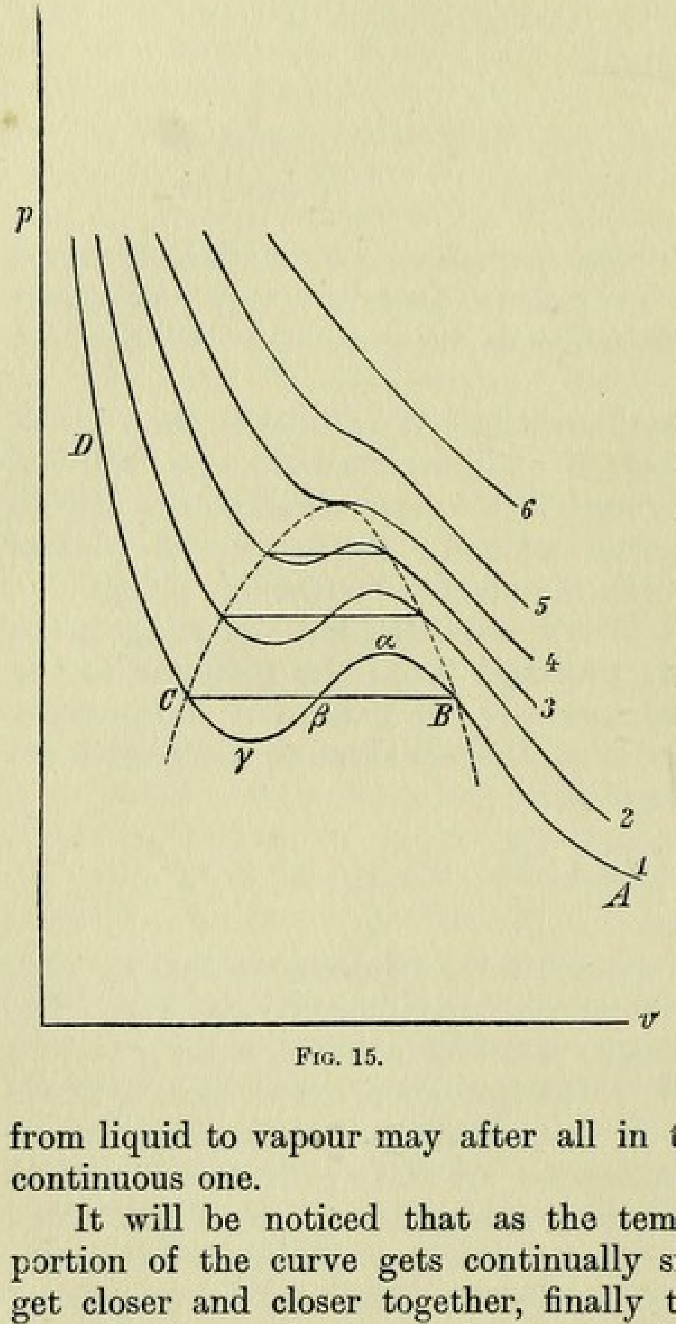

FIG. 15.

It will be noticed that as the temperature increases, the wavy portion of the curve gets continually smaller, and the three volumes get closer and closer together, finally to coalesce in a single point. Here the three solutions of the equation become identical, the volume of the liquid becomes equal to the volume of the substance as gas, and there is no longer any discontinuity or distinction between the liquid and gaseous states. In short, the substance at this point is in the critical condition: the curve is the curve of the critical temperature, the pressure is the critical pressure, and the volume is the critical volume.

When the three roots of a cubic equation become equal, certain relations exist between this triple root and the coefficients of the powers of the variable. If the equation is

$$x^3 - Ax^2 + Bx - C = 0,$$

and if the triple root is represented by ξ, the following relations hold good :—

$$3\xi = A\ ;\ 3\xi^2 = B\ ;\ \xi^3 = C.$$

In van der Waals's equation there are only the pressure and volume of the gas, the constants a and b, and the gas constant R. Now we can express the constant R in terms of the constants a and b as follows. Under normal conditions, let $p_0 = 1$, $v_0 = 1$, and $T_0 = 273$. Then the equation

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

becomes

$$(1 + a)(1 - b) = 273R$$

whence

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

or, if we make $\frac{1}{273} = \beta$, the coefficient of expansion, we have

$$R = \beta(1 + a)(1 - b).$$

Van der Waals's equation then becomes (cp. p. 97)

$$v^3 - \left(b + \frac{\beta T(1 + a)(1 - b)}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0.$$

If we denote now by ϕ, π, and θ the critical values of v, p, and T respectively, we obtain for the critical equation, in which the three roots become identical,

$$3\phi = b + \frac{\beta\theta(1 + a)(1 - b)}{\pi},$$

$$3\phi^2 = \frac{a}{\pi},$$

$$\phi^3 = \frac{ab}{\pi}\ ;$$

whence

$$\phi = 3b \text{ (critical volume)},$$

$$\pi = \frac{a}{27b^2} \text{ (critical pressure)},$$

$$\theta = \frac{8a}{27\beta b(1 + a)(1 - b)} \text{ (critical temperature)}.$$

Here we have general expressions for the critical values of a substance in terms of the constants which express the deviation of the substance from the laws for ideal gases; and conversely we can give the numerical values of these constants from the values of the critical data, viz.—

$$b = \frac{\phi}{3},$$
$$a = 3\pi\phi^2.$$

These relations have been tested in several cases, and a fair approximation of the calculated to the observed values has been found.

If in van der Waals's equation we express the values of the pressure, temperature, and volume as fractions of the corresponding critical values, and at the same time express these latter in terms of the deviation constants, the equation becomes

$$\left(\epsilon + \frac{3}{n^2}\right)(3n - 1) = 8m,$$

in which
$$\epsilon = \frac{p}{\pi};\ n = \frac{v}{\phi};\ m = \frac{T}{\theta}.$$

Here everything connected with the individual nature of the substance has disappeared, and we have an equation which applies under certain restrictions to all substances in the liquid or gaseous state, just as the gas equation holds good for all gases, independently of their specific nature.

The chief point to be noted here is that whereas for gases the temperature, pressure, and volume may be measured in the ordinary units without impairing the validity of the comparison of different gases, it is necessary in the case of liquids to effect the comparison under "corresponding" conditions, the temperatures of the two liquids to be compared being, for instance, not equal on the thermometric scale, but being equal fractions of the critical temperatures of the two substances.

It is one of the tasks of physical chemistry to compare the physical properties of different substances, and to trace, if possible, some connection between their magnitude and the chemical constitution of the substances considered. Now we know that most physical properties of substances vary with the temperature and pressure. The question therefore arises: At what temperature and pressure are we to compare the properties of different substances? It is evidently purely arbitrary to make the comparison at the so-called normal conditions of 0° and 760 mm., for these conditions have no relation whatever to the properties of the substances themselves, and are merely chosen for convenience' sake as being easily attainable in the circumstances in which we work. Van der Waals answers the question by saying that the properties ought to be compared at corresponding temperatures and pressures, meaning thereby at temperatures and pressures which are equal fractions of the critical values in the absolute scale. Suppose, for example, we were to compare ether and alcohol with respect to some particular property. The critical temperature of ether is 194° C., or 467 absolute; that of alcohol is 243° C., or 516 absolute. Let the property for the alcohol be measured at 60° C., then we shall have as the corresponding temperature x for ether $\frac{273+x}{467}=\frac{273+60}{516}$ or $x = 28°$ C. The pressure when small has not, as a rule, a great effect on the properties of liquids, so that in general we may make the comparison at the atmospheric pressure without committing any serious error. It should, however, be stated at once that the data for the comparison of different substances under corresponding conditions are for the most part still wanting, so that it is not known whether the theoretical conditions would lead to sensibly greater regularities than those observed among the properties when measured under more usual conditions.

The kinetic theory affords also some account of the phenomena of **solution**. If we take the case, for example, of the solution of a gas in a liquid, we can easily see that the gas molecules impinging on the surface of the liquid may be held there by the attraction of the molecules of the solvent. When, however, a number of the gas molecules have accumulated in the liquid, some of them, in virtue of their motion, will fly out from the surface of the solution, and this will happen the more frequently the more molecules there are dissolved in the liquid. But as the number of gas molecules striking the surface of the liquid remains constant at constant pressure, it will at last come to pass that the number of molecules entering and leaving the liquid will be the same. There is then equilibrium, and the liquid is saturated with the gas. As the number of gas molecules striking the liquid surface is proportional to the pressure, the number of molecules leaving that surface when the liquid is saturated, and consequently the number of molecules dissolved in the liquid, is likewise proportional to the pressure. This is Henry's Law, and Dalton's Law also follows at once; for in a gaseous mixture the number of molecules of each gas striking the surface is proportional to its partial pressure in the mixture, and independent of the other components. It will be seen from this explanation that there is a great similarity between the solution of a gas in a liquid and the phenomena of evaporation and condensation.

The same analogy appears when we consider the solution of a solid. When a soluble crystalline substance is introduced into a solvent, some of its particles become detached and enter the solvent. After a time certain of these detached particles come into contact with the solid again, and are retained by it. This give-and-take process goes on until the same number of particles leave the solid and return to it in a given time. No further apparent change then takes place, and the solution is saturated. The number of particles which return to the solid evidently depends on the number of them in unit volume of the solution, *i.e.* on the strength or concentration of the solution. If the solid is brought into contact with a stronger solution than the above, more particles will enter the crystal than will leave it, and so the crystal will increase in size. Such a solution is supersaturated with regard to the solid. In a weaker solution, fewer particles will come into contact with the solid and be retained by it than will leave it, *i.e.* the solution is unsaturated and the crystal will dissolve, in part at least.

In the chapter on evaporation and condensation we had occasion to refer to the vapour tension of liquids, meaning thereby the tendency of the liquids to pass into vapour under the specified conditions. There is equilibrium when the vapour tension of the liquid is balanced by the gaseous pressure of the vapour above the liquid. A similar term has been employed to express the tendency of a substance to pass into solution, the substance having a definite **solution tension** for each solvent it is brought into contact with. When the pressure of the dissolved substance in the solution is equal to the solution tension of the solid there is equilibrium. Here a new conception is introduced, namely, the pressure of a substance in solution. What this pressure is, and how it may be measured, will be seen in Chapter XVI.

A brief account of the Kinetic Theory will be found in

CLERK-MAXWELL, *Theory of Heat*, chap. xxii.

The student is also recommended to read, in connection with this chapter,

J. P. KUENEN, on "Condensation and Critical Phenomena," *Science Progress*, New Series, 1897, vol. **1**, p. 202 and p. 258.

DANIEL BERTHELOT gives an account of his method for molecular weights of gases in several papers in *Comptes rendus*, 1898, vol. **126**.

CHAPTER XI

THE PHASE RULE

A SUBSTANCE is in general capable of existing in more than one modification. For example, water may exist as ice, as liquid water, or as water vapour. Sulphur exists as vapour, liquid, and as two distinct solids, namely, as monoclinic and as rhombic sulphur. Para-azoxyanisole, as we have seen, forms not only solid and gaseous modifications, but can also exist as a crystalline liquid distinct from the ordinary non-crystalline liquid. All such modifications, when they exist together, are mechanically separable from each other, and are in this connection called **phases**. A single substance may assume the form of many different phases, but these phases cannot in general all exist together in stable equilibrium, being subject to certain restrictions regulating their coexistence, which may be stated in the form of definite rules.

As a familiar example we shall take the substance water in the three phases—ice, water, and vapour. The physical conditions determining the equilibrium of these phases are temperature and pressure. We know that at the pressure of 1 atmosphere, water is in equilibrium with ice at the temperature of zero centigrade, and with water vapour at the temperature of 100° centigrade. For a given pressure, then, there is a definite temperature of equilibrium between such a pair of phases; and we shall also find that for a definite temperature there is a definite equilibrium pressure. Consider the two phases, water and water vapour. To each temperature there corresponds a fixed vapour pressure, which is the pressure of water vapour, or the gaseous phase, which is in equilibrium with the water or liquid phase. By drawing the pressure-temperature diagram, therefore, of a substance, we are enabled to study conveniently the equilibrium between its phases.

In Fig. 16 the line OA represents the vapour-pressure curve of water, each point on the line corresponding to a certain pressure measured on the vertical axis, and to a certain temperature measured on the horizontal axis. For the sake of clearness, the curves in the diagram have all been drawn as straight lines. Ice, like water, has a vapour-pressure curve of its own, and this has been represented in the diagram by the line OB. It will be observed that the two vapour-pressure curves have not been represented as one continuous line, but as two lines intersecting at a point O. If we inquire into the meaning of this intersection, as interpreted from the diagram, we find that at a certain temperature *t* ice and water have the same vapour pressure, for the point O corresponding to this temperature belongs both to the vapour-pressure curve of water and the vapour-pressure curve of ice. It is easy now to show that there is in fact a temperature at which the vapour pressures of ice and water are identical. Water at its freezing point is in equilibrium with ice, *i.e.* ice and water can coexist at this temperature in any proportions whatever, and these proportions will remain unchanged if the mixture is surrounded only by objects of this same temperature. Now let the water and ice coexist, not, as is usual, under the pressure of one atmosphere, but under the pressure of their own vapour. The temperature of coexistence will no longer be exactly 0°, but a temperature very slightly higher; otherwise the conditions are unchanged. If the ice, at this equilibrium temperature between ice and water, have a vapour pressure higher than that of water at the same temperature, diffusion will tend to bring about equalisation of pressure, *i.e.* the pressure of vapour over the ice will become less than its own vapour pressure, so that the ice will evaporate; and the pressure of vapour over the water will become greater than its own vapour pressure, so that water will be formed by condensation. Ice will have

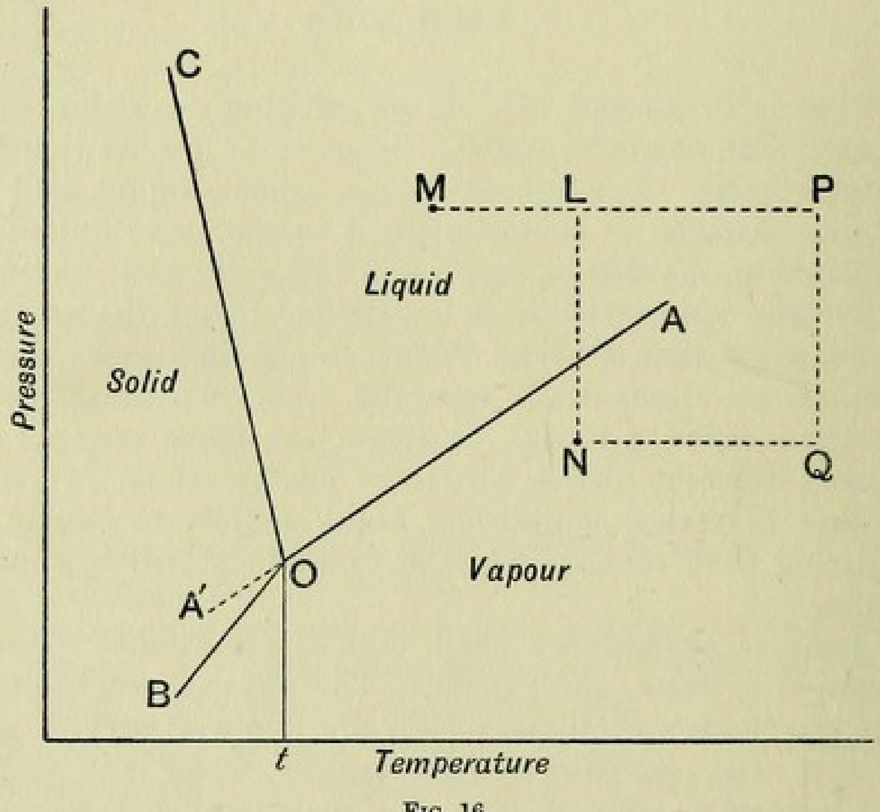

Fig. 16.

therefore been converted into water, which is contrary to our original assumption that the proportions of water and ice present are not under the circumstances subject to alteration Similarly, if water at the equilibrium temperature had a greater vapour pressure than ice, ice would be formed indirectly through the vapour phase at the expense of the liquid water, so that our assumption in this case also would be contradicted. There only remains, then, the alternative that the vapour pressures of ice and water are equal when the ice and water are in equilibrium, which is in accordance with the representation of the diagram. At any point on the line OA water and water vapour can coexist in equilibrium, at any point on the line OB ice and water vapour can coexist. At the point O, where these two lines intersect, all three phases can exist together in equilibrium, and such a point is therefore called a **triple point.**

When a substance can only exist in three phases, only one triple point is possible. The triple point in the case of water is not quite identical with the melting point of ice, because the melting point is, strictly speaking, defined as the temperature at which the solid and liquid are in equilibrium when the pressure upon them is equal to one atmosphere. At the triple point the pressure is not equal to the atmospheric pressure of 760 mm. but to the vapour pressure of ice or water, which is only 4 mm. Now, it has been shown, both theoretically (cp. Chap. XXVIII.) and experimentally, that pressure lowers the equilibrium temperature of ice and water by about 0·007° per atmosphere, so that the freezing point under atmospheric pressure is about 0·007° lower than the triple point. The effect of pressure on the melting point of ice may be represented in the diagram by the line OC, inclined from the triple point towards the pressure axis. At any point on this line, ice and water are in equilibrium with each other, the temperature of equilibrium falling with increase of pressure.

The diagram for equilibrium of the three phases of water consists therefore of three curves meeting in a point, the triple point. At any other point on the curves, two phases can coexist in equilibrium :—

(*a*) Water and water vapour on OA ;
(*b*) Ice and water vapour on OB ;
(*c*) Water and ice on OC.

At O, the common point of intersection, all three phases are in equilibrium together. The three lines divide the whole field of the diagram into three regions. At pressures and temperatures represented by any point in the region AOB water can only exist permanently in the state of vapour. At any point in the region AOC it can only exist as liquid water, and at any point in the region BOC it only exists as ice. The curve OA separates the region of liquid from the region of vapour, but the separation is not complete. The curve is the curve of vapour pressures, and, as we have already seen, there is a limiting pressure beyond which the vapour pressure of a liquid cannot rise. This is the critical pressure of the substance, and it is attained at the critical temperature. The curve OA, therefore, ceases abruptly at a point A, the values of the pressure and temperature at which are the critical values. Beyond A there is no distinction between liquid and vapour; the two phases have become identical.

It is possible to pass from a point M in the liquid region to a point N in the gaseous region in an infinite number of ways, which may be represented on the diagram by straight or curved lines. If these lines cut the line OA, there is discontinuity in the passage, for at the pressure and temperature represented by the point of intersection the two phases will coexist. For example, we may pass from M to N, by means of lines parallel to the axes, along the path MLN. The line ML represents increase of temperature at constant pressure; the line LN diminution of pressure at constant temperature. The pressure at L is greater than the vapour pressure of the liquid at the constant temperature considered, and so the substance exists at this point as liquid only. As the pressure is gradually released, a point is at last reached at which it is exactly equal to the vapour pressure of the liquid. The liquid now begins to evaporate, and the two phases exist together, the point at which this occurs being the point of intersection of LN with OA. No further reduction of pressure can be effected until all the liquid has been converted into vapour, after which the pressure may be diminished until it attains the value represented by the point N. If, on the other hand, we follow the line MPQN, which does not cut the line OA, we can pass from the state of liquid at M to the state of vapour at N without any discontinuity whatever. We first increase the temperature, following the line MLP, to a value above the critical temperature, the pressure being all the time above the critical value. This takes us into the region where there is no distinction between liquid and vapour, so that by first reducing the pressure and then lowering the temperature we pass without any break to a substance in the truly vaporous state at N, the substance at no time having been in the state of two distinct phases.

In what has been said above as to the condition of the substance in the various regions of the diagram, it has been assumed that stable states only are under consideration. If we disregard this restriction, then we may have, for example, liquid water in the region BOC, for water may easily be cooled below its freezing point without actually freezing, and exist as liquid at points to the left of O. Such supercooled water has a vapour-pressure curve which is the continuation of the curve OA, and has been represented in the diagram by the dotted line OA′. This curve lies above the vapour-pressure curve for ice, so that at any given temperature below the freezing point the vapour pressure of the supercooled liquid is greater than the vapour pressure of the solid. This rule holds good for all substances, and we find in general that the vapour pressure of the stable phase is less than the vapour pressure of the unstable phase.

It should be noted that the instability in such examples is only relative. A supercooled liquid may be kept for a very long time without any solid appearing (cp. Chap. VIII.), but as soon as the smallest particle of the substance in the more stable solid phase is introduced, the less stable, or, as it has been called, the **metastable** phase is transformed into it. That the metastable substance should have a higher vapour pressure than the stable substance is not surprising, if we consider that the phase of higher vapour pressure will always tend to pass into the phase of lower vapour pressure when the two substances are allowed to evaporate into the same space, although they are not themselves in contact. The vapour of the substance of higher vapour pressure will on account of that higher pressure diffuse towards the substance of lower vapour pressure and there condense. More of the metastable phase will then evaporate in order to restore equilibrium between itself and the vapour, with the result that there will again be diffusion and condensation on the stable phase until all the metastable phase has been thus indirectly converted by evaporation into the stable phase. The vapour at pressures and temperatures represented by points on the line OA′ is in an unstable state with regard to the solid ice, being supersaturated, although it is only saturated with regard to the supercooled liquid. It is likewise possible to supersaturate vapour at temperatures above the freezing point, *i.e.* to have the substance in the state of vapour in the region COA; and also to have a liquid substance in the region AO*t* by superheating. Water, for example, if free from dissolved gases, may be heated to 200° or over at the atmospheric pressure without boiling. It has always been found impossible, on the other hand, to heat a solid above its melting point. Water in the form of ice has never been observed in the region COA.

We shall next proceed to the consideration of a substance capable of existence in more than three phases, taking sulphur as our example. Here we have not only the liquid and vaporous phases, but the two solid phases of rhombic and monoclinic sulphur. Rhombic sulphur is the crystalline modification usually met with, and this on heating rapidly melts at 115°. If we keep it at a temperature of 100,° however, for a considerable time, we find that it becomes converted into the other modification, monoclinic sulphur. This latter on heating does not melt at 115° but at 120°, in accordance with the general rule that each crystalline modification of a substance has its own melting point. If the monoclinic sulphur be cooled to the ordinary temperature, it gradually passes again into the rhombic modification. We should be inclined, therefore, to say that at the ordinary temperature rhombic sulphur is in a stable state, while monoclinic sulphur is in a metastable condition. At 100° the reverse is the case: here monoclinic sulphur is the stable variety, and rhombic sulphur the metastable variety.

We have seen that in the case of solid and liquid there is a temperature at which both phases are stable together, namely, the melting point. Above or below this temperature only one of the phases is stable. We should therefore expect by analogy that there is a temperature at which the two solid phases of sulphur should be equally stable, *i.e.* should be able to coexist without any tendency of the one to be converted into the other. Careful experiment has revealed such a temperature. At 95·6°, the **transition or inversion temperature,** both rhombic and monoclinic sulphur are stable, and can exist either separately or mixed together in any proportions. Below this temperature the monoclinic phase gradually passes into the rhombic phase; above it, the rhombic phase gradually passes into the monoclinic. A transition temperature of this sort is then quite comparable to a melting point, the chief difference being that while a solid can never be heated above its melting point without actually fusing, a substance like rhombic sulphur may be heated above its transition point without undergoing transformation. It is thus possible to investigate the properties of rhombic sulphur up to its melting point, 115°, although between 95·6° and that temperature it is in a metastable condition, and is apt to suffer transformation into the stable monoclinic modification. The transition point, like the melting point, is affected by pressure, and in the case of sulphur increase of pressure has the effect of raising the transition temperature.

The transition point of sulphur is most easily determined by means of the change in density which occurs when the sulphur passes from one crystalline modification to the other. The instrument employed is termed a **dilatometer,** and resembles in construction a thermometer with a large bulb, which is made to contain a mixture of the two kinds of crystals together with a suitable liquid (best one in which the substance is slightly soluble). If the dilatometer is immersed in a bath whose temperature is constant and slightly above the inversion point, the liquid in the capillary will rise owing to the monoclinic sulphur which is formed having a larger volume than the rhombic sulphur from which it was produced. If, on the other hand, the dilatometer is immersed in a bath whose temperature is slightly below the inversion point, the level of the liquid will slowly fall owing to the reverse transformation. Thus at 96·1° a slow rise was observed in the case of sulphur, and at 95·1° a slow fall. It was therefore concluded that the transition point is intermediate between these two temperatures, say 95·6°. With some substances the transition takes place so slowly that many hours, or even days, must elapse before it can be determined with certainty if expansion or contraction is taking place. This dilatometric method is very generally available, but may be supplemented by vapour pressure or solubility determinations, the temperature at which the two phases have the same vapour pressure or the same solubility being the transition point (p. 115).

The transition phenomena may be represented diagrammatically by means of temperature-pressure curves (Fig. 17). The line OB in the figure represents the vapour-pressure curve of rhombic sulphur; OA is the vapour-pressure curve of monoclinic sulphur. These vapour-pressure curves must meet at the transition point, for at that temperature both modifications are equally stable and must have the same vapour pressure. Below that temperature the vapour pressure of the metastable monoclinic phase must be greater than that of the stable rhombic phase. The line OA′, therefore, which is the prolongation of the line OA, represents the vapour-pressure curve of monoclinic sulphur below the transition point. Above 95·6° rhombic sulphur is the metastable phase, and consequently has the greater vapour pressure. This is represented in the diagram by the dotted line OB′, which is the continuation of the line OB. The line OC gives the effect of pressure on the transition point, sloping upwards away from the pressure axis in order to represent rise of transition point with rise of pressure. The point O thus corresponds very closely to the point O of Fig. 16, being like it a triple point at which there is stable equilibrium of three phases, viz. rhombic, monoclinic, and gaseous.

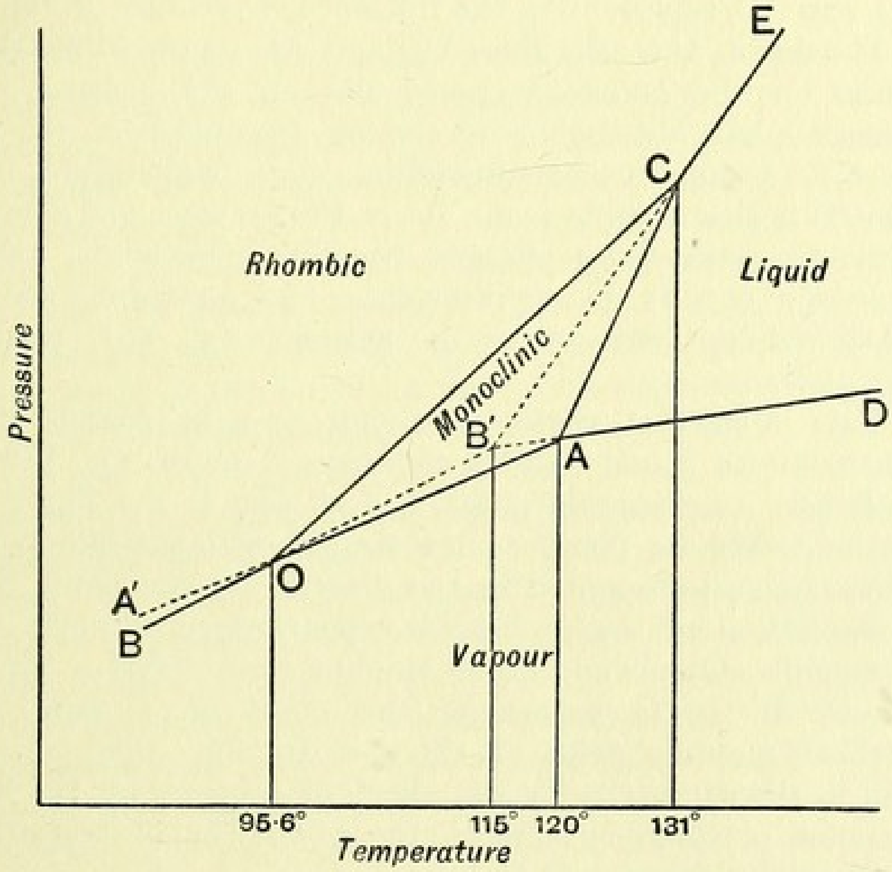

Fig. 17.[1]

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[1] The point C in the actual diagram would lie very much higher than is here represented.

The lines OA, OB, and OC diverging from O represent as before the conditions of equilibrium between pairs of phases, and the dotted lines OA′ and OB′ similar conditions in metastable regions.

It has been already stated that monoclinic sulphur melts at 120°. At this point also a triple point must exist, for here monoclinic sulphur, liquid sulphur, and sulphur vapour are in equilibrium. The melting point of monoclinic sulphur is raised by pressure, instead of being lowered, as is the case with water. We have therefore three curves intersecting at A, namely, OA, representing the vapour pressure of monoclinic sulphur; AD, representing the vapour pressure of liquid sulphur; and AC, representing the influence of pressure on the melting point. It happens that the lines OC and AC representing the effect of pressure on the transition point and on the melting point of monoclinic sulphur, although both sloping upwards from the pressure axis, meet at a point C, corresponding to a temperature of 131°. This point C is also a triple point, for at the pressure and temperature which it represents, three phases—rhombic, monoclinic, and liquid sulphur—can coexist in equilibrium. At pressures above this, monoclinic sulphur has no stable existence at any temperature whatever.

We have seen that rhombic sulphur may be heated above its transition point to a temperature at which it melts, viz. 115°. The rhombic is here a metastable phase, and so also is the liquid formed by its fusion. We are therefore now dealing with a triple point in a metastable region, represented in the diagram by the point B′, which is the intersection of the prolonged vapour-pressure curves OB and DA for rhombic sulphur and liquid sulphur respectively. The dotted curve from B′ to C represents the effect of pressure on the "metastable" melting point of rhombic sulphur, this curve being continued in the curve CE for the effect of pressure on the "stable" melting point of rhombic sulphur, the possibility of transition into monoclinic sulphur ceasing at C.

The chief features of the diagram may thus be represented as follows, metastable conditions being enclosed in brackets :—

REGIONS—DIVARIANT SYSTEMS.

BOCE	Rhombic
ECAD	Liquid
BOAD	Vapour
OCA	Monoclinic

CURVES—MONOVARIANT SYSTEMS.

BO, (OB′)	Rhombic, vapour
OA, (OA′)	Monoclinic, vapour
AD, (AB′)	Liquid, vapour
OC	Rhombic, monoclinic
AC	Liquid, monoclinic
CE, (CB′)	Rhombic, liquid

TRIPLE POINTS—NONVARIANT SYSTEMS.

O	Rhombic, monoclinic, vapour
A	Monoclinic, liquid, vapour
C	Rhombic, monoclinic, liquid
(B′)	(Rhombic, liquid, vapour)

Monoclinic sulphur offers the peculiarity that its range of existence is limited on all sides. It can only exist in the stable condition between certain temperatures and certain pressures, the extreme limits being given by the temperature and pressure values at O and C.

Diagrams similar to the sulphur diagram can be drawn for most other substances that exist in more than one crystalline modification. For example, para-azoxyanisole yields a similar figure, although one of the crystalline modifications is in this case a liquid. The two chief triple points are here the points at which the solid crystal passes into the liquid crystal, and where the liquid crystal passes into an ordinary liquid. The first point is usually spoken of as the "melting point" of the substance, and the second as its transition point. These points therefore occur in the reverse order to the corresponding points for sulphur, but otherwise the diagram is much the same.

In the case of a single substance, there is only one point, the triple point, at which any three phases can exist together. On this account, a system consisting of three phases of a single substance is called a nonvariant system, for if we change any of the conditions—here temperature or pressure—one or more of the phases will cease to exist. When the system consists of two phases, it is said to be monovariant, there being for each temperature one pressure, and for each pressure one temperature, at which there is equilibrium. When the system consists of only one phase, it is said to be divariant, for within certain limits both the temperature and the pressure may be changed arbitrarily and independently. The regions in the diagram therefore correspond to divariant systems; the curves to monovariant systems; and the triple points to nonvariant systems.

When the systems considered contain two distinct components, say salt and water, and not one, as in the preceding instances, the phenomena become more complicated; for here, besides temperature and pressure, we have a third condition, viz. concentration, entering into the determination of phases. The liquid phase, for example, may be pure water, or it may be a salt solution of any concentration up to saturation. The **phase rule** developed by Willard Gibbs furnishes us, however, with general methods for treating such systems theoretically. It states, for instance, that if the number of phases exceeds the number of components by 2, the system is **nonvariant**. As we have seen, this is true for one component, and it is equally true for two components. With the components salt and water we have a nonvariant system when the four phases, salt, ice, saturated solution, and vapour, coexist. There is only one temperature, one pressure, and one concentration at which the equilibrium of these four phases can take place; the point at which these particular values are assumed is called a quadruple point, and it coincides practically with what we have hitherto called the cryohydric point (cp. p. 69).

Again, the phase rule states that if the number of phases exceeds the number of components by 1, the system is **monovariant**. If, therefore, there are three phases with the components salt and water, a monovariant system will result. Suppose the phases are salt, solution, and water vapour. If we fix one of the conditions, say the temperature, the other conditions adjust themselves to certain definite values. At the given temperature, the salt solution assumes a definite concentration, viz. that of the saturated solution. This solution of definite concentration has a definite vapour pressure, less than that of pure water. By fixing the temperature, therefore, we also fix the concentration and the pressure. Suppose, again, that the three phases are ice, salt solution, and water vapour. Let the concentration of the solution be fixed, and it will be seen that the temperature and pressure adjust themselves to definite values. First, a solution of the given concentration can only be in equilibrium with ice at a certain temperature fixed by the rule for the lowering of the freezing point in salt solutions (cp. p. 67). At this temperature the solution being of a fixed concentration will have a vapour pressure defined by the law of the lowering of vapour pressure in solutions. By fixing the concentration, therefore, we likewise fix the temperature and pressure of equilibrium.

If the number of phases is equal to the number of components, the phase rule states that the system is **divariant**. Let the two phases in our example with two components be salt and solution, and let the temperature be fixed. The pressure and concentration are no longer fixed as in the last case, but may vary in such a way that a given variation in the pressure produces a concomitant variation in the concentration of the saturated solution. It is necessary, of course, that the pressure should be above a certain limiting value in order that the third phase, of vapour, should not appear. That the concentration of the saturated solution, *i.e.* the solubility of the salt, changes with the pressure has been experimentally ascertained in a number of cases. Sometimes the solubility increases with pressure, sometimes it diminishes, according as the volume of the solution is less or greater than the volume of the solvent and dissolved substances separately. If the two phases considered be salt-solution and vapour, it is obvious that although the pressure is fixed, the concentration and the temperature are not thereby defined. An increase of concentration will counteract the effect of a rise in the temperature, so that concentration and temperature may be made to undergo concomitant variations even though the pressure remains constant.

If the number of phases is less than the number of components by 1, the system is then, according to the phase rule, **trivariant**. In the case of two components, the trivariant system has only one phase, and with our example of salt and water, the salt solution may be taken as the most representative phase, since it contains both components. If the temperature and pressure are both fixed, we are still at liberty to vary the concentration as we choose, *i.e.* a change of pressure at the fixed temperature causes no concomitant change in the concentration. Here, then, we meet with the greatest degree of freedom in varying the conditions in the case of two components, as we cannot reduce the number of phases further.

An instructive exemplification of the phase rule is afforded by the distillation of two partially miscible liquids. It has been stated on p. 87 that when a mixture of such liquids is distilled, a distillate of definite composition is obtained as long as two separate layers are present, the composition of the layers themselves remaining unaltered. When one of the layers vanishes, the composition of both residue and distillate varies continuously. In the first case, where we have two liquid phases and one vaporous phase, the number of phases exceeds the number of components by 1, so that the system is monovariant. Consequently if we fix the pressure at the atmospheric value, the temperature of the equilibrium and the concentrations of the three phases are also fixed. The constant temperature is the constant boiling point of the mixture, and the vapour has a constant composition, as have also the two layers of liquid. As the distillation progresses the only change that occurs is in the proportions in which the three phases are present. If one of the layers of liquid disappears before the other, which will in general happen if the distillation is continued, the number of phases becomes equal to the number of components, and the system is divariant. Fixing the pressure therefore no longer involves a fixed temperature and fixed concentrations : these are now subject to variation. The variations of the different magnitudes are however not independent, but concomitant, definite compositions of vapour and liquid corresponding to each temperature.

With two components we sometimes get diagrams for melting and transition points which closely resemble those obtained for one component, when instead of pressure we substitute concentration and neglect pressure altogether. Thus with the two components paratoluidine and water, we may draw the following diagram (Fig. 18). On the vertical axis concentrations are measured instead of pressures, and on the horizontal axis temperatures are plotted as before.

The line BO represents the concentrations of the solutions in equilibrium with solid paratoluidine at different temperatures, *i.e.* it is the solubility curve of solid paratoluidine in water. Under water, paratoluidine melts at about 44·2°, slightly lower than the temperature of fusion of the dry substance.[1]

If we heat the system above this temperature, the solid phase disappears, and a liquid phase takes its place. Now, the liquid phase has its own solubility curve LO, and this must cut the solubility curve of the solid at the point at which the solid melts. This can be shown in the same way as that adopted to prove that water and ice have the same vapour pressure at the melting point, by substituting in this case solubility for vapour pressure. In general, we may say that if two phases are in equilibrium with each other, and one of them is in equilibrium with a third phase, then the second of the original pair will also be in equilibrium with the third phase. We see that there is thus considerable resemblance between the melting point of a substance under its own saturated vapour and the melting point of a substance under its own saturated solution. If we bear in mind that concentration of a solution corresponds to pressure of a gas (Chap. XVI.), the reason for the resemblance of the solubility and pressure diagrams becomes apparent.

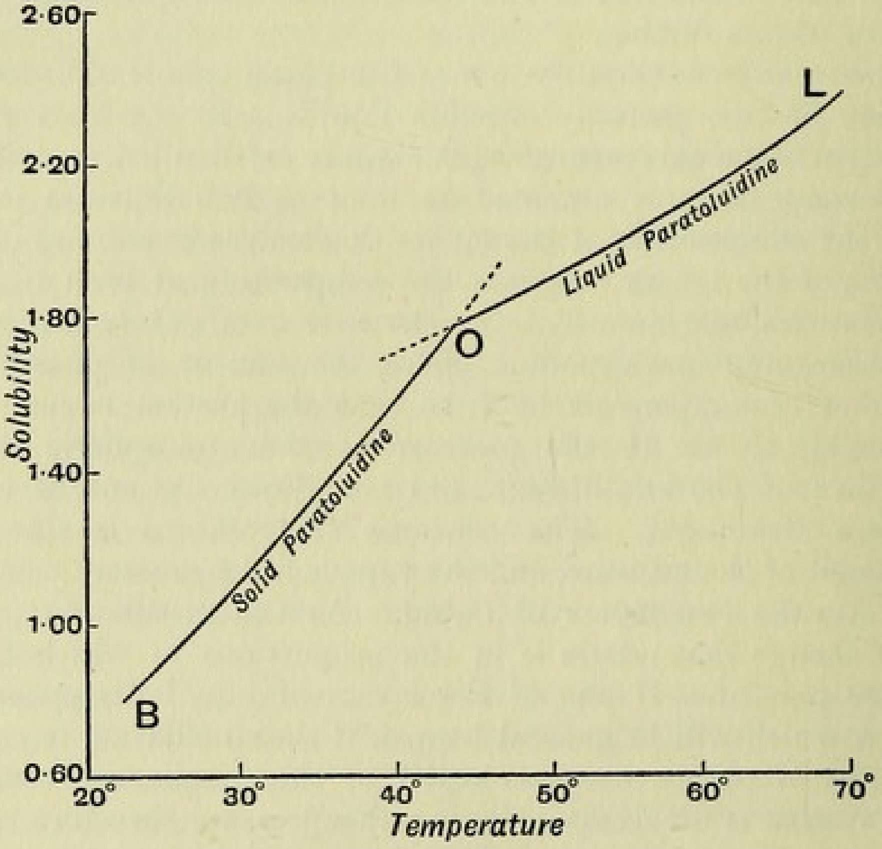

Fig. 18.

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[1] The reason for the lower melting point of paratoluidine under water is evident. Any substance soluble in water dissolves, when melted under its aqueous solution, a portion of the water with which it is in contact. The solid paratoluidine is thus not in equilibrium with pure fused paratoluidine, for which the fusing point is highest (cp. p. 73), but with a solution of water in paratoluidine.

The similarity is also observable in the case of transition points. If we consider the two components, sulphur and an organic liquid capable of dissolving it, the general rule referred to in the preceding paragraph teaches us that at the transition point of rhombic and monoclinic sulphur the solubility of rhombic and monoclinic modifications in the solvent must be the same. For if a certain solution is in equilibrium with one of the modifications, it must be in equilibrium with the second also, since at the transition point the two modifications are in equilibrium with each other. We may say shortly, therefore, that the vapour-pressure curves and the solubility curves of two modifications of the same substance cut at the transition point. This actually gives us in some cases a practical method of determining the transition point. Sometimes the transition of one modification into the other proceeds with such extreme slowness that it is almost impossible to observe the transition temperature directly. If, however, we investigate carefully the vapour pressures or the solubilities of the two modifications at different temperatures, we can construct curves of vapour pressure or solubility; these curves will be found to intersect, and the point of intersection may be taken as the point of transition.

Hydrated salts present many interesting aspects when viewed from the standpoint of the phase rule. The components here are the anhydrous salt and water, and the number of phases which they form may be very great, each solid hydrate being a phase distinct from the others. Let us take as our first example sodium sulphate in the form of the decahydrate $Na_2SO_4, 10H_2O$, and the anhydrous salt Na_2SO_4. The solubility curves of these solids have been already given on p. 54, the concentrations being referred to the two components, anhydrous salt and water. The two solubility curves intersect at 33°, *i.e.* the two solids are at that temperature in equilibrium with the same solution. They must, therefore, according to the rule already given, be in equilibrium with each other, *i.e.* 33° is the temperature of transition of the decahydrate phase into the anhydrous phase. This may be confirmed directly by heating the decahydrate alone. At 33° it melts, but the fusion is not complete, for besides the liquid phase, a new solid phase, the anhydrous salt, comes into existence. We have therefore at 33° the four phases of decahydrate, anhydrous salt, saturated solution, and water vapour, all in equilibrium. This point is thus a quadruple point, and as the system consists of two components and four phases, it is nonvariant. Consequently, if we alter the temperature, pressure of vapour, or the concentration of the solution, the equilibrium will be disturbed. If the alteration is only slight and temporary, the equilibrium will re-establish itself; if the alteration is permanent, some of the phases will disappear.

Many instances like the above are known. The essential feature is that one hydrate loses water, forming a solution and a lower hydrate or anhydrous salt. When this is the case there is a definite transition temperature from one hydrate to the other, the higher hydrate, *i.e.* that with the greater amount of water of crystallisation, existing below the transition temperature, and the lower hydrate above this point.

Sometimes a hydrate on being heated melts without separation of a new solid phase. An example of this kind is to be found in the ordinary yellow hydrate of **ferric chloride,** $Fe_2Cl_6, 12H_2O$, already referred to on page 72. This hydrate on heating melts completely at 37°, the liquid having the same composition as the solid. Here, then, we are dealing with a melting point in the ordinary sense, the three phases of solid, liquid, and vapour existing together. If the system consisted of only one component, the number of phases at the melting point would exceed the number of components by 2, and the system would be nonvariant. But the number of components is 2, and the number of phases at the melting point exceeds the number of components by 1 only, so that the system is monovariant according to the phase rule. This is as much as to say that we are not fixed down to absolutely definite values of temperature, pressure, and concentration for the equilibrium of the solid, liquid, and vaporous phases, but may alter any one of these conditions within limits, the alteration of one being attended by concomitant alterations in the two other factors. For example, we may change the concentration of the liquid by adding one or other of the components to it. Such a change in the composition of the liquid phase will bring about a certain definite change in the temperature of equilibrium and in the vapour pressure. If, on the other hand, we alter the temperature, it will be found that the vapour pressure and the concentration of the liquid phase will undergo corresponding variations.

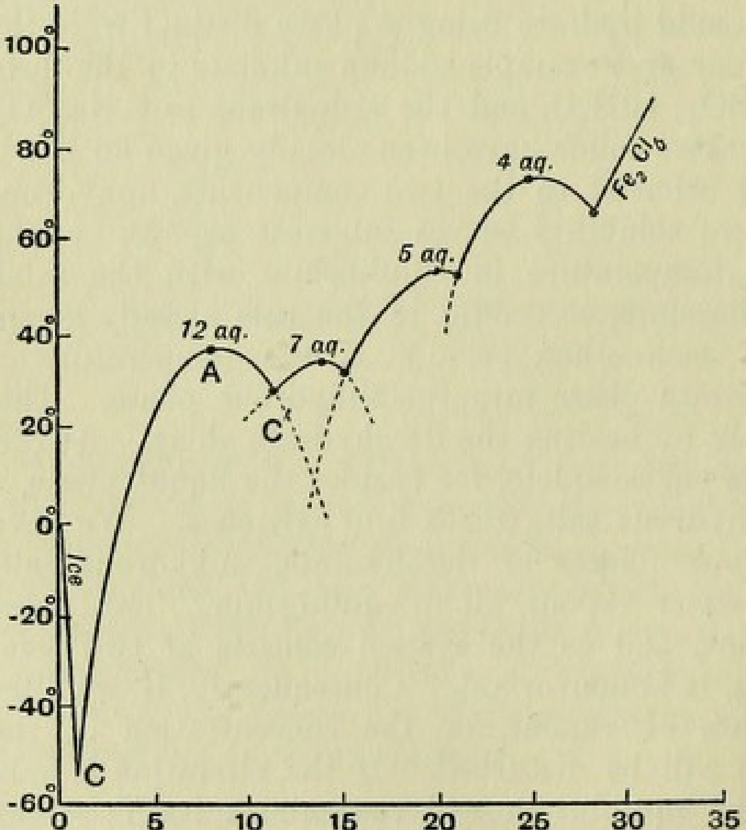


Fig. 19.

The curves of temperature and concentration for the hydrates of ferric chloride are given in Fig. 19. In this diagram pressure is not considered, and the curves represent equilibrium curves between solid and liquid phases. The line on the left represents the temperatures at which ice is in equilibrium with solutions of ferric chloride of various concentrations; it is, in short, the freezing-point curve of ferric chloride solutions (cp. p. 72). The curve CAC′ gives the equilibrium of solid dodecahydrate with ferric chloride solution; it is the solubility curve of the dodecahydrate. The point C, where it intersects the ice curve, is the cryohydric point, and lies at - 55°. At a temperature of 37° the liquid with which the dodecahydrate is in equilibrium has the same composition as the dodecahydrate itself. This temperature may therefore be called the melting point of the dodecahydrate, and it is the maximum temperature at which the hydrate can exist either by itself or in contact with any solution of ferric chloride. Addition of either water or ferric chloride to the liquid will lower the temperature at which the dodecahydrate will separate from the solution.

If we follow the curve for the dodecahydrate to greater concentrations, we find that another hydrate may make its appearance at C′, which lies at about 27°. It will be seen that this point resembles the cryohydric point C, inasmuch as it is a quadruple point, the four phases being the dodecahydrate, the new heptahydrate $Fe_2Cl_6, 7H_2O$, the saturated solution, and aqueous vapour. The only difference between the equilibrium here and at the cryohydric point is that the two solid phases are both hydrates, while at the cryohydric point one of the solid phases is ice. The point C′ corresponds to the point of intersection in the sodium sulphate diagram (Fig. 4, p. 54). It is the intersection of the solubility curves of the dodecahydrate and the heptahydrate, and therefore represents the transition point of these two phases. An investigation of the curve of the heptahydrate shows that it is of the same nature as the curve of the dodecahydrate. It reaches a maximum as before, the concentration of the solution and the temperature there being the composition and melting point of the hydrate. This curve for the heptahydrate finally cuts the curve of a lower hydrate, and similar curves are repeated until at last the solubility curve of the anhydrous salt is reached. The curve for each hydrate reaches a maximum temperature, which is the melting point of the hydrate, and cuts the curves for other hydrates at temperatures which are transition temperatures.

In the preceding instances we have seen how water may be removed from hydrates by continually raising the temperature, solution being at the same time present. Now, it is possible in many cases to remove the water of crystallisation from a hydrate without any solution being formed at all. This can be done most conveniently by placing the hydrate in a vacuous desiccator over a substance such as sulphuric acid or phosphorus pentoxide. The hydrate is at a given temperature in equilibrium with a small, and in most cases measurable, pressure of water vapour, *i.e.* it has a vapour pressure just as a solution has. If the pressure of water vapour above the hydrate is kept beneath this value, the hydrate will lose water and be converted into a lower hydrate or the anhydrous salt. In an evacuated desiccator containing phosphorus pentoxide the pressure of water vapour is practically kept at zero, so that the loss of water by the hydrate goes on continuously. Copper sulphate in the form of the pentahydrate $CuSO_4, 5H_2O$, for example, gradually loses water under these conditions, and is converted into the greenish-white monohydrate $CuSO_4, H_2O$. The vapour pressure of this hydrate is so small at the ordinary temperature that it remains practically unchanged in the desiccator.

In this mode of **dehydration of a hydrate**, we have only three phases coexisting, viz. the higher hydrate, the lower hydrate, and aqueous vapour. The liquid phase is entirely wanting. Now, the system consists of two components, the anhydrous salt and water, so that the number of phases exceeds the number of components only by one. The system is therefore monovariant, *i.e.* we can change one of the conditions without destroying the equilibrium altogether, the other conditions at the same time undergoing concomitant alterations. It should be noted that the condition of concentration is here practically absent, for there is no phase present in which the concentration varies continuously as it does in a solution.

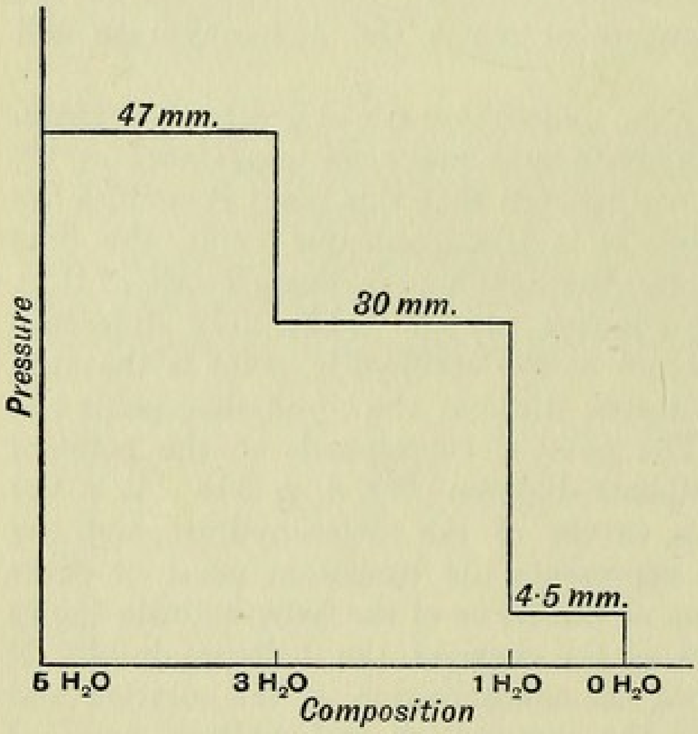


Fig. 20.

The effect of passing from one hydrate to another at constant temperature is seen in the accompanying diagram (Fig. 20), which represents the dehydration of copper sulphate pentahydrate at 50°. The dehydration does not proceed in one step from the pentahydrate to the anhydrous salt, but in three stages, two intermediate hydrates being formed. Each of these hydrates has its own vapour pressure; and where two hydrates coexist, the observed vapour-pressure is the vapour pressure of the higher hydrate. Pressures have been tabulated on the vertical axis, and composition in molecules on the horizontal axis. Until the molecule of copper sulphate has lost two molecules of water, the vapour pressure remains constant at 47 mm., after which there is a sudden drop to 30 mm. The first of these values is the pressure of the pentahydrate; the second is the pressure of the trihydrate formed as the first step in the dehydration. This value of the pressure is retained until two more molecules of water have been lost, when it sinks suddenly to 4·5 mm. This indicates that a monohydrate with a vapour pressure of 4·5 mm. has been formed. Further dehydration produces no diminution of the pressure until all the water has been lost, when, of course, the pressure altogether disappears. This method of systematic measurement of vapour pressure during the dehydration of a hydrate at constant temperature can be used to ascertain the existence of intermediate hydrates, which may not be easily prepared in other ways.

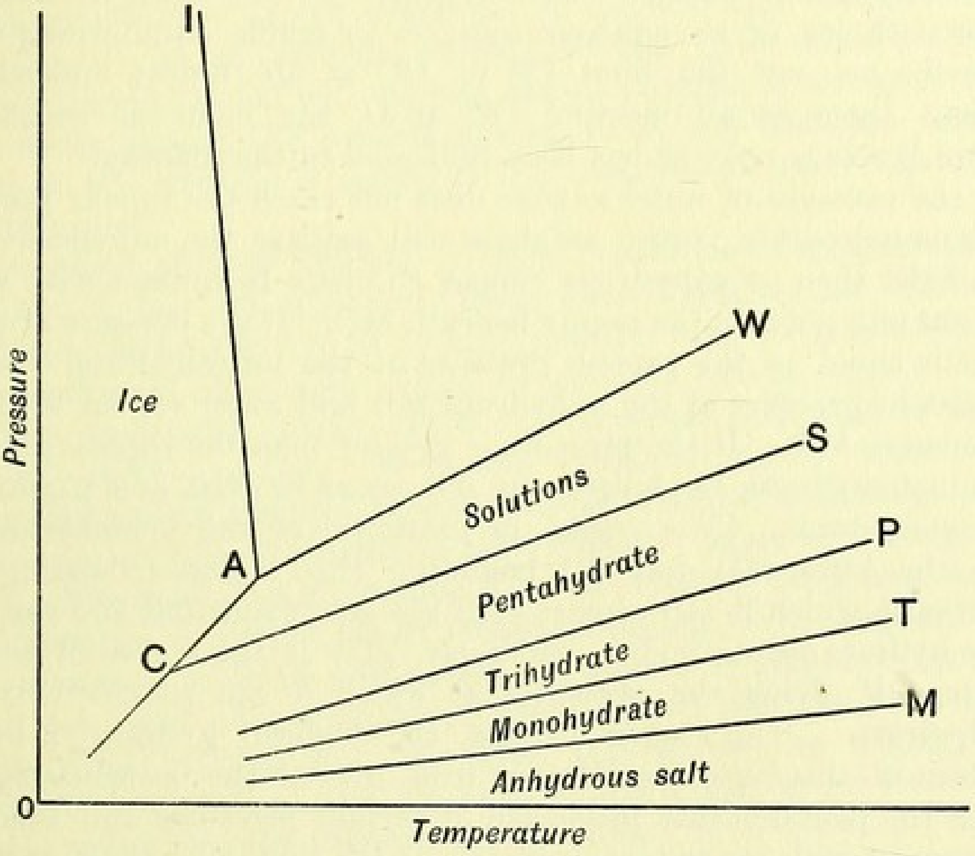


Fig. 21.

If the dehydration were conducted at another temperature than 50°, a similar diagram would result; the values of the pressures for the different temperatures would, however, be all higher or all lower than before. As the system with three phases is a monovariant one, the temperature and the pressure may be altered without the equilibrium being destroyed, but to a given alteration of the one there corresponds a definite alteration of the other. Each hydrate, therefore, has a vapour-pressure curve precisely like that of liquid water. These curves are represented in the temperature-pressure diagram of Fig. 21 by the lines OM, OT, OP, for the monohydrate, trihydrate, and pentahydrate respectively. The vapour-pressure curve of ice is represented by the line OA, and that of water by the line AW, the point

A where these curves intersect being the freezing point, or more correctly the triple point. SC is the curve of vapour pressures of solutions saturated with the pentahydrate at different temperatures. This curve has a smaller vapour pressure than that of pure water, and consequently cuts the curve for ice at a temperature below the freezing point. The line SC is the curve for the equilibrium of the three phases, pentahydrate, solution, and vapour. At the point C, where it cuts the ice curve, the three phases are also in equilibrium with ice, so that C represents the cryohydric point for copper sulphate. As the lower hydrates do not seem to exist in contact with ice or an aqueous solution in stable equilibrium, these curves do not cut the lines CS or OC at all, unless, indeed, we represent them as all meeting OC at O, the point at which the pressure becomes zero, as has been indicated in the diagram.

If the pressure of water vapour does not reach the vapour pressure of the monohydrate, copper sulphate will exist as the anhydrous salt. It can exist then as anhydrous copper sulphate in contact with water vapour at any point in the region beneath MO. If the pressure of water vapour is equal to the vapour pressure of the monohydrate, this salt can exist in presence of the anhydrous salt and water vapour at points on the curve MO. If the pressure is greater than the vapour pressure of the monohydrate, the anhydrous salt ceases to exist, and passes into the monohydrate. The region of existence of the monohydrate is MOT, the lines MO and TO bounding this region indicating the pressures at which it can coexist with the anhydrous salt and the next higher hydrate respectively. Similarly, TOP is the region of the trihydrate, OP giving the pressures at which it can coexist with the pentahydrate. The region of this, the highest, hydrate is POCS. The form of this region is different from that of the previous regions, because the pentahydrate phase can at certain pressures and temperatures coexist with ice as is represented by the line OC. If the pressure of water vapour is increased to values above those given by the vapour-pressure curve of the pentahydrate CS, some of the vapour will condense with formation of a new phase, viz. solution. The region of the existence of solutions is SCAW, bounded by the vapour-pressure curve of the saturated solutions, of ice, and of pure liquid water respectively.

The diagram throws some light on the behaviour of hydrated salts when exposed to an atmosphere containing the ordinary amount of moisture. The pressure of water vapour in a well-ventilated laboratory in this country is about 8 to 10 mm. on the average. If the vapour pressure of a hydrate is greater than this amount at the atmospheric temperature, the hydrate will lose water, *i.e.* will **effloresce**. This is the case, for example, with common washing soda, $Na_2CO_3, 10H_2O$, which, when exposed to the atmosphere, loses water in the form of vapour, with production of a lower hydrate. If, on the other hand, the pressure of water vapour in the atmosphere is greater than the vapour pressure of the hydrate, the water vapour may condense, and a higher hydrate or a solution may be formed. Thus, if anhydrous copper sulphate, or one of the lower hydrates of this salt be exposed to the atmosphere, the water vapour will be slowly absorbed with ultimate formation of the pentahydrate, for all the hydrates of copper sulphate have a lower vapour pressure than the pressure of the water vapour usually found in the atmosphere. If calcium choride or its common hydrate, $CaCl_2, 6H_2O$, is exposed to the air, it **deliquesces**, *i.e.* forms a liquid phase. Here the vapour pressures of the hydrate and of the saturated solution are lower than the pressure of water vapour commonly in the atmosphere, amounting to only 2 or 3 mm. at the ordinary temperature. The result is that a solution is formed which will become more and more dilute by absorption of water vapour, the process coming to an end when the vapour pressure of the solution is equal to the pressure of water vapour in the atmosphere.

Formation of New Phases.—Under conditions where a new phase *may* appear, it does not necessarily follow that it *must* appear. When a crystalline solid is heated to its melting point, it invariably melts if any further heating is attempted. Here we have the new phase, the liquid making its appearance as soon as the conditions are such that its stable existence becomes possible. If we cool the liquid, on the other hand, we may easily reach temperatures considerably below its freezing point without any solidification actually taking place. Here the new phase, the crystalline solid, does not appear when its existence becomes possible, but may remain unformed for an indefinite period. We meet with the same reluctance to form new phases at transition points. Rhombic sulphur can exist at temperatures above 95·6°, the transition point into monoclinic sulphur, and the latter may remain for a long time unchanged even at the ordinary temperature, which is far below the transition point into the rhombic modification.

New hydrates of well-known substances are constantly being discovered since investigations have been directed to their formation, although it is practically certain that conditions compatible with their existence must have previously been encountered in actual work with these substances.

Although sodium sulphate in the form of the decahydrate is efflorescent under ordinary atmospheric conditions, its vapour pressure being greater than the pressure of water vapour in the atmosphere, yet it may, if perfectly pure, remain for a long time in the air without a trace of efflorescence being observable. On the other hand, there are probably salts which are under the atmospheric conditions capable of taking up moisture to form a higher hydrate, and yet remain unaffected in the air. In each case, removal or absorption of water would result in the formation of a new phase, but the tendency to the formation of the new phases is so small that their formation may be delayed or never occur at all. It must be borne in mind that the reluctance to the production of new phases only applies to the first appearance of the new phase. As soon as the smallest particle of it appears, or is introduced from without, its formation goes on steadily and in many cases very rapidly. Supersaturated solutions of sodium thiosulphate, for example, may be kept for years without showing any tendency to crystallise, but if the merest trace of the solid crystalline phase is introduced, the whole mass becomes solid in the course of a few seconds. Similarly water, if perfectly air-free, may be heated to a temperature much above its boiling point, but in such a case, when the smallest bubble of vapour is formed in the interior of the liquid, the whole passes into the new vaporous phase with explosive violence.

When ice and a salt (or other substance soluble in water) are brought together at a temperature below the freezing point, there is the possibility of the formation of a new phase—the solution—and this phase generally forms, the temperature then under favourable conditions falling to the cryohydric point. It is questionable, however, if this is invariably the case; and it seems quite possible that two substances in the solid state might be brought together at a temperature above the cryohydric point without liquefaction taking place.

It is evident from what has been said in this chapter that it is not always the phase most stable under the given conditions which actually exists. A metastable phase may exist for an indefinite time without passing into the most stable phase, provided that this latter phase is entirely absent. As soon as the stable and metastable phases are brought into contact, however, the former begins to be produced at the expense of the latter. The transition from the metastable to the stable phase takes place as a rule fairly rapidly, but in some instances the transformation is so slow as to be practically unobservable. Strongly overcooled liquids, for example, crystallise with extreme slowness, even after they have been brought together with the stable crystalline phase (cp. p. 66). The crystalline modifications of silica (quartz and tridymite) are at ordinary temperatures so far beneath their temperature of transformation, if such exists, that they show no tendency to reciprocal transformation, and both forms must be accounted stable. The same holds good for the two forms of calcium carbonate, arragonite and calcspar. Yellow phosphorus is at ordinary temperatures metastable with regard to red phosphorus, which is the stable form, yet in the dark it keeps for an indefinite time without undergoing much alteration, even although it may be in contact with red phosphorus.

When we come to inquire what phase will be formed when there is the possibility of formation of several different phases, we find that it is not, as we might be inclined to expect, always the most stable phase that is formed, but rather a metastable phase, which may thereafter pass into the stable phase. A substance, then, in passing from an unstable to the most stable phase very frequently goes through phases of intermediate degrees of stability, so that the transformation does not occur directly, but in a series of steps. Liquid phosphorus, for instance, which is itself metastable with regard to red phosphorus, does not on cooling pass into the latter, most stable, modification, but into the metastable yellow phosphorus. Molten sulphur, again, when quickly cooled by pouring into cold water, does not pass directly into the stable rhombic sulphur, but into the comparatively unstable plastic sulphur, which then in its turn undergoes transformation into more stable varieties. It is a common experience in organic chemistry to obtain substances first in the form of oils which afterwards crystallise, sometimes only after long standing. The alkali salts of organic acids, for example, on acidification with a mineral acid in aqueous solution, very frequently do not yield the free acid in the most stable solid form, but as an oily liquid, which crystallises with more or less rapidity. Thus if solid paranitrophenol is dissolved in caustic soda solution, and the solution then acidified with hydrochloric acid, the paranitrophenol is liberated as an oil which crystallises after a few minutes.

If we consider that the least stable phase of a substance has always the greatest vapour pressure, or, if we are dealing with solutions, the greatest solubility, the formation of intermediate metastable phases is not perhaps so remarkable as might at first sight appear. In the above instance of paranitrophenol, the system before acidification consists of a liquid phase only, since for our present purpose we may neglect the vapour phase altogether. On acidification, the new phase may not make its appearance for some moments, owing to the general reluctance exhibited in the formation of new phases, and the new phase which eventually does make its appearance is that which entails least alteration in the system, *i.e.* that which leaves most in the solution. In other words, the more soluble and less stable phase is formed first, the less soluble and more stable phase only appearing as a product of the transformation of the former.

A very complete, non-mathematical exposition of the subject dealt with in this chapter is given by W. D. BANCROFT in his book *The Phase Rule* (Ithaca, New York).

For details of Calcium Chloride and its Hydrates, and Ferric Chloride and its Hydrates, see ROOZEBOOM, *Zeit. für physikal. Chem.* **4**, 31 (1889) and **10**, 477 (1892) respectively.

CHAPTER XII

THERMOCHEMICAL CHANGE

A CHEMICAL change is almost invariably attended by a heat change, the latter being generally of such a nature that heat is given out during the progress of the action. Vigorous reactions are accompanied by considerable evolution of heat; in feeble reactions, on the other hand, the heat evolution is comparatively small as a rule, and in some cases gives place to heat absorption. In special circumstances there may be neither evolution nor absorption of heat, but instances of this kind are practically confined to the reciprocal transformation of optical isomerides.

From the fact that vigour of chemical action frequently goes hand in hand with heat evolution, it was at one time thought that measuring the amount of heat evolved in any given action was tantamount to measuring the chemical affinity of the substances taking part in the action; but this point of view has of late years been entirely given up owing to practical difficulties in reconciling it with the facts, and to a general advance in our theoretical knowledge of the subject. If heat evolution were to be taken as an accurate measure of chemical affinity, there is an obvious difficulty in explaining why certain changes take place with absorption of heat, since this would correspond to a negative chemical affinity, and there would therefore be no reason, chemically speaking, why the action should take place at all. By introducing the heats of attendant physical changes in a somewhat arbitrary way, it was found possible to explain away the exceptions, but the explanations were in many instances so laboured that it became expedient to drop the rule altogether, in the strict sense, and be content with the recognition of a general parallelism between the amount of heat evolved in an action and the readiness with which it takes place.

The amount of heat change attendant on a chemical change is perfectly definite in ordinary circumstances, and is easily susceptible of exact measurement. A gram of zinc when dissolved in sulphuric acid will always occasion the same heat development if the conditions of the chemical action are the same. If the conditions are different, the thermal effect will also be different. Thus it is necessary in the first place to ensure that in each case exactly the same chemical action occurs. The action of zinc on sulphuric acid differs according as the acid is concentrated or dilute. In the former case, zinc sulphate and sulphur dioxide are the chief products, in the latter case zinc sulphate and hydrogen. These are essentially different chemical actions, and evolve different amounts of heat for a given quantity of zinc dissolved. But even if we ensure that the only products are zinc sulphate and hydrogen, there will still be a difference in the heat development if the sulphuric acid in two cases is at different degrees of dilution. The difference here, however, will be slight, and may for most purposes be neglected. Again, a difference in the temperature at which the action takes place will occasion a difference in the heat evolution; but in this case also the difference is comparatively slight, and negligible for small variations of temperature. Lastly, if the zinc and sulphuric acid form part of a voltaic circuit, as in a Daniell or a Grove cell, the heat evolution is then very different from what it is if the chemical action is not accompanied by the generation of an electric current.

From the standpoint of the conservation of energy, these phenomena are easily understood. Each substance, under given conditions, possesses a certain definite amount of **intrinsic energy**, so that if we are dealing with a system of substances, a definite amount of energy is associated with that system as long as it remains unchanged. If it changes now into another group of substances, each of these will have its own intrinsic energy, and the new system will in general have a different amount of energy from that of the original system. Suppose the second system has less energy than the first. From the law of conservation, it is plain that the difference of energy between the two systems cannot be lost, but must be transformed into some other kind of energy. Now the energy difference between two systems is usually accounted for as heat, and in our example the heat evolved during the solution of zinc in dilute sulphuric acid measures the difference of the intrinsic energy of the zinc and dilute sulphuric on the one hand, and hydrogen and dilute zinc sulphate on the other. If pure sulphuric is taken instead of a mixture of sulphuric acid and water, the second system is now sulphur dioxide and zinc sulphate, mostly in the solid anhydrous state—a system which has quite a different amount of intrinsic energy associated with it from hydrogen and dilute aqueous solution of zinc sulphate, so that the energy differences (and therefore the heat evolved) are widely divergent in the two cases. When the zinc and sulphuric acid form part of a galvanic cell, the initial and final systems are the same as above, so that there is the same energy difference as before; but now all the energy does not pass into heat, some of it being transformed into electric energy, which takes the shape of an electric current passing outside the system. The consequence is that much less heat is obtained by the solution of the zinc in this case than was obtained when no electric current was generated.

Dealing now with smaller heat effects, we find that the intrinsic energy of a system is not the same at one temperature as it is at another; for if we wish to raise the temperature we must supply energy in the form of heat to the system, the quantity supplied depending on the heat capacity of the substances which compose the system. In changing from one system to another, therefore, at different temperatures, different amounts of heat wlll be evolved, for in general the heat capacities of the two systems will be different. If we dilute a solution of sulphuric acid or of zinc sulphate, we find that a heat change accompanies the process, and as this heat of dilution is not as a rule the same for two substances, the total thermal effect depends on the concentration of the solutions employed.

From the principle of the conservation of energy we see that if we have in a chemical change the same initial system and the same final system, the same thermal effect will always be produced no matter how we pass from the first system to the second, provided that no other form of energy than heat is concerned in the transformation. Hess, who originally worked this out experimentally, gives the following numerical example. Pure sulphuric acid was in one experiment neutralised with ammonia in dilute aqueous solution; in other experiments it was first of all diluted with varying amounts of water before neutralisation, the heats of dilution and the heats of neutralisation being noted in each case. The experiment resulted as follows:—

Mols. Water.	Heat of Dilution.	Heat of Neutralisation.	Sum.
0	0	595·8	595·8
1	77·8	518·9	596·7
2	116·7	480·5	597·2
5	155·6	446·2	601·8

The first column gives the number of molecules of water which were added to one molecule of sulphuric acid; the second gives the number of heat units evolved on the addition of the water; and the third gives the number of heat units evolved on the neutralisation of the resulting solution by dilute ammonia. It will be noticed that the sum of the two heats is very nearly the same in the four cases, for in each the starting-point is from pure sulphuric acid and dilute ammonia, and the product is dilute ammonium sulphate.

This constancy of the total heat evolved is frequently made use of in thermochemistry for the determination of heat changes not easily accessible to direct measurement. Yellow phosphorus, for example, on conversion into red phosphorus is known to give out a considerable amount of heat, but the direct determination of this amount is a matter of some difficulty. An indirect determination, on the other hand, may be made with the greatest ease. Favre found that when a gram-atom of yellow phosphorus is oxidised to an aqueous solution of phosphoric acid by means of hypochlorous acid, the oxidation is attended by the disengagement of 2386 heat units. A gram-atom of red phosphorus in similar circumstances yields 2113 heat units. If now a gram-atom of yellow phosphorus were first converted into red phosphorus, and this then oxidised to phosphoric acid, the total heat evolution would be 2386 heat units, since the sum must be equal to the heat evolved in the direct oxidation. But the second part of the action, viz. the oxidation of the red phosphorus, yields 2113 units, so the first stage of the action, viz. the transformation of the yellow into the red phosphorus, must yield $2386 - 2113 = 273$ units.

Of the heat units referred to on p. 6, the most convenient for thermochemical purposes is the centuple unit, denoted by K, which is the quantity of heat required to raise the temperature of 1 gram of water from 0° C. to 100° C. With this unit the ordinary heats of reaction for molecular quantities are represented by numbers such as those in the preceding paragraph, not inconveniently large and not requiring the use of fractional values, since the degree of accuracy in the experimental determinations corresponds in favourable circumstances to about one unit.

We have no means of determining the amount of intrinsic energy in any substance; we can only measure differences between the intrinsic energies of certain substances, or systems of substances. If all substances were mutually convertible, directly or indirectly, we might take one substance as standard, and refer all intrinsic energies to it by means of numbers stating the quantity of energy possessed by the substance in excess of the standard. But chemical substances are not mutually convertible without restriction. In particular, the elements cannot be converted into each other by any means in our power. We are therefore unable to compare the intrinsic energies of the elements together, and so for purposes of calculation we may adopt any value for them that we please. The easiest system is to make the intrinsic energies of all the elements equal to 0, and refer all other intrinsic energies to this value for the elements. If in the equation

$$Pb + I_2 = PbI_2,$$

we take the ordinary chemical symbols of the elements and compounds as signifying the amounts of intrinsic energy in the substances, as well as the quantities of the substances themselves, the equation does not balance, for in the conversion of lead and iodine into lead iodide there is heat evolution, viz. 398 K for one gram atom of lead, so that the equation to be an accurate energy equation should read

$$Pb + I_2 = PbI_2 + 398 \text{ K}.$$

The intrinsic energy of a gram molecule of lead iodide is 398 K less than the sum of the intrinsic energies of the atoms from which it is formed, and is therefore equal to − 398 K, since the sum of the intrinsic energies of the elements is zero. If we actually write the amounts of energy associated with the various substances, we have the equation

$$\begin{array}{ccccccc} Pb & + & I_2 & = & PbI_2 & & \\ 0 & + & 0 & = & -398\text{ K} & + & 398\text{ K.} \end{array}$$

Now, the heat given out on the production of lead iodide, or any other substance from its elements, is called the **heat of formation** of the substance, and we see from the above instance that this must be equal to the intrinsic energy of the substance with the sign reversed; for on the left-hand side of the equation the sum of the energies is always equal to zero, being the intrinsic energy of elements alone, so that the sum of the energies on the right-hand side must also be zero, and the intrinsic energy of the compound thus equal to its heat of formation with the sign reversed. The heats of formation of compounds from their elements are for this reason very important in thermochemical calculations, their practical use being as follows. If from the sum of the heats of formation on the right hand of an ordinary chemical equation we subtract the sum of the heats of formation on the left hand, we obtain the heat given out or absorbed during the reaction. If the difference has the positive sign, the heat is evolved; if it has the negative sign, the heat is absorbed. If we reverse the signs of the heats of formation, *i.e.* if we write the values of the intrinsic energies, and subtract the sum on the right hand from the sum on the left, we arrive at the same result.

As an example, we may take the displacement of copper from copper sulphate by metallic iron according to the equation

$$Fe + CuSO_4, Aq = Cu + FeSO_4, Aq\ ;$$

where Aq indicates that the substance to whose formula it is attached is in aqueous solution. The heat of formation of copper sulphate in solution is 1984 K, and of ferrous sulphate under the same conditions 2356 K. The two metals have of course no heats of formation. If we subtract, therefore, the heat of formation of copper sulphate from that of ferrous sulphate, we get the heat of reaction required, viz. 372 K. Writing the equation with the values of the intrinsic energies, we have

$$\begin{array}{lllllll} Fe & + & CuSO_4 & = & Cu & + & FeSO_4 \\ 0 & - & 1984\text{ K} & = & 0 & - & 2356\text{ K} + 372\text{ K.} \end{array}$$

If we know the heat of a reaction and the heats of formation of all the substances but one concerned in the action, we can calculate the heat of formation of that substance directly from the energy equation. For example, the heat of neutralisation of hydrochloric acid by caustic soda, when both substances are in aqueous solution, is 137 K, the heats of formation of dissolved hydrochloric acid, dissolved caustic soda, and liquid water respectively being 393 K, 1118 K, and 683 K. If we let

x represent the unknown heat of formation of sodium chloride in aqueous solution, we obtain the following equation:—

$$\begin{array}{lllll} \mathrm{HCl, Aq} & + \ \mathrm{NaOH, Aq} & = \mathrm{NaCl, Aq} & + & \mathrm{H_2O} \\ -393\ \mathrm{K} & -\ 1118\ \mathrm{K} & = -x & & -\ 683\ \mathrm{K} + 137\ \mathrm{K}, \end{array}$$

whence $x = 965$ K.

When an element like sulphur exists in more than one modification, it is necessary to specify which modification we assume to have zero intrinsic energy, as there is always a heat change in passing from one modification to another. As a rule, the commonest or the most stable variety is taken as the standard as convenience dictates. Heats of formation of sulphur compounds are generally referred to rhombic sulphur; those of phosphorus compounds to yellow phosphorus.

In the case of carbon compounds we seldom deal directly with heats of formation, but rather with **heats of combustion,** on account of their practical importance, and also on account of the ease with which they can be determined. The heat of formation, however, can easily be calculated from the heat of combustion. We find, for example, that methane has a heat of combustion equal to 2138 K, the products of combustion being carbon dioxide and water. Now, the heat of formation of carbon dioxide from carbon in the form of diamond is 943 K, and of water 683 K. For the heat of formation of methane we have therefore the following equation:—

$$\begin{array}{lllll} \mathrm{CH_4} + & 2\mathrm{O_2} = & \mathrm{CO_2} & + & 2\mathrm{H_2O} \\ -x + & 0 = & -943\ \mathrm{K} - & 2 \times 683\ \mathrm{K} & + \ 2138\ \mathrm{K}, \end{array}$$

whence $x = 171$ K. We see from this that the combustion of methane gives out less heat than we should get by burning the same quantity of carbon and hydrogen as the free elements, and this is true of most carbon compounds. The difference between the heat of combustion of a hydrocarbon and that of the carbon and hydrogen composing it is not as a rule very great, so that a calculation of the latter gives an approximate value for the former. Thus the heat of combustion of the carbon and hydrogen in amylene, C_5H_{10}, would be $5 \times 943\ \mathrm{K} + 5 \times 683\ \mathrm{K} = 8130\ \mathrm{K}$. The heat of combustion of amylene vapour was found by direct experiment to be 8076 K, a number differing only slightly from the preceding one.

When a carbon compound contains oxygen as well as hydrogen, its heat of combustion may be calculated roughly by means of "Welter's rule." According to this rule, the oxygen is subtracted from the molecular formula together with as much hydrogen as will suffice to convert it completely into water, the heat of combustion of the carbon and hydrogen in the residue then giving an approximate value of the heat of combustion of the whole compound. As an example we may take propionic acid, $C_3H_6O_2$, whose heat of combustion has been found by direct experiment to be 3865 K. If we subtract

$2H_2O$ from the molecular formula, we are left with the residue C_3H_2, the elements of which have the heat of combustion

$$3 \times 943 \text{ K} + 683 \text{ K} = 3512 \text{ K}.$$

It is evident that the approximation is here by no means close, the error in this case being about 10 per cent. A better result may usually be obtained by subtracting the oxygen, not with the corresponding quantity of hydrogen, but with the corresponding quantity of carbon, and then estimating the heat of combustion of the elements in the residue. In the above example we subtract CO_2 from the formula $C_3H_6O_2$, and have C_2H_6 left as residue. This gives the heat of combustion $2 \times 943 + 3 \times 683 = 3935$ K, a much better approximation to the experimental value. As another instance of the two methods of calculation, we may take cane sugar, $C_{12}H_{22}O_{11}$. By Welter's rule we subtract $11H_2O$ from the molecule, and for the residue C_{12} get the heat of combustion $12 \times 943 = 11,316$ K. By the other method we subtract $5{\cdot}5CO_2$ in order to dispose of the 11 atoms of oxygen, and obtain the residue $6{\cdot}5C$ and $11H_2$. The heat of combustion of these quantities of the elements is $6{\cdot}5 \times 943 + 11 \times 683 = 13,642$ K. The value experimentally found is 13,540 K, a number much closer to the second calculated value than to the first.

Some hydrocarbons have a greater heat of combustion than that of the carbon and hydrogen contained in them. The heat of combustion of acetylene, for example, is 3100 K; the heat of combustion of the two atoms of carbon and the two atoms of hydrogen contained in its molecule being $2 \times 943 + 683 = 2569$ K. This corresponds to a heat of formation of -531 K, *i.e.* this amount of heat is absorbed on formation of acetylene from its elements. We have here, then, an example of an **endothermic** compound formed from its elements with heat absorption, in contradistinction to the bulk of compounds, which are **exothermic**, *i.e.* are formed from their elements with evolution of heat. Other common examples of endothermic compounds are carbon disulphide, which is formed with a heat absorption of 287 K, and gaseous hydriodic acid, which is formed with a heat absorption of 61 K. Endothermic compounds like these are comparatively unstable, and give out heat on their decomposition. Hydriodic acid gas, for instance, is decomposed by gentle heating; carbon disulphide can be split up into its elements by mechanical shock; and carbon and hydrogen may be regenerated from acetylene by the passage of electric sparks through the gas. The substance hydrazoic acid, or azoimide, N_3H, has a large negative heat of formation, which is no doubt closely associated with its extremely explosive properties.

Such endothermic compounds are formed directly from their elements with difficulty, if they can be formed at all. At ordinary temperatures their direct formation does not take place, but if the elements are brought into contact at a very high temperature, then combination may occur. Thus carbon disulphide is formed by passing sulphur vapour over red-hot carbon. Acetylene is produced when carbon and hydrogen are brought into contact at the very high temperature of the electric arc. This behaviour is exactly opposite to what we find with the common exothermic compounds, which are stable enough at ordinary temperatures, but are frequently decomposed by high temperatures.

It has already been stated that for thermochemical purposes it is necessary to specify exactly the condition of each of the substances concerned in the action under discussion. This is not only true for the chemical condition, but also for the **physical state** of the substances. We must know whether the substances are in the solid, liquid, or gaseous state, or, if they are in the state of solution, in what solvent, and at what dilution. This is so because change of physical state is accompanied by heat change, which must be taken into account in thermochemical investigations. Liquid sulphur, on combining with oxygen to give sulphur dioxide, will not give out the same amount of heat as rhombic sulphur, for the latter on melting absorbs about 3 K, which must therefore be added to the heat of combustion of the rhombic sulphur. The correction for the difference between the solid and liquid states is often small, and never amounts to more than about 50 K. If the substance is in the state of vapour, the heat of vaporisation must be added to the thermochemical data for the liquid. This correction is often considerable, amounting approximately to one-fourth of the value of the boiling point of the substance on the absolute scale (Trouton's rule). Thus the correction for water according to this rule would be $0{\cdot}25 \times 373 = 93$ K, the actual heat of vaporisation at 100° being 97 K. The heat of formation of liquid water at the ordinary temperature from oxygen and hydrogen is 683 K, the number we have used throughout in the above calculations. At 100° the heat of formation of liquid water is somewhat less, viz. 676 K. If, now, we want to find the heat of formation of gaseous water at 100°, we must subtract the heat of vaporisation of the liquid, viz. 97 K, and thus obtain 579 K as the heat of formation of water vapour.

There is still another circumstance which must be taken into consideration when a chemical action is accompanied by the disappearance or formation of gases; or, in general, when the action is accompanied by a great **change of volume**. Each gram molecule of gas generated performs an amount of work equal to $0{\cdot}02T$ K, for, as we have seen, the equation $pv = RT$ becomes $pv = 2T$ for the gram molecule, and R has the value 2 in small calories, or 0·02 in centuple calories (see p. 30). This amount of heat, then, is absorbed on production of the gas. If, on the other hand, a gram molecule of gas disappears, a corresponding amount of heat is produced in the action. At 27° the actual amount per gram molecule is $0{\cdot}02 \times (27 + 273) = 6$ K, the value being the same for all gases. This correction is of importance in the case of carbon compounds, which, under ordinary circumstances, are burned at the atmospheric pressure, the volume increasing considerably during the combustion. The actual thermochemical measurement is usually made, on the other hand, in a closed "calorimetric bomb," the volume thus remaining constant. If we consider the combustion of toluene, for instance, we have the following volume relations :—

$$\mathrm{C_7H_8} + \underset{\text{9 vols.}}{\mathrm{9O_2}} = \underset{\text{7 vols.}}{\mathrm{7CO_2}} + \mathrm{4H_2O}\,;$$

or, if the substances are all in the gaseous state,

$$\underset{\text{1 vol.}}{\mathrm{C_7H_8}} + \underset{\text{9 vols.}}{\mathrm{9O_2}} = \underset{\text{7 vols.}}{\mathrm{7CO_2}} + \underset{\text{4 vols.}}{\mathrm{4H_2O}}.$$

Each volume in the above equations is the gaseous gram-molecular volume, the volume of the liquid substances being negligible. If both the toluene and the water formed by its combustion are in the liquid state, there is a shrinkage of two volumes on completion of the combustion. If all the substances are in the gaseous state, there is an expansion of one volume. On the supposition that the combustion takes place in the calorimetric bomb at 27° with evolution of m centuple calories, then if the liquid toluene is burned at constant pressure, we shall have a heat evolution of $m + 12$ K. Suppose now that the toluene is burned as vapour at 27° by passing a stream of air or oxygen through the liquid and igniting the mixture at a jet, the water vapour being carried off without condensing; and suppose further that the heat of vaporisation of toluene and water at this temperature are t and w respectively, then we can calculate the heat of combustion under these conditions as follows. To vaporise the gram molecule of toluene, t heat units are absorbed, and this heat is given out again when the toluene ceases to exist as such, so to the heat of combustion of the liquid we must add this heat of vaporisation. But the water obtained in the previous case was liquid water, in the formation of which from vapour there was evolved w heat units per gram molecule. This amount of heat is not given out if the water remains in the gaseous state, so that from the heat of combustion given above we must now subtract $4w$. Finally, there is now an expansion of one volume, so that 6 K must be subtracted from the heat of combustion at constant volume. The heat of combustion under the circumstances is therefore $m + t - 4w - 6$ K.

The apparatus used to measure heats of chemical change is essentially the same as that used in physics for measuring heat quantities, and in particular the water calorimeter is universally employed. The chemical action is allowed to take place in a chamber immersed in a known amount of water of known temperature, and the change of temperature brought about in this water by the chemical action is noted. As the apparatus itself, viz. vessels, thermometers, stirrers, etc., is heated along with the water it contains, its water equivalent, *i.e.* the quantity of water which has the same heat capacity as the apparatus, must be determined and added to the quantity of water actually employed in the experiment. This can be done by adding a known quantity of heat to the apparatus and ascertaining the resultant change of temperature in the water of the calorimeter.

The chief source of error in such experiments lies in heat exchange with external objects by conduction and radiation. To reduce this error to a minimum, the chemical action must be made to go as fast as possible, and the temperature of the calorimeter must never be allowed to depart greatly from the temperature of the room in which the experiment is made. Conduction is avoided by having the calorimeter surrounded by one or two vessels with stagnant air spaces between them, contact between the vessels being made by a bad heat conductor, such as cork, and reduced to as few points as possible.

If the calorimeter is constructed to contain half a litre of water, the heat capacity of the apparatus is small in comparison, and by the use of a thermometer which can measure differences of temperature to a thousandth of a degree, very accurate results can be obtained with a relatively small expenditure of material. The most convenient form for the calorimeter is that of a cylinder, whose height is one and a half times to twice its diameter, so that in many cases an ordinary beaker serves the purpose very well, a larger beaker with a cover being the surrounding vessel.

For further information concerning the methods and results of thermochemistry, the student may consult MUIR AND WILSON, *Elements of Thermal Chemistry*.

CHAPTER XIII

VARIATION OF PHYSICAL PROPERTIES IN HOMOLOGOUS SERIES

In the homologous series of organic chemistry, for example the series of the saturated alcohols, there is a close resemblance in chemical properties amongst the members, so that it is possible to give general methods for the preparation of the substances and general types of action into which they enter. The actual readiness with which the substances are formed or are acted on by other substances, may, and usually does, differ from case to case, there being a gradation in chemical activity as successive members of the series are considered. Sodium, for instance, acts on the alcohols with formation of sodium alkyl oxides and hydrogen according to the equation

$$2ROH + 2Na = 2RONa + H_2,$$

but the vigour of the action is very different according as the alcohol is one high or low in the series. With methyl alcohol ($CH_3 . OH$) and with ethyl alcohol ($C_2H_5 . OH$) the action is brisk; with amyl alcohol ($C_5H_{11} . OH$) it is already sluggish at the ordinary temperature.

Corresponding to this gradation of chemical activity within the series we have a gradation in physical properties, and here, on account of the accuracy with which these physical properties can be measured, the differences are more readily observed and more readily brought under general rules. We may take first for consideration the specific gravities in the series of normal primary saturated alcohols, which are exhibited in the following table (p. 135). The values of the specific gravity are for 0°, and are referred to the specific gravity of water at 0°.

It will be seen that as the molecular weight of the alcohol increases, the specific gravity increases likewise. The difference in composition from step to step is one atom of carbon and two atoms of hydrogen; and to this constant difference, CH_2, there corresponds a continually diminishing difference in the values of the specific gravities as the series is ascended.

		Specific Gravity.	Difference.
Methyl alcohol	$CH_3 . OH$	0·812	
			– ·006
Ethyl ,,	$C_2H_5 . OH$	0·806	
			+ ·011
Propyl ,,	$C_3H_7 . OH$	0·817	
			+ ·006
Butyl ,,	$C_4H_9 . OH$	0·823	
			+ ·006
Amyl ,,	$C_5H_{11} . OH$	0·829	
			+ ·004
Hexyl ,,	$C_6H_{13} . OH$	0·833	
			+ ·003
Heptyl ,,	$C_7H_{15} . OH$	0·836	
			+ ·003
Octyl ,,	$C_8H_{17} . OH$	0·839	
			+ ·003
Nonyl ,,	$C_9H_{19} . OH$	0·842	

An exception is found in the first member of the series. Reasoning by analogy from the other members, we should expect methyl alcohol to have a considerably lower specific gravity than ethyl alcohol, but instead of this it has a higher specific gravity, the value being intermediate between those for the second and third members of the series. The exceptional behaviour of the first member of a series is not confined to this series, or to this property, being of frequent occurrence amongst organic compounds.

If instead of considering the specific gravities of the compounds (*i.e.* the weights which occupy unit volume) we consider the **molecular volumes** (*i.e.* the volumes occupied by the molecular weights), we are enabled to bring greater regularities to light. The specific volume v is the reciprocal of the density d, and the molecular volume V is the product of the specific volume and the molecular weight, or the molecular weight divided by the density. The values of $v = \frac{1}{d}$, and $V = \frac{M}{d}$ are contained in the following table :—

		M	v	Difference.	V	Difference.
Methyl alcohol	CH_3OH	32	1·231		39·4	
				+10		+17·7
Ethyl ,,	C_2H_5OH	46	1·241		57·1	
				–17		+16·3
Propyl ,,	C_3H_7OH	60	1·224		73·4	
				– 9		+16·5
Butyl ,,	C_4H_9OH	74	1·215		89·9	
				– 9		+16·2
Amyl ,,	$C_5H_{11}OH$	88	1·206		106·1	
				– 5		+16·4
Hexyl ,,	$C_6H_{13}OH$	102	1·201		122·5	
				– 5		+16·2
Heptyl ,,	$C_7H_{15}OH$	116	1·196		138·7	
				– 4		+16·2
Octyl ,,	$C_8H_{17}OH$	130	1·192		154·9	
				– 4		+16·2
Nonyl ,,	$C_9H_{19}OH$	144	1·188		171·1	

The regularity exhibited by the molecular volumes is much more striking than that displayed by the specific volume or by the specific gravity. Here the difference between neighbouring members, instead of continuously diminishing, remains practically constant throughout the series. The volume occupied by the molecular weight of the alcohol is increased by 16·2 units for every addition of CH_2 to the molecule of the alcohol. The value 16·2 may therefore be looked upon as the "molecular" volume of CH_2 under the given conditions, and in this particular homologous series. Under other conditions the value for CH_2 may be, and is, different. The volume of organic compounds is usually affected greatly by temperature; the coefficient of expansion of ethyl alcohol being, for example, some twenty times as great as that of water at the ordinary temperature. It is therefore of importance to determine under what conditions the volumes of different compounds are to be compared, more especially when they belong to different series. In the above instances the specific gravities were measured at 0° (and compared with water at 0°). This choice of temperature is evidently arbitrary, bearing no relation to the properties of the compounds themselves, but as far as we have seen it has the merit of leading to regular results.

Kopp found, by studying a great many liquid substances, that if the molecular volume of each was determined at its own boiling point, not only were the regularities within each series preserved, but the same regularity held good for practically all series. No matter what homologous series was studied, Kopp found that a difference of composition of CH_2 corresponded to a constant difference in the molecular volume, the value being in his units 22. It must be noted that this volume is not absolutely constant, but is merely an average, the actual differences being liable to slight fluctuations about the mean. The value is greater than that obtained when the homologous compounds are all measured at the same temperature, because, as we shall see, the boiling points in homologous series rise as the series is ascended. Thus the molecular volumes of two neighbouring compounds measured at their respective boiling points will show a greater difference than if they were measured at the same temperature, for the molecular volume of the compound with greater molecular weight is ascertained at a higher temperature than the molecular volume of the substance with lower molecular weight, and there is therefore the expansion between the two temperatures to be added to the value that would be obtained if both were measured at the boiling point of the lower compound. Besides this regularity others come to light. It was found by Kopp that the densities of isomeric compounds (measured at their boiling points) were equal, and consequently that their molecular volumes were also equal under these conditions. For example, he found the following numbers for compounds having the formula $C_6H_{12}O_2$:—

	Molecular Volume.
Methyl valerate	149·2
Ethyl butyrate	149·3
Butyl acetate	149·3
Amyl formate	149·8

When the measurements are made at the same temperature, this constancy is not displayed if the boiling points of the isomeric substances are widely different. Thus for the butyl alcohols we have, when the densities are all measured at 20° (against water at 4°)—

		Boiling Point.	Density.
Normal primary	$C_2H_5 . CH_2 . CH_2OH$	117°	0·810
Iso-primary	$(CH_3)_2 . CH . CH_2OH$	107°	0·806
Tertiary	$(CH_3)_3 . C . OH$	83°	0·786

The alcohol with highest boiling point has the greatest density, *i.e.* the smallest volume when the measurements are all made at one temperature. Its higher boiling point, however, allows of greater expansion, so that when the determinations are made at the boiling points, the increase of volume due to the higher temperature to some extent compensates for the smaller original volume at 20°. The choice of the boiling points of the compounds as the temperatures at which the comparisons are to be made, although it involves the properties of the compounds themselves, is still to a certain extent arbitrary, inasmuch as they are the temperatures at which all the substances have an arbitrary vapour pressure, viz. 76 cm. The justification of this choice lies in the fact that the observed regularities under these conditions are great. Another mode of working up the volume data will be found in Chapter XVIII.

The heat evolved by the complete combustion of an organic compound (the carbon becoming carbon dioxide, and the hydrogen becoming water) is an example of a property exhibiting constant differences between neighbouring members of a homologous series when molecular quantities are compared. The following table contains the **heats of combustion** of gram-molecular weights of the fatty acids expressed in centuple calories (p. 129) :—

Acid.			Difference.
Formic	CH_2O	590 K	
			1543
Acetic	$C_2H_4O_2$	2133 ,,	
			1546
Propionic	$C_3H_6O_2$	3679 ,,	
			1548
Butyric	$C_4H_8O_2$	5227 ,,	
			1540
Valeric	$C_5H_{10}O_2$	6767 ,,	
			1545
Caproic	$C_6H_{12}O_2$	8312 ,,	

For each difference in composition of CH_2 there is a difference in the molecular heat of combustion amounting on the average to 1543 K.

This difference is found to be practically the same in all homologous series. Thus for the alcohols we have—

Alcohol.			Difference.
Methyl	CH_4O	1685 K	
			1561 K
Ethyl	C_2H_6O	3246 ,,	
			1565 ,,
Propyl	C_3H_8O	4811 ,,	
			1565 ,,
Butyl	$C_4H_{10}O$	6376 ,,	
			1558 ,,
Amyl	$C_5H_{12}O$	7934 ,,	

A property which in general varies regularly in homologous series is the **boiling point.** As we ascend a simple series the boiling point invariably rises, but the rise at each succeeding step in general grows smaller and smaller as the molecular weight increases. The following table gives the boiling points of some of the normal saturated hydrocarbons. In the second column under t is the boiling point at 76 cm. in the centigrade scale; under T we have the boiling point in the absolute scale, *i.e.* $t + 273$.

Hydrocarbon.	t	t (calculated).	T	Difference.
C_7H_{16}	100·5	100·8	373·5	
				25·0
C_8H_{18}	125·5	126·1	398·5	
				24·0
C_9H_{20}	149·5	149·9	422·5	
				23·5
$C_{10}H_{22}$	173·0	172·5	446·0	
				21·5
$C_{11}H_{24}$	194·5	193·8	467·5	
				20·0
$C_{12}H_{26}$	214·5	214·2	487·5	
				19·5
$C_{13}H_{28}$	234·0	234·3	507·0	
				18·5
$C_{14}H_{30}$	252·5	253·0	525·5	
				18·0
$C_{15}H_{32}$	270·5	271·1	543·5	
				17·0
$C_{16}H_{34}$	287·5	288·9	560·5	

The boiling points of most series exhibit a regularity similar to the above, but the differences are not usually so great as is the case with the hydrocarbons. The boiling points of most members of a homologous series can be expressed by a fairly simple formula. If M is the molecular weight of the compound, T its boiling point in the absolute scale, and a and b constants for the series, then in general

$$T = aM^b.$$

The values under "t calculated" in the above table were obtained by means of a formula of this kind, the constants for the series being $a = 37·38$ and $b = 0·5$. In some series (*e.g.* the alcohols, the alkyl bromides, and the alkyl iodides) a formula of this type cannot successfully be applied, but in most cases it gives accurate results.

The student must again be reminded that the boiling point of a series of compounds is a magnitude arbitrarily selected in so far as the pressure under which the compound boils is itself quite arbitrarily chosen equal to the average pressure of the atmosphere. It is found, however, that a formula of the above type is capable of expressing the relation between boiling points and molecular weights under any pressure. In the same series the constant a has different values for different pressures, whilst the constant b retains the same value for all the pressures. Thus the boiling points of the above series of hydrocarbons under 3 cm. pressure may be expressed by the formula

$$T = 29{\cdot}68M^{0{\cdot}5},$$

instead of

$$T = 37{\cdot}38M^{0{\cdot}5},$$

which is valid for 76 cm. The constancy of b for different pressures leads to the following results. If we take two substances belonging to the same series, we have for their boiling points at a certain pressure p

$$T = aM^b, \text{ and } T_1 = aM_1{}^b.$$

At another pressure p' we have the boiling points

$$T' = a'M^b, \text{ and } T_1{}' = a'M_1{}^b.$$

M, M_1 and b remain the same throughout; so, by dividing each equation of the first pair by the corresponding equation of the second pair, we obtain

$$\frac{T}{T'} = \frac{a}{a'} \text{ and } \frac{T_1}{T_1{}'} = \frac{a}{a'}, \text{ whence } \frac{T}{T'} = \frac{T_1}{T_1{}'}.$$

That is, if b remains constant for different pressures, the ratio of the boiling points (expressed in the absolute scale) at any two given pressures will remain the same for all members of the homologous series. Transposing the last equation, we have

$$\frac{T'}{T_1{}'} = \frac{T}{T_1},$$

i.e. the ratio of the absolute boiling points of two substances belonging to the same homologous series is independent of the pressure.

The boiling points of isomeric substances are in general not the same, as may be seen, for example, in the case of the butyl alcohols given in the table on p. 137. We usually find, as here, that the isomers containing the longest carbon chain boil at a higher temperature than those with branched carbon chains.

As a rule, the boiling point of the first member of a homologous series is considerably higher than that calculated from the formula which includes the other members of the series. This abnormally high boiling point is displayed still more markedly when, instead of one characteristic group, the first member of the series has two. Thus, for example, in the simplest series of the dicyano-derivatives, the first member has a boiling point which is actually higher than those of the three succeeding members :—

			Difference.
Malonic nitrile	$(CN)_2CH_2$	218°	
			− 21
Methyl-malonic nitrile	$(CN)_2CH . CH_3$	197°	
			+ 9
Ethyl-malonic nitrile	$(CN)_2CH . CH_2CH_3$	206°	
			+ 10
Propyl-malonic nitrile	$(CN)_2C_2H . CH_2CHCH_3$	216°	

The glycols behave similarly :—

Ethylene glycol	$CH_2(OH) . CH_2(OH)$	197°	
			− 9
Methyl-ethylene glycol	$CH_2(OH) . CH(OH) . CH_3$	188°	
			+ 4
Ethyl-ethylene glycol	$CH_2(OH) . CH(OH) . CH_2CH_3$	192°	

The **melting points** in homologous series often show the peculiarity that the substances with an even number of carbon atoms form a regular series by themselves, and those with an odd number of carbon atoms form a regular series by themselves. The following table contains the melting points of the higher fatty acids :—

Acid (Even).		Melting Point.		Acid (Odd)	
Caproic	$C_6H_{12}O_2$	− 1·5			
			− 10·5	$C_7H_{14}O_2$	Œnanthylic
Caprylic	$C_8H_{16}O_2$	+ 16·5			
			+ 12·5	$C_9H_{18}O_2$	Pelargonic
Capric	$C_{10}H_{20}O_2$	+ 31·4			
			+ 28	$C_{11}H_{22}O_2$	Undecylic
Lauric	$C_{12}H_{24}O_2$	+ 44			
			+ 40·5	$C_{13}H_{26}O_2$	Tridecylic
Myristic	$C_{14}H_{28}O_2$	+ 54			
			+ 51	$C_{15}H_{30}O_2$	Pentadecylic
Palmitic	$C_{16}H_{32}O_2$	+ 62			
			+ 60	$C_{17}H_{34}O_2$	Margaric
Stearic	$C_{18}H_{36}O_2$	+ 68			
			+ 66·5	$C_{19}H_{38}O_2$	Nondecylic
Arachic	$C_{20}H_{40}O_2$	+ 75			

If we take the successive members of the series, we find an alternate rise and fall in the melting point as we pass from one acid to the next. If, however, we separate the acids into those with an even and those with an odd number of carbon atoms, we have a rise in the melting point in each series. It will be observed here again that the differences decrease as we ascend the series.

In some homologous series the difference between the homologues with even and those with uneven numbers of carbon atoms is so marked that in the one case we may have the melting point rise, and in the other case fall, as we ascend. The normal saturated dibasic acids afford an instance in point:—

Acid (Even).		Melting Point.		Acid (Odd).	
Succinic	$C_4H_6O_4$	181°			
			98°	$C_5H_8O_4$	Glutaric
Adipic	$C_6H_{10}O_4$	149°			
			103°	$C_7H_{12}O_4$	Pimelic
Suberic	$C_8H_{14}O_4$	141°			
			107°	$C_9H_{16}O_4$	Azelaic
Sebacic	$C_{10}H_{18}O_4$	133°			
			110°	$C_{11}H_{20}O_4$	Nonane-dicarboxylic
Decane-dicarboxylic	$C_{12}H_{22}O_4$	127°			
			113°	$C_{13}H_{24}O_4$	Brassylic
Dodecane-dicarboxylic	$C_{14}H_{26}O_4$	123°			

In the even series the melting point falls, in the odd series the melting point rises, as the molecular weight increases. Once more the rise or fall diminishes in magnitude step by step as we ascend the series.

The student may have observed that in these melting-point tables the lowest members of the series have been omitted. This is so because they do not fall under the general scheme which includes the higher members of the series. For example, the first member of the normal dibasic acids, oxalic acid, $C_2H_2O_4$, melts at 189°, and the second member, malonic acid, $C_3H_4O_4$, melts at 133°. It is evident that the melting points are not included in the general scheme which suffices for the other members of the series. In the series of the fatty acids the same irregularity is displayed. Acetic acid, $C_2H_4O_2$, which, if the fall observable as we descend the series were maintained to the end, should melt many degrees below zero, in reality melts at + 16·5°. In general, we may say that the lowest member (or members) of a series departs from the regular behaviour exhibited by the higher members amongst themselves. Exceptions to this rule occur, but they are comparatively rare.

The separation of the members of a series into those with even and those with odd numbers of carbon atoms sometimes appears in other properties besides the melting points. Thus in the same series of the normal dibasic acids we have the **solubility** of the odd members in water considerably greater than the solubility of the even members, as the following table shows:—

Acid (Even).		Solubility.		Acid (Odd).	
Oxalic	$C_2H_2O_4$	8·8			
			140	$C_3H_4O_4$	Malonic
Succinic	$C_4H_6O_4$	6·9			
			...	$C_5H_8O_4$	Glutaric
Adipic	$C_6H_{10}O_4$	1·5			
			4·5	$C_7H_{12}O_4$	Pimelic
Suberic	$C_8H_{14}O_4$	0·142			
			0·12	$C_9H_{16}O_4$	Azelaic
Sebacic	$C_{10}H_{18}O_4$	0·01			
			0·014	$C_{11}H_{20}O_4$	Nonane-dicarboxylic
Decane-dicarboxylic	$C_{12}H_{22}O_4$	0·003			
			0·004	$C_{13}H_{24}O_4$	Brassylic

The solubilities are given as parts of acid dissolved by 100 parts of water at the ordinary temperature (15° – 20°). It will be seen that in the separate series the solubility in water falls off very rapidly as the number of carbon atoms in the molecule increases. This is in accordance with what was stated in the chapter on solubility. The solubility of an acid in water is probably connected with the presence in it of the hydroxyl (– OH) or carboxyl (– COOH) group (cp. p. 59). Other things being equal, the greater the proportion of hydroxyl (or carboxyl) in the molecule, the greater will be its solubility. As we go up the series the proportion which the hydroxyl bears towards the rest of the molecule diminishes, and along with this goes on diminution of the solubility in water.

It is evident from the above tables that in this particular series there is some fundamental difference between the homologues with an even and those with an odd number of carbon atoms. This difference is probably to be sought for in some property affecting the substance in the solid state, for both the melting point and the solubility are here properties of the solids, *i.e.* it is the presence of the solid that determines both. The liquid may be supercooled when not in contact with the solid, and the solution may be supersaturated if the solid is not present. But the solid cannot be heated above its point of fusion without melting, and the solution in contact with it is always exactly saturated. It is in this sense that we say that it is the solid that determines the melting point and the solubility—not the liquid or the solution.

The analogy that we see between solubility and fusing point in the above tables is an example of a rule of fairly general applicability. We usually find that, when we compare similar substances, fusibility and solubility go together. If we consider a set of isomeric substances, for instance, we find that the order of solubility is usually the same as the order of fusibility, *i.e.* the most soluble isomer has the lowest melting point.

The order of the solubility of isomers is frequently independent of the nature of the solvent. Thus, if one of two isomers is more soluble in water than the other, it will still be the more soluble if alcohol, ether, benzene, etc., be the solvents employed instead of water. In some special cases, not only the order but even the ratio of the two isomers remains nearly the same for all solvents. For example, it has been found that meta-nitraniline is, on the average, 1·3 times more soluble than para-nitraniline in 13 different solvents, the ratio of solubility only varying from 1·15 to 1·48. It has also been found that the order of solubility of corresponding salts of isomeric acids is also very frequently the order of solubility of the acids themselves. It must be borne in mind, however, that these rules are all liable to well-marked exceptions.

CHAPTER XIV

RELATION OF PHYSICAL PROPERTIES TO COMPOSITION AND CONSTITUTION

THE properties of substances, when studied in relation to their composition and structure, have been divided into three classes. In the first class we have those properties which are possessed by the atoms unchanged, no matter in what physical or chemical state these atoms may exist. Such properties are called **additive**, and the best instance of an additive property is found in weight (or mass). Each atom retains its weight unaltered, whether it exists in the free state or whether it is combined with other atoms. When atoms combine, the weight of the compound is the sum of the weights of the component atoms. This is only another way of stating one of the fundamental assumptions of the atomic theory (Chap. II.), the assumption, namely, which takes account of the indestructibility of matter. Weight is the additive property *par excellence*, no other property being additive in the strict sense, although in the case of some properties there is an approximation to the additive character.

We have seen in homologous series that there exists between neighbouring members a difference in molecular volume which is practically constant. For a difference in composition of CH_2 there is the constant difference of 22 in the molecular volume, and this difference retains nearly the same value for all homologous series. We may therefore attribute the value 22 to the group CH_2, for whenever the methylene group enters a molecule the molecular volume is increased by this amount. Here we are evidently dealing with an additive property, but the additive character is modified by other influences, for the difference 22 is not absolutely constant, but fluctuates slightly about this value. It should be noted, also, that this number only holds good for the liquid state, for the measurements from which it is derived were all made at the boiling points of the liquid substances. By comparing the molecular volumes of liquids differing in composition in various definite ways, Kopp was able to establish a set of approximate rules such as the following :—

(*a*) When two atoms of hydrogen are replaced by one atom of oxygen, there is a very slight increase in the molecular volume.

(*b*) One atom of carbon may replace two atoms of hydrogen without sensible alteration of the molecular volume.

From these rules, in conjunction with the preceding one, we may draw the following deductions:—If the increase of molecular volume for CH_2 is 22, and if one atom of carbon is equivalent to two atoms of hydrogen, we may assign the value 11 to an atom of carbon, and the value $11 \div 2 = 5{\cdot}5$ to the atom of hydrogen. These values, then, are assumed to be the **atomic volumes** of carbon and hydrogen. Since there is a slight increase in the molecular volume when two atoms of hydrogen are replaced by one atom of oxygen which is attached to the same carbon atom, the atomic volume of oxygen must be somewhat greater than 11. On the average it is 12·1. It is found, however, that when hydrogen is replaced by hydroxyl, the increase of molecular volume is not 12·1, corresponding to the addition of one oxygen atom, but only about 7·8. When oxygen, therefore, is attached to one carbon atom, it contributes more to the molecular volume than when it is partially attached to carbon and partially to hydrogen. Here we come across an influence which modifies the additive character of all properties except weight, namely, the influence of structure or constitution. The molecular volume is not a purely additive property—it is in part **constitutive,** *i.e.* is dependent not merely on the number and kind of atoms in the molecule but also on their arrangement. We must therefore attribute to oxygen two atomic volumes—12·2 when it is attached to carbon so as to form the carbonyl group (CO), and 7·8 when it is part of the hydroxyl group, or is attached to two different carbon atoms, as in the ethers.

We are now in a position to deduce the molecular volume of a compound containing only carbon, hydrogen, and oxygen, by adding together the volume values of its constituent atoms. Thus, a compound of the formula $C_aH_bO_cO'_d$, where O′ denotes oxygen in a hydroxyl group, has the molecular volume

$$V = 11a + 5{\cdot}5b + 12{\cdot}2c + 7{\cdot}8d,$$

if the molecular volume is determined at the boiling point of the liquid. For example, in valeric acid, $C_4H_9 . CO . OH$, we have $a = 5$, $b = 10$, $c = 1$, $d = 1$, so that

$$V = 55 + 55 + 12{\cdot}2 + 7{\cdot}8 = 130.$$

The molecular volume as experimentally ascertained is 130·5. The agreement in the majority of cases is not so good, *e.g.* the molecular volume of ethyl oxalate found from the formula is 161, and that found by experiment 167. In this connection it must be remembered that Kopp's original rules are not strictly accurate, so that the deductions from them are always liable to slight error.

From the consideration of compounds containing other elements than those already referred to, values have been deduced for the atomic volumes of nitrogen, the halogens, sulphur, phosphorus, etc. Sulphur and nitrogen, like oxygen, have different values for the atomic volume according to the mode in which they are combined with other atoms.

When an element or radical exists in the liquid state, the molecular volume deduced from its compounds in general agrees with that of the free element or radical. Thus the volume of Br_2 deduced from bromine compounds would be 53·4, and the molecular volume of free bromine is actually 53·6. The value of NO_2 deduced from compounds containing it as a radical is 31·5, the value for the free oxide being 32·0.

No purely additive property can throw any light on the size of the molecule or its constitution, as each atom retains the numerical value of the property unchanged, whether it exists in the free state or whether it is combined with other atoms in any way whatever. As the value is therefore unaffected by the kind and extent of the combination, it can clearly give no indication as to what that mode or extent of combination may be (cp. Chap. XVIII. § 7). When the property is modified by constitutive influences, as is the case with the molecular volume of liquids, it may throw light on the constitution of a substance. Thus, if of two isomeric substances it were suspected that one contained an atom of carbonyl oxygen, whilst the other contained an atom of hydroxyl oxygen, that with the larger molecular volume would be the compound containing the carbonyl oxygen.

The **refractive power** of liquids is a property which, like the molecular volume, is in general additive in character, although modified by constitutional influences. The refractive index itself cannot be taken as a measure of the refractive power when its relation to the chemical nature of the substance is under investigation, for the index varies greatly with temperature, etc. A better measure is found in the specific refractive constant $\frac{n-1}{d}$, or $(n-1)v$, where n is the refractive index, d the density, and v the specific volume. This expression varies very slightly with the temperature, and is little influenced by the presence of other substances, so that it has frequently been used in the comparison of different liquids. Another specific refractive constant is given by the expression $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$, or $\frac{n^2-1}{n^2+2} \cdot v$, which was arrived at on theoretical grounds. When the values obtained by its aid are compared with the values of $(n-1)v$, it is found that they have an advantage over the latter, inasmuch as they are not only independent of the temperature, but also of the state of aggregation. With the empirical refraction constant there is considerable divergence between the values in the liquid and gaseous states, whilst the numbers obtained for the theoretical constant are the same in both cases. Thus for water at 10° we have

	$(n-1)v$	$\frac{n^2-1}{n^2+2} \cdot v$
Liquid	0·3338	0·2061
Gaseous	0·3101	0·2068

The **molecular refractive power** is the product of the molecular weight into the specific refractive power as measured by either of these expressions. Thus we have the "empirical" molecular refraction, $Mv(n-1)$, or $V(n-1)$, and the "theoretical" molecular refraction, $\frac{n^2-1}{n^2+2} \cdot Mv$, or $\frac{n^2-1}{n^2+2} \cdot V$. It is found that the molecular refraction of liquids as measured by either of the formulæ is essentially an additive property modified by constitutive influences, so that an atomic refraction for carbon, hydrogen, oxygen, chlorine, etc., may be calculated. If the refractive powers of each atom in the molecule be added together, the sum gives the molecular refraction of the compound. As is the case with the atomic volumes, different values have to be attributed to the atomic refraction of oxygen, according as it is carbonyl, or hydroxyl, or ether oxygen, a distinction in this case being necessary between the last two kinds which is not required for atomic volumes. When a substance contains an ethylene linkage, its atomic refraction is considerably higher than would be reckoned from the atomic refractions of the elements composing it; and when an acetylene linkage is known to exist in the molecule, the excess is even greater. "Atomic" refractions have therefore been attributed to "double bonds" and "triple bonds," which must be added to the atomic refractions of the elements themselves when the total molecular refraction is calculated.

Some liquids exhibit the phenomenon of **optical activity**—that is, when placed in the path of a polarised ray they rotate the plane of polarisation in one sense or the other. Substances which rotate the plane of polarisation in the direction of the hands of a watch are said to be dextrorotatory; substances which rotate it in the opposite direction are said to be lævorotatory. The **specific rotatory power** is usually denoted by the symbol $[\alpha]$, which is obtained by dividing the actual rotation observed in the polarimeter by the length of the layer of liquid through which the light passes, and by the density of the liquid at the temperature of observation. To obtain convenient numbers, the length is usually given in decimetres. The molecular rotation is the product of the specific rotation into the molecular weight, or more usually the hundredth part of this value, *i.e.*

$$[m] = \frac{M\alpha}{100dl} = V\frac{\alpha}{100l},$$

where α is the observed rotation, l the length of liquid, and d its density. It has been suggested that a better expression would be $[\delta] = \frac{\alpha}{l}\sqrt[3]{V}$, since we are obviously here concerned not so much with the molecular volume of the liquid as with the average distance between the centres of the molecules, the ray of light passing in a straight line through the liquid, and meeting a number of molecules proportional to the cube root of the molecular volume. Since the rotatory power varies with the temperature and with the wave length of the light employed, it is necessary to specify both of these in stating the value of the specific or molecular rotation.

When we inquire into the nature of liquids and dissolved substances which show optical activity, we find that they possess in every case one or more **asymmetric atoms** of carbon, tin, sulphur, or nitrogen, *i.e.* atoms which are directly united to elements or radicals all different from each other. If we imagine the four radicals attached to a carbon atom to be at the four corners of a tetrahedron, we find that we can arrange them in two essentially different ways, as is shown in the accompanying figures. Here the tetrahedra are supposed to be resting with one face on the paper, the summits being towards the reader. If we call the four different groups *a*, *b*, *c*, *d*, and place the group *d* at the summit, then in Fig. 22 the order *abc* is in the direction of the hands of a watch, and in Fig. 23 in the reverse direction. If two of the groups are made the same, the asymmetry vanishes, as we can see from the figures if we make $b = c$, for then the two figures become identical. No altogether satisfactory answer has yet been obtained to the question of what determines the value of the molecular rotation in any particular case. As we have seen, the rotation should vanish if two of the groups become identical, and it may also be perceived from the figures that if we interchange the positions of any two of the groups, the sign of the rotation will thereby be changed. If we suppose each of the groups to be endowed with some definite property causing the rotation, and denote the value of this function by α, β, γ, δ for the groups *a*, *b*, *c*, *d* respectively, the rotation of the asymmetric carbon atom must be

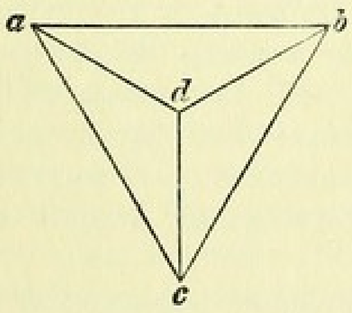


FIG. 22.

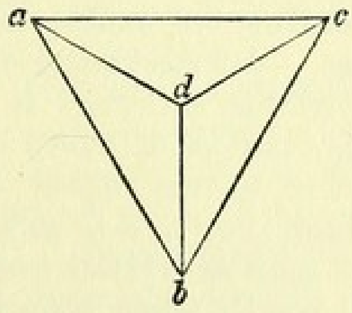


FIG. 23.

determined by an expression of the following or similar type:—

$$(\alpha - \beta)(\beta - \gamma)(\gamma - \delta)(\alpha - \gamma)(\alpha - \delta)(\beta - \delta).$$

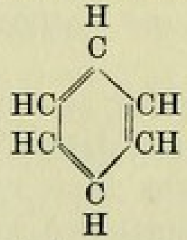
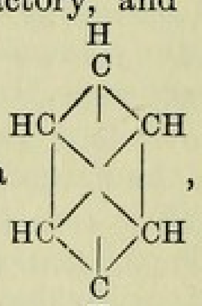
If the function becomes the same for two of the groups, the expression becomes zero, *i.e.* the rotation vanishes, and if we interchange any two throughout, the sign of the whole expression is changed, *i.e.* the rotation from dextrorotatory becomes lævorotatory, or *vice versa*. What the function is we do not know. It seems to be connected with the weight of the radicals, but cannot be the weight itself, since substances are known to be optically active which have two groups of equal weight attached to the asymmetric carbon atom. Certain regularities have been observed among the molecular rotations of members of homologous series, but numerous exceptions occur. Many of the apparent divergencies, however, may be accounted for by the assumption that different members of the same series may have different degrees of molecular complexity when in the liquid state (cp. Chap. XIX.).

Some crystalline substances, such as quartz, are optically active, but the activity here is not due to the arrangement of atoms within the molecule, but rather to a certain arrangement of the crystalline particles. A consequence of this is that the activity disappears when the crystalline structure is destroyed, *i.e.* when the substance passes into the fused or dissolved state. As a general rule, substances which are active in the liquid or dissolved state are not active when crystalline, but a few substances are known which exhibit optical activity both as crystals and as liquids.

All liquids when placed between the poles of a magnet or in the core of an electromagnet become optically active. The character of the **magnetic optical activity**, however, is essentially different from that exhibited by liquids which are naturally active. If we place a tube containing a naturally active liquid between the prisms of a polarising apparatus, and so adjust the prisms that no light passes through the system when we place a light-source at one end and the eye at the other; and if we then reverse the positions of the light-source and the eye, we find that the passage of the light is still obstructed. The sense and magnitude of the activity, then, are independent of the direction of the light. A naturally inactive liquid in a magnetic field behaves quite differently. If we first adjust the prisms so that no light passes, and then reverse the positions of eye and light-source, we find that light now traverses the system quite freely. We find, in fact, on readjusting the prisms to darkness, that a substance which appeared originally dextrorotatory is now to an equal extent lævorotatory. The difference in the nature of the activity may best be made clear by analogy. The action of a naturally active liquid resembles the action of a screw. If a screw is right handed (dextrorotatory) when viewed from one end of its axis, it is right handed when viewed from the other. A naturally active liquid if dextrorotatory when viewed from one end remains dextrorotatory though the direction of the light passing through it is reversed. The polarity of a magnetically active liquid resembles that of a muff. If the lie of the hair in a muff when viewed from one end of its axis is in the direction of the hands of a watch, it will be in the opposite direction if we view it from the other end of the axis. A magnetically active liquid is similarly dextro- or lævo-rotatory according to the direction in which the light passes through it, the magnetic field being supposed constant.

The **specific magnetic rotation** is usually given as the ratio of the specific rotation of the substance (determined as in naturally active liquids) to that of water under the same conditions: the molecular magnetic rotation is this value multiplied by the molecular weight of the substance and divided by 18, the supposed molecular weight of water. We find once more that when the molecular magnitudes for homologous substances are compared, there is a constant difference for the group CH_2, so that to this extent the property is an additive one. The constitutive influence, however, is much more marked here than in any of the previous instances; and the property is therefore valuable when applied to solving problems of constitution.

When a relation has been established between the constitution of well-known substances and the values of a certain property possessed by them, it is legitimate to draw inferences regarding the unknown constitution of other substances from the known value of this property in their case, the same rules being applied as to substances of known constitution. Of course, the worth of the deduction depends entirely on the number and variety of compounds which have been investigated, and on the exactness of the empirical rules established from the investigation. Melting points and boiling points, for example, are occasionally useful in indicating the probable structure of a compound, but it is seldom that the evidence based on them alone is to be treated with any degree of confidence. To take an instance in point, it was assumed that the decane dicarboxylic acid given in the table of melting points on page 141 has the normal structure, entirely on the strength of its melting point falling into the regular scheme displayed by the even members of the homologous series which are known to have the normal structure; for if its structure were not normal, it would in all probability have a melting point diverging widely from the scheme which included the members of the series which were known to be normal in reality. This evidence is slight, but for want of anything better it had a certain validity, although any well-established fact to the contrary would have been conclusive against it. It is now definitely known that the acid has the normal structure.

When the connection between the constitution and the value of a physical property is better marked and susceptible of being laid down in more definite rules, as is the case with the molecular refraction or magnetic rotation, greater confidence can be placed in the conclusions drawn from the value of the property in a particular compound as to the constitution of that compound. Great care, however, must be exercised in certain cases, for we are liable to draw conclusions which are not warranted by the facts. Thus, for example, from a consideration of the molecular refraction of aromatic compounds, it has been concluded that benzene has three ethylene linkings in the molecule, *i.e.* that Kekule's formula  is the correct one. Against this we must place the fact that benzene does not behave chemically as if it had a molecule containing three ethylene linkings, and at present the chemical evidence must be held to outweigh the evidence of the molecular refraction. The real difficulty in a case like this is that we can express the general chemical behaviour of the fatty compounds by means of three different kinds of carbon linking—simple, ethylenic, and acetylenic, all perfectly well defined chemically; whilst in the aromatic compounds we meet with something entirely new, and not readily brought into any of the above classes of carbon linking. How we are to represent this new kind of linking we do not at present know. Various attempts have been made, mostly based on the supposed properties of the tetrahedral carbon atom—some of them yielding ordinary static formulæ, some of them kinetic formulæ in which the carbon atoms are assumed to be in a state of constant vibration in a specified manner. These formulæ have all their peculiar merits and demerits. In view of the conflict of evidence, none can be held to be entirely satisfactory, and it may perhaps still be said that the least definite formula , which makes no assumptions as to the mode of linking of some of the bonds, is also the happiest in representing the known properties of aromatic compounds.

As we have seen in Chapter XIII., the molecular heat of combustion is essentially an additive property, though subject to modifications conditioned by differences in constitution. The modifications occasioned by changes of constitution are often very slight, so that as long as we are dealing with saturated compounds, it is found that isomeric substances have approximately the same heats of combustion. Thus for propyl alcohol we have 4986 K, and for isopropyl alcohol 4933 K;

for anthracene and phenanthrene, which both have the formula $C_{14}H_{10}$, we have 16,943 K and 16,935 K respectively. In other cases the differences are greater, but when substances of nearly the same character are considered, the differences are not of much importance. Unsaturated compounds exhibit great divergence from saturated compounds, and values have been attributed to the ethylene linkage and to the acetylene linkage. Conclusions, too, have been drawn as to the constitution of benzene from the heat of combustion. This amounts for benzene, C_6H_6, to 7878 K, the value for the isomeric substances, dipropargyl, $CH \vdots C.CH_2.CH_2.C \vdots CH$, and dimethyldiacetylene, $CH_3.C \vdots C.C \vdots C.CH_3$, being 8829 K and 8474 K respectively. Here the differences for the isomeric substances are great, owing to undoubted differences in the constitution—especially in the mode of linking of the carbon atoms. The exact nature of the differences in constitution corresponding to the differences in the heat of combustion is, however, as before, uncertain, for we have nothing but analogy to guide us, and are apt to assume that the rules that hold good for the fatty compounds have the same validity for aromatic compounds, which in all probability is not the case.

Some properties are exceedingly valuable in certain special cases for giving us an insight into the constitution of chemical compounds. For instance, if a new hydrocarbon displays optical activity, we know that in all likelihood it contains one or more asymmetrical carbon atoms, *i.e.* carbon atoms which are combined with four different kinds of atoms or groups of atoms; for all well-investigated optically active hydrocarbons have been proved to contain such asymmetric carbon atoms. Again, for organic acids we have the molecular conductivity in aqueous solution (cp. Chap. XXI.). This property, as we shall see, is closely related to the strengths of the acids, and also to their constitution. The molecular conductivity of acids varies with the strength of the solution in which they exist, and the actual variation is different according to the acid which is dissolved. There is a general rule, however, to which the variations for nearly all acids conform, and this enables us to calculate for each acid a constant independent of the strength of the solution whose conductivity is measured. It is this **dissociation constant** which is useful in the discussion of questions regarding the constitution of organic acids. In it there is scarcely a trace of an additive nature in the sense in which the term has hitherto been used. For example, the dissociation constants K for the fatty acids are—

		K.
Formic	$H.COOH$	0·0214
Acetic	$CH_3.COOH$	0·00180
Propionic	$C_2H_5.COOH$	0·00134
Butyric	$C_3H_7.COOH$	0·00149
Isobutyric	$C_3H_7.COOH$	0·00144
Valeric	$C_4H_9.COOH$	0·00161
Caproic	$C_5H_{11}.COOH$	0·00145

If we except the first number of the series, which as usual diverges from the others, we see that the constants have all approximately the same values, although constant additions are made to the molecule.

In the case of the normal dibasic acids of the oxalic series we have a very different table :—

		K.
Oxalic	$(COOH)_2$	10·0 (?)
Malonic	$CH_2(COOH)_2$	0·163
Succinic	$C_2H_4(COOH)_2$	0·00665
Glutaric	$C_3H_6(COOH)_2$	0·00475
Adipic	$C_4H_8(COOH)_2$	0·0037

Here the values of the constants sink steadily as the molecular weight increases, although the fall becomes less and less as we proceed. In the normal acids the carbon atoms are supposed to be linked to each other in a continuous chain. The two carboxyl groups are therefore at opposite ends of the chain. Now, in the fatty monobasic acids, in which there is only one carboxyl group, the addition of CH_2 has little influence on the dissociation constant. We therefore attribute the great diminution of the value in the series of dibasic acids to the increasing distance of the carboxyl groups from each other. In oxalic acid the carboxyl groups are directly attached, and their proximity is assumed to increase the dissociation constant. Each separate group has acid properties, and the two groups reinforce each other's acidity. In a higher member of the series, *e.g.* adipic acid, it is true that we have still two acid groups, but they are so far apart that we suppose them to have little reciprocal influence in increasing the acid properties. This mode of viewing the relation between constitution and dissociation constant leads on the whole to consistent results where the constitution has been well ascertained.

When chlorine replaces hydrogen in an organic acid, the strength of the acid, and with it the dissociation constant, is increased. Thus trichloracetic acid is very much stronger than acetic acid from which it is derived, being comparable in point of strength with the ordinary mineral acids. The dissociation constants of the chloracetic acids are shown in the following table :—

Acid.	Formula.	K.
Acetic	$CH_3 . COOH$	0·0018
Monochloracetic	$CH_2Cl . COOH$	0·155
Dichloracetic	$CHCl_2 . COOH$	5·14
Trichloracetic	$CCl_3 . COOH$	120

The replacement of hydrogen by chlorine obviously does not correspond to a constant addition to the dissociation constant, but rather to multiplication by a factor, although here the factor at successive stages diminishes.

The influence of other replacing atoms and groups is seen in the following derivatives of acetic acid :—

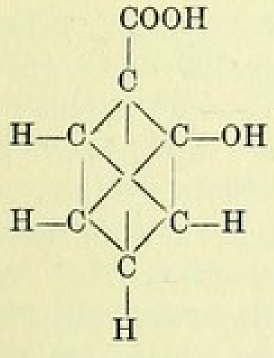
Acid.	Formula.	K.
Acetic	$CH_3 . COOH$	0·0018
Glycollic	$CH_2(OH) . COOH$	0·0152
Thioglycollic	$CH_2(SH) . COOH$	0·0225
Bromacetic	$CH_2Br . COOH$	0·138
Chloracetic	$CH_2Cl . COOH$	0·155
Malonic	$CH_2(COOH) . COOH$	0·163
Sulphocyanacetic	$CH_2(SCN) . COOH$	0·265
Cyanacetic	$CH_2(CN) . COOH$	0·370

From the table it appears that the influence of a chlorine atom is almost as great as the influence of another carboxyl group, although much less than the influence of a cyanogen group. Reasoning on the same lines as those adopted in treating the constants of the normal dibasic acids, we should expect that the farther removed any of these substituting atoms or radicals are from the the carboxyl group, the less will be their influence on the dissociation constant. This expectation is in general justified. We have, for example, the following constants for the hydroxyl derivatives of propionic acid :—

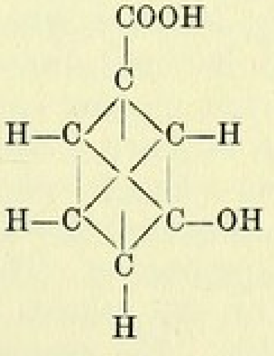
Acid.	Formula.	K.
Propionic	$CH_3 . CH_2 . COOH$	0·00134
β-Lactic	$CH_2(OH) . CH_2 . COOH$	0·00311
α-Lactic	$CH_3 . CH(OH) . COOH$	0·0138
Glyceric	$CH_2(OH) . CH(OH) . COOH$	0·0228

The influence of the hydroxyl group in the *α*-position is much more marked than the influence of the same group in the *β*-position. When there is a hydroxyl group attached to each carbon atom, the influence is greater still.

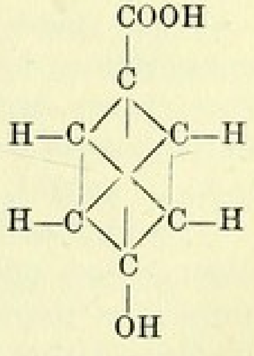
In the aromatic series we meet with peculiarities not easily explicable. Benzoic acid, $C_6H_5 . COOH$, has the constant 0·0060, whilst the three hydroxyl acids have the values given below :—



Salicylic.
K = 0·102



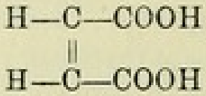
Metahydroxybenzoic.
0·0087



Parahydroxybenzoic.
0·0029

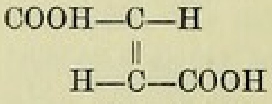
In the orthohydroxyl acid, where the carboxyl and hydroxyl groups are on neighbouring carbon atoms, we have a great increase over the value of the constant of the parent acid. In the meta acid the effect on the constant is comparatively slight. In the para acid, contrary to expectation, we have an actual diminution instead of an increase. It is obvious from a consideration of these results that very great caution must be exercised in drawing conclusions for aromatic bodies from rules derived from the study of fatty compounds.

The so-called geometrical or space isomerism is often accompanied with striking differences in the values of the dissociation constants. From the saturated dibasic acid, succinic acid, $COOH . CH_2 . CH_2 . COOH$, are derived two unsaturated acids, maleïc acid and fumaric acid, which both in all probability have the structural formula $COOH . CH : CH . COOH$. We often express the difference between these two acids by writing their formulæ thus :—



$$\begin{array}{l}\text{H—C—COOH}\\ \quad\ \|\\ \text{H—C—COOH}\end{array}$$

Maleïc acid.
K = 1·17



$$\begin{array}{l}\text{COOH—C—H}\\ \qquad\quad\ \|\\ \qquad\text{H—C—COOH}\end{array}$$

Fumaric acid.
K = 0·093

the difference corresponding to a supposed difference in the arrangement of the hydrogen and carboxyl groups on the carbon tetrahedra. The dissociation constants are much greater than that of succinic acid, and the constant of maleïc acid is twelve times that of fumaric acid. The above mode of formulation might lead us to expect such a difference, for in maleïc acid the two carboxyl groups are on the same side of the central plane, and in fumaric acid on different sides, and consequently more remote from each other.

From the purely chemical point of view, the investigation of the relationship between the value of physical properties and the constitution of chemical compounds is chiefly important as affording a means of ascertaining the otherwise unknown constitution of certain compounds by a determination of their physical constants. Too much reliance, however, should not be placed on this mode of settling chemical constitutions. The interpretation of the results is often doubtful, and that most frequently in cases where the determination of the constitution by chemical methods presents special difficulty. To sum up, we may say that the physical method usually offers valuable indications of the direction in which a chemical solution of the problem is to be sought, rather than a final solution of the problem itself.

Besides additive and constitutive properties, we have what have been called **colligative** properties. The numerical value of these properties depends only on the *number* of molecules concerned, not on their nature or magnitude. For example, if we take equal numbers of gaseous molecules of any kinds whatever, they will always occupy the same volume when under the same conditions (Avogadro's Law). The gaseous volume then is a colligative property. We make use of these properties in the determination of molecular weights, and they will therefore be further referred to under that heading.

CHAPTER XV

THE PROPERTIES OF DISSOLVED SUBSTANCES

If we ask ourselves the question: "To which state of aggregation is the state of a substance in solution comparable?" we find that there are only two answers admissible, viz. the liquid state or the gaseous state. It is obvious that when a solid is dissolved in a liquid it at once loses the properties which are characteristic of the solid state. Its particles become mobile, and all properties which depend on regular arrangement of particles disappear. Thus the solid may be a double-refracting crystal; its solution exhibits none of the phenomena of double refraction. It may be an optically active solid, and yet its solution may show no signs of optical activity. In such cases the passage of the substance into solution exhibits considerable analogy to the passage of the substance into the liquid state. A double-refracting crystal almost invariably loses its double refraction when it melts, and most substances which are optically active in the crystalline state are inactive after fusion. The analogy which here holds good between the dissolved and the liquid states might, however, be equally well applied to the dissolved and the gaseous states. It is true that the solution of a substance in a liquid solvent is itself a liquid, but it by no means follows that the state of the substance within the solution is accurately comparable to that of a liquid. Indeed, if we look a little more closely into the matter we find that in the case of dilute solutions, at least, there is far more likelihood of the dissolved substance being in a condition comparable with that of a gas.

One of the characteristic properties of a gas is its power of diffusion. If its pressure (or what is proportional to its pressure, its density or its concentration) is greater at one part of the space containing it than at another, the gas will move from the region of higher to the region of lower pressure or concentration, until by this process of diffusion the pressure or concentration is everywhere equalised. This process of diffusion goes on independently of the presence of another gas. A coloured gas such as bromine vapour may be seen to diffuse against gravity into another gas, say air, until the colour of the contents of the cylinder is everywhere of the same depth. The rate at which the diffusion takes place is, however, greatly influenced by the presence of another gas, the rate becoming rapidly less as the concentration of the other gas increases. This may be easily rendered evident by taking two cylinders, one evacuated, and one containing air, and breaking a bulb containing liquid bromine at the bottom of each. In the cylinder containing air the diffusion takes place slowly, an hour perhaps elapsing before the bromine vapour reaches the top of the vessel. In the evacuated cylinder the diffusion is apparently instantaneous. The particles of the foreign gas thus obstruct the movement of the particles of bromine, and render the process of diffusion slower.

Now, in the case of a substance in solution we have the same process of **diffusion** as we have with gases. If we take a solution of a coloured substance, such as bromine itself, or preferably a coloured salt like copper sulphate, and place it in the bottom of a cylinder, afterwards covering it with a layer of pure water, we find that the colour of the copper sulphate solution gradually rises in the cylinder, proving that the copper sulphate is moving from a region of greater concentration to a region of less or no concentration. In this case also the diffusion is against gravity, for the solution of copper sulphate if concentrated has a much higher specific gravity than water, so that the centre of gravity of the liquid will be raised as the copper sulphate becomes more uniformly distributed throughout it.

It is true that the diffusion of a dissolved substance is very much slower than the diffusion of a gas, months or even years elapsing before uniform concentration is attained in a cylinder not more than a foot high. But the difference is only a difference in degree, for it has been shown that gases under great pressures mix with extreme slowness against the action of gravity, many of the characteristic phenomena of the critical point, where the pressure is high, being obscured owing to this cause, unless the substances are mechanically mixed by stirring.

Even solids have the property of mixing by diffusion. Thus Roberts-Austen, who kept surfaces of gold and lead in contact during long periods at the ordinary temperature, was able after four years to detect the presence of gold in the layer of lead 7 mm. distant from the surface of contact. This phenomenon is quite in accordance with the conception of solid solutions to which reference has already been made (p. 74).

When we come to consider the arrangement of the particles of a substance in dilute solution relatively to each other, we again find a resemblance to the gaseous state, as in the case of chlorine water, for instance. Water at the ordinary temperature takes up about 2·2 times its volume of chlorine. As the dissolved chlorine is uniformly distributed in the solution, the average distance between the chlorine particles in the chlorine water is not very much less than the average distance between the particles in the chlorine gas; and if the chlorine water is only half saturated with chlorine, the distance between the particles is practically the same as the distance between the particles of the gas. So far, then, as the relative position of the particles of a gas and of the same substance in dilute solution is concerned, there is great similarity between the two states; and as the particles of a gas at low pressure have very little influence on each other, so we may suppose that the particles of a substance in dilute solution are mutually independent. If we ask what concentration of a solution is comparable to the concentration of a gas under ordinary conditions, we find that although the concentration is comparatively small, it is still such as may be frequently met with in ordinary laboratory work. A gram molecule of a gas at 0° and 760 mm. occupies 22·4 litres; a solution then containing a gram molecule of dissolved substance in 22·4 litres at 0° will be equally concentrated with a gas under standard conditions. This solution in the terminology of volumetric analysis is about twenty-second normal, and solutions twentieth or even fiftieth normal are by no means uncommon in volumetric work. There is therefore an *a priori* probability that the state of a substance in dilute solution resembles in some respects the state of a gas, and it would not be surprising, therefore, to find that dissolved substances obey laws comparable to the gas laws. In the sequel we shall see that this is actually true.

In order to get some idea of the **effect of the solvent** on a dissolved substance, we shall consider briefly some properties of substances which are easily measurable both for the substances themselves and for their solutions. It is evident that the properties most suited for study in this respect are those which are possessed by the dissolved substance alone and not by the solvent. We get a good example of such a property in the case of optically active liquids dissolved in optically inactive solvents. We can easily measure the specific rotation given by oil of turpentine, say, in the pure state and in various inactive solvents. If the solvent has no influence on the dissolved body, the specific rotation ought to remain the same whether the substance is in solution or whether it is in a state of purity. The specific rotation of lævorotatory oil of turpentine is 37·01°. Solutions containing 10 per cent of this substance dissolved in various solvents gave the following specific rotations, as calculated by the formula $[a]=\frac{av}{lp}$, where p is the number of grams of active substance in v cubic centimetres of solution (see p. 146):—

Solvent.	Specific Rotation.
Alcohol	38·49°
Benzene	39·45°
Acetic acid	40·22°

There is evidently here an action of the solvent, for these numbers are all different from the number obtained for the pure substance, and not only are they thus divergent, but they differ also from each other. The optically active liquid alkaloid, nicotine, shows the same behaviour in still more striking fashion. The specific rotation of the pure substance is 161·5°; the specific rotation of a 15 per cent solution in alcohol is 141·6°, and that of a 15 per cent solution in water is only 75·5°. Here the specific rotation of the nicotine sinks to less than half its original value when the substance is dissolved in about six times its own weight of water, so that we cannot avoid the inference that the water exercises some powerful influence on the nicotine dissolved in it. In the other instances given above the solvents also play an important part in modifying the properties of the substances dissolved in them, although to a less extent than is the case with nicotine; and it will be observed that each solvent exerts its own peculiar influence. The extent to which the rotatory power is affected by the solvent depends on the strength of the solution. The less of the active substance there is in the solution the more does its specific rotation diverge from the value for the pure substance. This may be seen in the accompanying diagram (Fig. 24), which gives the specific rotation of ethyl tartrate alone and in solutions of varying concentrations. The effect of water is again specially great, the specific

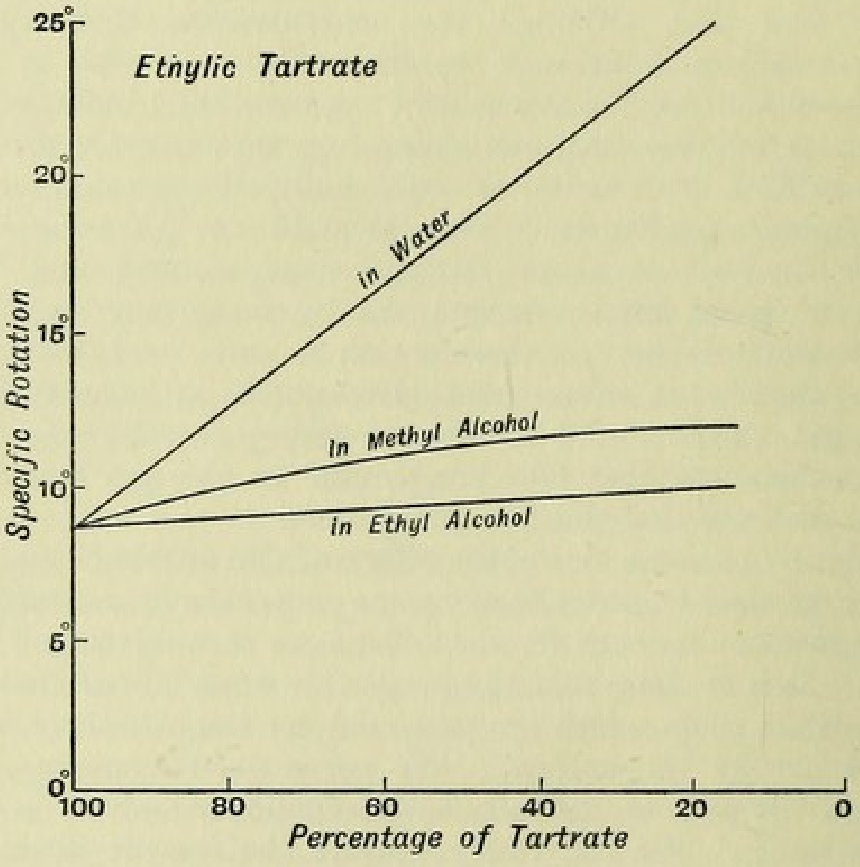


FIG. 24.

rotation in 14 per cent aqueous solution being three times as great as the rotation for the pure ester.

It has been suggested that the value of the specific rotation of the same substance in different solvents varies owing to a variation in the molecular complexity (Chap. XIX.) of the dissolved substances. Whilst this may be true in some instances, the explanation is not sufficiently wide to cover all the observed facts.

A curious regularity appears when we consider the rotations of aqueous solutions of different salts of optically active acids and bases. In order to obtain comparable numbers for the different salts, it is necessary to work, not with specific rotations, but with molecular rotations, *i.e.* the products of the specific rotation and the molecular weight. If we take, for example, the more soluble salts of camphoric acid, it appears that the value of the molecular rotation tends towards the same limit in each case as the dilution increases. This is clearly shown in Fig. 25, where the percentage strength of the solution is plotted on the horizontal axis, and molecular rotations on the vertical axis. The values for the molecular rotations are obtained by multiplying the specific rotations by the molecular weights, and dividing by 100 in order to get convenient numbers. The curves, which are wide apart at the higher concentrations, come closer and closer together as the strength of solution diminishes, and might ultimately meet in the same point at zero concentration. This final concurrence, however,

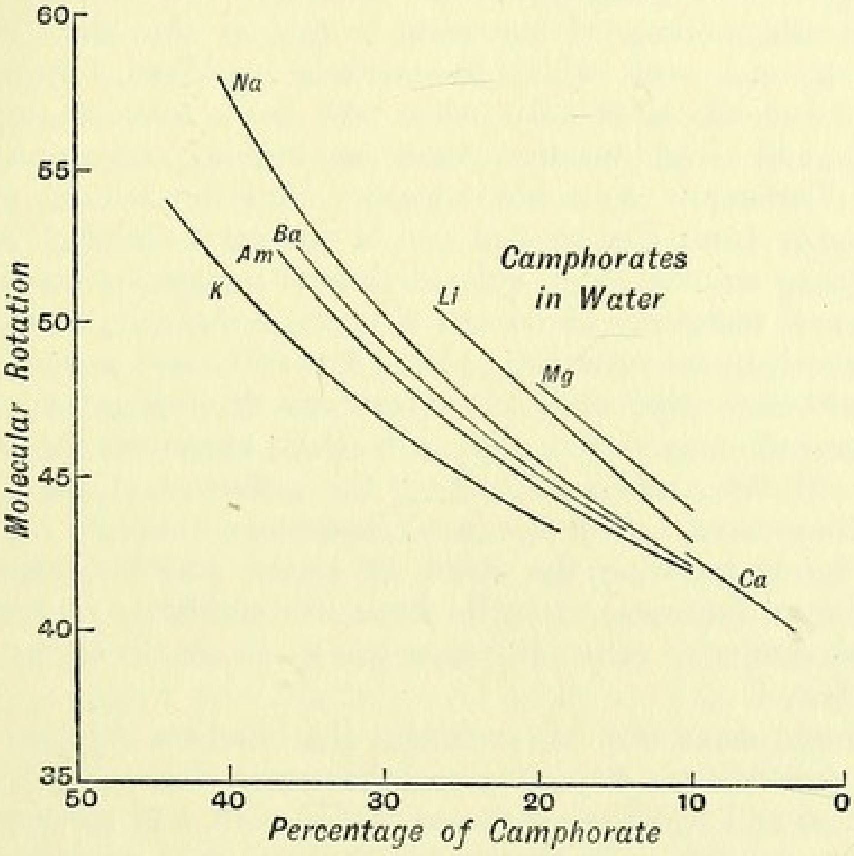


Fig. 25.

cannot be established directly owing to the difficulty of obtaining readings of sufficient exactness with very dilute solutions.[1] The same regularity appears with the soluble salts of other optically active acids, such as malic acid, tartaric acid, and quinic acid; and also with the soluble salts of optically active bases, such as the alkaloids quinine, cinchonine, etc. We may say then, in general, that the molecular rotation of the salts of an optically active acid or base always tends to a definite limiting value as the concentration of the solution diminishes. This regularity is known as **Oudemans' Law,** and we may now attempt its interpretation.

Taking the camphorates as our example, we note in the first place that the activity of the salts is due to the acid—the bases, potash, soda, etc., with which the acid is combined, being optically inactive. Indeed, it is only when we have such a combination of active acid with inactive base, or active base with inactive acid, that Oudemans' Law holds good. Now the salts of camphoric acid, to judge from the general run of the curves in Fig. 25, would in very strong solution have quite divergent molecular rotations; and this we know definitely to be the case with the salts of malic acid, some of which in strong solution have a positive and some a negative rotation, although their rotations at extreme dilution are all negative. Where the influence of the solvent is least, therefore, the salts have different molecular rotations; where the influence of the solvent is greatest, they have nearly the same molecular rotation. The water therefore tends to bring the acidic, or active, portion of the salts in some way into the same state, for from the similarity of rotation we must argue similarity of condition, as this is no chance agreement, but a general law.

This might come about in several ways, but here we shall consider only one possibility. Suppose that the water decomposed the salts into free acid and free base progressively as more and more water was added to the solution. In the strong solutions only a relatively small proportion of the gram-molecular weight of the salt will be decomposed, so that the total molecular rotation will be made up of a relatively small rotation for the free acid, and a relatively large rotation for the acid still bound up with the base in the form of salt. As the different salts have different rotations, their strong solutions will differ considerably in their molecular rotations, as the total rotation is here due mostly to the salt. It is quite different with dilute solutions in which, on our assumption, the salt is almost entirely decomposed into free acid and free base. Here the total rotation is due almost wholly to the acid in each case, the undecomposed salt contributing very little to the total; so that no matter what the salt is,

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[1] The salts of α-bromosulphocamphoric acid have a very high rotatory power, and it is therefore possible to investigate them in centinormal aqueous solutions. At this dilution the molecular rotations of the soluble salts are identical.

the value of the molecular rotation will be the same. The assumption, then, of the progressive decomposition of the salt into acid and base under the influence of the solvent water would thus account for the phenomena of molecular rotation in dilute solutions; but it is on other grounds an improbable one, and fails to explain the numerical value of the limiting molecular rotation for the following reason. A consideration of the curves of Fig. 25 shows that if they intersect on the line of zero concentration at all, it will be at a value of about 39°. This value, therefore, would be on the above assumption the molecular rotation of camphoric acid in dilute solution; but the value actually found for a solution of camphoric acid of 0·6 per cent strength is 93°, an altogether different number. We must therefore conclude that the supposition of a decomposition into acid and base by the water is untenable, and endeavour to find another explanation. It will be seen that the essence of the explanation attempted above is the assumption of the independence of the inactive basic and the active acidic portion of the salt in dilute solution. If on any hypothesis of the action of the water we can suppose that the active negative part of the salt is removed from the influence of the inactive positive part of the salt as the dilution increases, we have a sufficient explanation of the constancy of the molecular rotation in weak solutions, and it only remains to select such a hypothesis as shall conform with the other properties of dilute solutions, and give a rational account of the numerical value of the limiting rotation. We shall meet with such a hypothesis in a later chapter.

When we deal with properties which are possessed by solvent and dissolved substance alike, it is more difficult to ascertain definitely if the property of the dissolved substance has been changed by the fact of its having passed into solution. As a rule we find that the sum of the values of the property for substance and solvent is not the value for the solution. For example, the volume of solvent and solute is never exactly equal to the volume of the resulting solution, although in some instances, such as cane sugar and water, this is nearly the case. Very frequently we find that solution is accompanied by contraction in volume. When water and alcohol are mixed in equal measures there is a contraction of about 3 per cent of the total volume. This shrinkage may be due to a change in the specific volume of the water or the alcohol, or both, so that it is by no means easy to apportion the total volume change between the two substances. Even when we take a solution and dilute it by adding more of the solvent, we generally find that a change of volume occurs, a contraction on dilution being the usual result (cp. Chap. XVIII. § 7).

There is an undoubted regularity in the density of aqueous salt solutions. If we consider, for example, the density of normal solutions of a number of salts, we find that the difference in density between a chloride and the corresponding bromide is constant; that the difference between a chloride and the corresponding sulphate is constant; in short, that the difference between corresponding salts of two acids is approximately constant, no matter what the base is with which the acids are combined. On the other hand, we find that the difference in the densities of equivalent solutions of corresponding salts of two bases is always the same, and independent of the acid with which they are united. Examples are given in the following table, where the densities are those of normal solutions:—

	Cl	Br	I	$\frac{1}{2}SO_4$	NO_3
K	1·0444	1·0800	1·1135	1·0662	1·0591
NH_4	1·0157	1·0520	1·0847	1·0378	1·0307
Difference	0·0287	0·0280	0·0288	0·0284	0·0284

	K	Na	NH_4	$\frac{1}{2}Sr$	$\frac{1}{2}Ba$
NO_3	1·0591	1·0540	1·0307	1·0811	1·1028
Cl	1·0444	1·0396	1·0157	1·0667	1·0887
Difference	0·0147	0·0144	0·0150	0·0144	0·0141

From a consideration of this table, it is evident that we can obtain the density of the normal solution of any salt by adding to the density of a salt chosen as standard two numbers, or moduli, one of which is characteristic of the base of the salt, and the other characteristic of the acidic portion of the salt. This regularity is known as Valson's **Law of Moduli.** Valson chose ammonium chloride as his standard, because its normal solution had the smallest density of any of the salts he investigated.

The moduli for the principal series of salts are given below:—

NH_4	0·0000	Cl	0·0000
K	0·0296	Br	0·0370
Na	0·0235	I	0·0733
$\frac{1}{2}Ba$	0·0739	NO_3	0·0160
$\frac{1}{2}Ca$	0·0282	$\frac{1}{2}SO_4$	0·0200
$\frac{1}{2}Mg$	0·0221		
$\frac{1}{2}Zn$	0·0410		
$\frac{1}{2}Cu$	0·0413		
Ag	0·1069		

If these moduli are added to the density of normal ammonium chloride solution, viz. 1·0153, the densities of the other normal salt solutions are obtained, the values holding good for 18°. Thus, if we wish to know the density of an equivalent normal solution of copper sulphate, we add to 1·0153 the modulus of copper plus the modulus of the sulphates, viz. $0·0413 + 0·0200$, and obtain 1·0766 as the result, in good accordance with the experimental number.

Not only is the law of moduli valid for normal solutions, but also for solutions of other (moderate) concentrations, the moduli being multiplied by the strength of the solution expressed in terms of a normal solution as unity, and then added to the density of the ammonium chloride solution of corresponding strength. We have the following values for the densities of various ammonium chloride solutions, which can be used as standards :—

Normality.	Density.
1	1·0153
2	1·0299
3	1·0438
4	1·0577

Should we wish to know the density of a thrice normal solution of calcium bromide, we add to 1·0438 three times the sum of 0·0282 and 0·0370, viz. 0·1956, and obtain 1·2394, the value actually found by experiment being 1·2395.

It is found that other properties of salt solutions besides the density are susceptible of similar treatment by the method of moduli. One salt solution is taken as standard, and from the value for it the values of the others may be obtained by adding the modulus for the acidic portion and the modulus for the basic portion of the salt under consideration. It will be observed that, strictly speaking, the optical rotations of dilute salt solutions are treated by means of moduli. If we take an inactive salt as standard, we can get the value of the rotation of any salt by adding together a modulus for the acidic and a modulus for the basic portion of the salt. Thus if we compare in the case of the camphorates dilute solutions of equivalent strengths, we find that their rotations are all practically the same, and equal to what we may term the modulus for the acidic portion of the salt, the moduli for the different inactive basic portions being all equal to zero.

From what has been said above, it will appear already that the properties of a substance in general undergo an alteration when the substance is dissolved in a liquid. The question as to whether the process of solution is to be regarded as chemical or physical has been much discussed, and this alteration in the value of well-defined properties has led many chemists to the conclusion that solution must be classed amongst the chemical processes. There can be no reasonable doubt that the dissolved substance and the solvent react on each other so as to influence each other's properties, but at present we are without any satisfactory theory as to the origin or nature of this influence, and even without empirical regularities, except in a few special cases, to enable us to say in any given instance how the influence is most likely to become apparent. On the other hand, if we look upon dilute solutions with respect to volume, pressure, and temperature relations as affecting the dissolved substance, we find we can neglect the influence of the solvent altogether, and still obtain simple laws of the most general applicability, as will be shown in the succeeding chapters.

T. S. Patterson, "Influence of Solvents on the Rotation of Optically Active Compounds," *Journal of the Chemical Society* (1901), **79**, 167, 477 ; (1902), **81**, 1097, 1134.

CHAPTER XVI

OSMOTIC PRESSURE AND THE GAS LAWS FOR DILUTE SOLUTIONS

We have seen in the preceding chapter that in some respects there is considerable analogy between the state of a substance existing as gas and the state of a substance in dilute solution. In the present chapter it will be shown that the analogy is more than superficial, and that laws exist for substances in dilute solution which are quite comparable with the simple laws for gases. These gas laws (cp. Chap. IV.) connect together the volume, pressure, and temperature of the gaseous substances to which they apply, so that we have first to consider what we are to understand by the volume, pressure, and temperature of a substance in solution. The temperature of a substance in solution is evidently the temperature of the solution itself. The volume of a gas we take to be the volume in which the substance as gas is uniformly distributed. Now the volume in which a dissolved substance is uniformly distributed is the volume of the solution, so that this volume corresponds to gaseous volume. There still remains to find for solutions the analogue of gaseous pressure. In the case of gases, the pressure we consider is that on the walls of the containing vessel, and may be measured directly. With substances in solution it is different: here the pressure on the walls of the containing vessel is not the pressure of the dissolved substance, but is the gravitational pressure of solvent and solute combined. If we could exactly counteract the force of gravitation, there would be no pressure of the liquid on the walls of the vessel at all. There is therefore for substances in dilute solution no obvious magnitude corresponding to gaseous pressure; and yet, until this magnitude was discovered, no progress was made in the theory of dilute solutions.

An experiment with gases will serve to show in what direction the analogue of gaseous pressure might be sought. In the case of the liquid solution we have two substances, and we wish to estimate the pressure of one of them. Can we in the case of a mixture of two gases find a method for measuring directly not only the total pressure of the two gases, but the partial pressure contributed by one of them?

There is a theoretical method by means of which we can do this, and experiments have been made which go far to confirm the theory. Suppose that of two gases, *A* and *B*, one of them, *B*, can pass through a certain diaphragm, whilst *A* cannot. Let the gas *A* be enclosed in a vessel made of the material through which *A* cannot pass, and let the vessel be connected with a manometer which will measure the pressure of the gas within it. Suppose that the original pressure of *A* within the vessel is half an atmosphere, and let the vessel and its contents be immersed in the gas *B*, whose pressure is maintained steadily at one atmosphere. The gas *B* by supposition can pass freely through the material of which the vessel enclosing *A* is constructed, and it will do so until its pressure inside the vessel is equal to its pressure outside the vessel, viz. one atmosphere. For, if there is to be equilibrium between the gas inside the vessel and the same gas outside the vessel, there must be no difference of pressure of *B* throughout the whole space which it occupies, for the gas *A* exerts no appreciable influence on *B*. Inside the vessel there is now a total pressure of one and a half atmospheres, one atmosphere being the partial pressure of *B*, and half an atmosphere being the partial pressure of *A*, which has remained constant at its original value, owing to the impermeability of the vessel to this gas. Outside the vessel we still have the pressure of one atmosphere, so that the internal pressure registered when equilibrium occurs is half an atmosphere greater than the pressure outside the vessel. The excess of pressure inside is evidently due to the gas *A* which cannot pass through the diaphragm, so that, by taking the difference in pressure on the two sides of the diaphragm, we obtain the partial pressure of the substance to which the diaphragm is impermeable. It is not an easy matter to get a diaphragm which is quite permeable to one gas, and quite impermeable to another; but palladium at a moderately high temperature fulfils the conditions fairly well. Palladium has the property of absorbing hydrogen at ordinary temperatures, and parting with the absorbed gas again when heated in a vacuum to temperatures above 100°. It exhibits this behaviour with regard to no other gas, so that at temperatures of about 200° it forms a diaphragm permeable to hydrogen, but impermeable to gases such as nitrogen, carbon monoxide, or carbon dioxide. Experiments have been made with one of these gases inside a palladium tube, and an atmosphere of hydrogen at known pressure outside the tube. Theoretically, one would expect the internal pressure to increase by an amount equal to the external pressure of hydrogen. This was found to be nearly but not quite the case, the actual increase amounting in different experiments to from 90 to 97 per cent of the theoretical increase. Still the result is close enough to show that this method of measuring the pressure due to one substance in a mixture might be applied in other cases with success.

Let us now deal with a liquid solution, say a solution of cane sugar in water. If we could procure a **semipermeable diaphragm** of the proper kind, *i.e.* one which would be permeable to water and impermeable to sugar, we might be in a position to ascertain the pressure in the solution due to the presence of the sugar, and find how it varied with the concentration of the solution, the temperature, etc.

Pfeffer, the plant physiologist, while working at the osmotic phenomena in vegetable cells, prepared various membranes which proved to be perfectly permeable to water, and impermeable to some substances dissolved by the water. Such membranes had been previously discovered by Moritz Traube, who, however, did not give them such a form as to permit of accurate work being done with them. They are essentially precipitation membranes, and their formation can be easily studied on a small scale. If a solution of copper acetate is added to a solution of potassium ferrocyanide, a chocolate-brown precipitate of copper ferrocyanide is produced; and if the two solutions are brought together very carefully, mechanical mixing being avoided, the precipitate assumes the form of a fine film or membrane separating the two, and impermeable to both the dissolved substances. The experiment may be carried out in the following fashion, which was proposed by Traube. A piece of narrow glass tubing about 6 inches in length is left open at one end, and closed at the other by means of a piece of rubber tubing provided with a clip. Into this tube a few drops of a 2·8 per cent solution of copper acetate are sucked up, by compressing the rubber beneath the clip with the fingers and then releasing it. The tube is now lowered into a test-tube containing a few cubic centimetres of a 2·4 per cent solution of potassium ferrocyanide. If the liquid in the inner tube forms a plane surface at its mouth, which can be secured by a slight movement of the rubber tubing, the copper ferrocyanide is deposited as a fine transparent film which closes the opening of the tube. That diffusion of the dissolved salts is prevented by this membrane is evident from the fact that the membrane remains transparent and of excessive tenuity for a very considerable period, showing that the copper and potassium salts no longer come into contact. A substance such as barium chloride, which is easily recognisable in small quantities, may be added to one of the membrane-forming solutions, best to that which is to be placed in the inner tube, and it will be found that even when gravitation would aid the mixing, none of the barium chloride passes through the septum.

Whilst these experiments show the possibility of existence of membranes permeable to a liquid solvent and not to certain substances which might be dissolved in it, they are of no use for an investigation into the pressure exercised by dissolved substances, for the films are so delicate as to be ruptured by very slight pressures or mechanical disturbance. Pfeffer solved the problem by depositing such films in the pores of unglazed vessels of fine earthenware, such as those employed in experiments on the diffusion of gases. This he did by placing one of the membrane-forming solutions in the inside of the porous pot and the other solution outside. The two solutions gradually penetrating the wall from opposite directions, at last meet in the interior of the wall, and there deposit a semipermeable film across the pores in which they meet. The film, although as delicate in this as in the former case, is now capable of withstanding a much higher pressure, on account of the support which the material of the porous cell affords it. If the film is to be exposed to high pressures, great precautions have to be taken in its preparation, so as to avoid all possibility of rupture of the membrane; but if it is merely desired to show the phenomena qualitatively, it may be done simply as follows.

The most convenient form of porous vessel to use is that of a bulb provided with a neck into which a rubber stopper may be inserted. These bulbs are used in gas diffusion experiments, and need no further preparation than washing and soaking for a day in running water. The neck of the bulb is dried and coated inside and outside with melted paraffin wax, which is allowed to solidify. A solution of copper sulphate (2·5 grams per litre) is introduced into the bulb up to a level above the bottom of the paraffin coating, and the bulb is then placed in a beaker, into which is poured a solution of potassium ferrocyanide (2·1 grams per litre) until the bulb is immersed up to the neck. After standing for some hours the bulb is taken out of the solution, emptied, and rinsed with water. If now the bulb is filled with a strong solution of sugar, and placed in pure water, the water will pass into the interior through the semipermeable membrane. This is best seen by inserting into the neck a well-fitting stopper through which passes a length of narrow glass tubing open at both ends. As the water passes into the interior of the bulb, the solution rises in the narrow glass tube, and the pressure on the inner surface of the semipermeable diaphragm increases. Owing to the resistance the water experiences in passing through the fine pores of the bulb the process is a slow one, but in the course of an hour a rise of several inches may be noted, and in twenty-four hours the solution may have risen from six to ten feet in the tube. As a rule, the membrane prepared in this way without any special precautions being taken, breaks down when the pressure exceeds ten feet of water, and the level of the liquid no longer rises.

With a perfect membrane capable of resisting high pressures it becomes a question when the increase of pressure within the bulb will come to an end. Pfeffer devoted his attention to this question, and attained the following results. For a given solution the pressure rises slowly until a certain maximum value is reached, after which the pressure remains constant. This maximum pressure, called by Pfeffer the **osmotic pressure,** varies with the nature of the dissolved substance. The following table contains the maximum pressures in centimetres of mercury observed for one per cent solutions of the undernoted substances :—

Cane sugar	47·1
Dextrine	16·6
Potassium nitrate	178
Potassium sulphate	193
Gum	7·2

The pressure was found to be dependent on the strength of the solution, being very nearly proportional to the concentration of the solution, as may be seen from the following table for cane sugar, concentrations being given in percentages, and pressures in centimetres of mercury :—

Concentration.	Pressure.	Ratio.
1	53·5	53·5
2	101·6	50·8
2·74	151·8	55·4
4	208·2	52·1
6	307·5	51·3

For potassium nitrate the ratios are less constant :—

Concentration.	Pressure.	Ratio.
0·80	130·4	163
1·43	218·5	153
3·3	436·8	133

As the concentration increases, the ratio of pressure to concentration here diminishes, but Pfeffer showed that this was really due to the membrane not being perfectly impermeable to potassium nitrate, a small quantity of the salt escaping, especially at the higher pressures, so that the proper maximum was never reached.

Temperature also influences the maximum pressure, as the following results with a one per cent sugar solution serve to show :—

Temperature.	Pressure.
6·8°	50·5
13·2	52·1
14·2	53·1
22·0	54·8

There is obviously here a regular increase of pressure with rise of temperature.

All these experiments were made by Pfeffer in 1877, but it was not until 1887 that van 't Hoff published a complete theory of dilute solutions which takes them as its experimental basis. The semipermeable membrane furnishes us with a means of directly measuring a pressure due to the presence of the dissolved substance, so that we may take it as the analogue in dilute solutions of gaseous pressure in gases. It should be noted that this pressure does not necessarily depend for its existence on the presence of a semipermeable diaphragm, but is only rendered evident and measurable by its means.

We are now in possession of all the magnitudes necessary to enable us to investigate the pressure, volume, and temperature relations of substances in dilute solutions, and to compare the numerical results of the investigation with the corresponding relations for gases. The pressure we consider is the osmotic pressure; the temperature is the temperature of the solution; and the volume is the volume occupied by the solution.

Pfeffer's results show, in the first place, that the osmotic pressure at constant temperature is proportional to the concentration of the solution, *i.e.* to the amount of substance in a given volume. In other words, the osmotic pressure of a given quantity of substance is inversely proportional to the volume of the solution which contains it. Here, then, is a law in perfect analogy to Boyle's law for gases: the volume varies inversely as the pressure.

Let us now consider the **effect of temperature** on the osmotic pressure, the volume of the solution remaining constant. As we have seen, the osmotic pressure increases with the temperature just as gas pressure does. To determine the exact amount of the increase, Pfeffer made special experiments, with the following results:—

Cane Sugar.

Temperature C.	Temperature Abs.	Osmotic Pressure.
14·2	287·2	51·0
32·0	305	54·4 (54·2)
15·5	288·5	52·1
36·0	309·0	56·7 (55·8)

Sodium Tartrate.

Temperature C.	Temperature Abs.	Osmotic Pressure.
13·3	286·3	143·2
36·6	309·6	156·4 (154·9)
13·3	286·3	90·8
37·3	310·3	98·3 (98·4)

From these figures it is evident that there is a close proportionality between the absolute temperature of a given solution and its osmotic pressure. In each pair of experiments the osmotic pressure at the higher temperature has been calculated from the experimental value of the osmotic pressure at the lower temperature, on the assumption that the osmotic pressure is proportional to the absolute temperature, and the calculated value has been placed within brackets alongside the pressure actually measured. The difference between the observed and calculated values is not greater than the error of experiment. Here, then, we have another law exactly comparable to the law for gaseous substances: If the volume is kept the same, the pressure is proportional to the absolute temperature (cp. p. 28, Law 3).

Combining these two laws for dilute solutions, we may now say that the product of the osmotic pressure and the volume is proportional to the absolute temperature, *i.e.* we may write the equation

$$pv = RT$$

for substances in dilute solution as well as for gases, and it only remains now to find how the constant R is related to the corresponding constant for substances in the gaseous state. On p. 30 we calculated the value of this constant for a gram molecule of a gas, and we shall now proceed to evaluate it from Pfeffer's data for a gram molecule of sugar dissolved in water.

For a one per cent solution of cane sugar at 0° Pfeffer observed that the osmotic pressure was 49·3 centimetres of mercury. This corresponds to a pressure of $49 \cdot 3 \times 13 \cdot 59$ gram centimetres (cp. p. 3). The gram-molecular weight of cane sugar is 342, and consequently the volume of a one per cent solution containing the gram-molecular weight is nearly 34,200 cubic centimetres. The absolute temperature of the solution is 273, so that we have for the constant—

$$R = \frac{49 \cdot 3 \times 13 \cdot 59 \times 34{,}200}{273} = 83{,}900,$$

a value practically identical with the value obtained for the gas constant, which in the same units we found to be 84,700.

So far, then, as pressure, temperature, and volume relations are concerned, the analogy between gases and substances in dilute solution is complete. The identity of the constant in the two cases shows that the osmotic pressure of a dissolved substance is numerically equal to the gaseous pressure which the substance would exert were it contained as a gas in the same volume as is occupied by the solution. In fact, if we imagine that the solvent is suddenly annihilated, we should have the osmotic pressure on the semipermeable membrane replaced by a gaseous pressure of equal magnitude. This similarity between gaseous and dissolved substances is of the utmost importance, for it enables us to transfer to dissolved substances conclusions arrived at from the consideration of the temperature, volume, and pressure relations of gases. For example, it at once enables us to determine the molecular weights of dissolved substances from simultaneous measurements of the temperature, volume, and osmotic pressure of the solution, just as the molecular weights of gases and vapours are determined from similar magnitudes. The accurate measurement of osmotic pressure is an experimental task of the utmost difficulty, and has been attempted by only one or two investigators, so that molecular weights can hardly be determined directly in this way. There are, however, other magnitudes, susceptible of easy and exact measurement, which are known to be proportional to the osmotic pressure, and these are now made use of for molecular-weight determinations, as will be shown in a subsequent chapter.

In osmotic pressure we can recognise the **cause of diffusion** of substances in solution. Just as in gases we have movement from regions of higher to regions of lower pressure, so in solutions we have movement from regions of higher osmotic pressure to regions of lower osmotic pressure. Osmotic pressure, then, we take to be the driving force in solutions, and if we calculate its value, we find it to be very considerable. Thus the osmotic pressure of a normal solution is over 22 atmospheres (cp. p. 157), or 330 lbs. per square inch. In spite of this high driving power, the process of diffusion in solution is, as we have seen, a very slow one. It has been calculated that the force necessary to drive a gram of dissolved urea through water at the rate of 1 cm. per second is equal to forty thousand tons weight. The resistance, then, which the water offers to the movement of the dissolved substance is enormous. This we must take to be due to the smallness of the dissolved particles. A substance in the state of fine dust may take many days to settle, even in a perfectly still atmosphere, while the same weight of substance in the compact state would fall to the ground in as many seconds. The driving force in the two cases is the same, namely, the gravitational attraction of the earth for the given substance, but the resistance which the air offers to the small particles is incomparably greater than that offered to the compact mass.

It should be borne in mind that the osmotic pressure in a solution may be regarded as always present, whether a semipermeable membrane renders it visible or not. The osmotic pressure in the ordinary reagent bottles of the laboratory is of the dimensions of 50 atmospheres. This pressure is of course not borne by the walls of the bottle, nor is it apparent at the free surface of the liquid. Where the liquid comes in contact with the enclosing vessel, there we find a liquid surface, and a consideration of the magnitude of the forces at work in the phenomena of surface tension leads us to believe that the pressure at right angles to the free surface of a liquid, and directed towards the interior of the liquid, is measurable in hundreds and even thousands of atmospheres. Osmotic pressures, then, large as they are in ordinary solutions, are small compared to the surface pressures in liquids, and their existence is consequently not evident at the free surface of liquids. It is only when these surface pressures are got rid of that we can measure osmotic pressures directly. The liquid solvent can easily penetrate the semipermeable membrane, so at the semipermeable membrane there is not in the ordinary sense a liquid surface, and consequently there is no surface pressure of the ordinary type. This continuity of the liquid through the semipermeable partition gives us, therefore, the opportunity of determining differences of internal pressure in the solution and the solvent.

Various hypotheses have been put forward to explain the nature of osmotic pressure, but none of them can be accounted satisfactory. They are based upon more or less probable suppositions as to the nature of the movement of the dissolved molecules, the degree of attraction between them and the particles of the solvent, the capillary phenomena in the "pores" of the semipermeable partition, and the like. Our ignorance of such matters is, however, so great that no profitable conclusions have hitherto been arrived at.

One thing may be said about osmotic pressure which is independent of any supposition as to its nature, and has indeed been already indicated in what has preceded. The osmotic pressure of any solution is independent of the **nature of the semipermeable membrane.** Pfeffer tested several membranes besides membranes of copper ferrocyanide. For example, membranes of Prussian blue or of tannate of gelatine can be deposited in a porous cell in the manner described for copper ferrocyanide, and have a similar action with regard to water and substances held by it in solution. Pfeffer found that in general the osmotic pressure of any one solution varied with the nature of the membrane he employed, but this was in reality due to the membranes not being perfectly impermeable to the dissolved substance, so that the maximum pressures recorded did not correspond to the actual osmotic pressure, but fell short of it in a degree dependent on the extent to which the membrane leaked. A theoretical proof may be given that the nature of the membrane does not influence the value of the osmotic pressure provided that it is perfectly impermeable to the dissolved substance. Suppose two membranes to exist, one of which, A, generates with a given solution and solvent a higher osmotic pressure than the other membrane B. If the pressure in the vessel containing the solution is less than the osmotic pressure, liquid will flow through the membrane from solvent to solution; if it is greater than the osmotic pressure, liquid will flow from the solution to the solvent. Let the solution, solvent, and diaphragms be combined into one working system, as in the figure. If the solution is originally at a greater pressure than corresponds to the value of the osmotic pressure generated by B, solvent will flow out through the diaphragm, and the pressure inside will diminish and tend to reach this value. But as soon as the pressure diminishes to a value less than the osmotic pressure generated by A, solvent will flow through A into the cell. The pressure inside will still be too great for B, and solvent will therefore continue to flow out. There will thus be a continuous flow of solvent

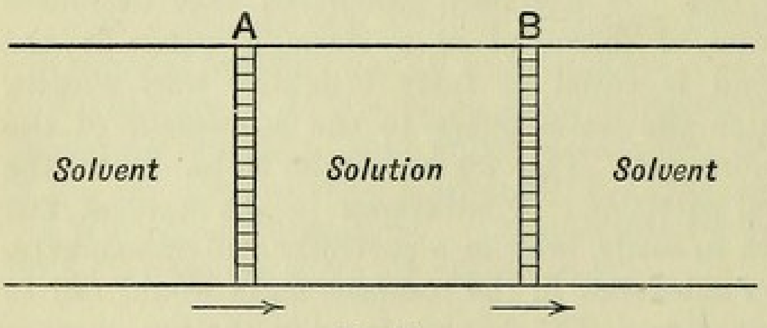


Fig. 26.

through the cell from left to right, and as the conditions are not changed by this transference, the flow might go on indefinitely and the current be made use of to perform work, *i.e.* in this way we could obtain a perpetual motion (cp. Chap. XXVIII.). Since this is impossible, our assumption that the osmotic pressures generated by the two diaphragms are different must be incorrect, and we are forced to conclude that the osmotic pressure of a solution is independent of the diaphragm used in measuring it, provided that the diaphragm is completely impermeable to the dissolved substance.

Although the direct measurement of osmotic pressure is surrounded by so many difficulties, it is often possible to tell whether a solution has an osmotic pressure greater than, equal to, or less than another solution of the same or a different substance. This may be done either with the aid of a precipitation membrane such as Traube employed, or by means of a natural semipermeable membrane. When a precipitation membrane is formed at the end of a tube as described above, the two solutions which form the precipitate have in general different osmotic pressures. But the solvent water moves through the membrane from the solution with less to the solution with greater osmotic pressure. If the solution outside the cell has the greater concentration it gains water, becomes more dilute in the immediate neighbourhood of the membrane, and rises in the external liquid owing to its lesser specific gravity. This is easily rendered visible by means of a Töpler apparatus, which detects very small differences in the refractive power of liquids. If the external solution has a smaller osmotic pressure than the internal solution, water will be transferred inwards through the membrane, and the external solution will become more concentrated in the neighbourhood of the membrane, the change betraying itself by differences in density and refractive power as before. If, finally, the two solutions have equal osmotic pressures, no transference of water takes place, and there is consequently no change in the density or refraction of the solutions. We have here, then, a method for determining when two membrane-forming solutions are isosmotic, or **isotonic**, a term sometimes applied to solutions having the same osmotic pressure.

A method making use of natural semipermeable membranes is the following. It is known that the protoplasm of vegetable cells has a sort of skin which serves to a certain extent as a semipermeable membrane, for it keeps dissolved substances in the cell sap from passing outwards, while it admits of the free passage of water. If the protoplasm of the cell then is brought into contact with pure water or a solution of smaller osmotic pressure than the cell contents, water will pass through the skin inwards to the protoplasm. If, on the other hand, the cell content has a smaller osmotic pressure than the solution with which the protoplasm is brought into contact, water will pass outwards through the skin. Should the external solution finally have the same osmotic pressure as the solution within the protoplasmic skin, there will be no transference of water between the cell and the external solution. In the case of some cells, the passage of water to or from the protoplasm is easily visible on account of the apparent increase or diminution of the volume. Thus when a suitable vegetable cell is brought into contact with a solution of higher osmotic pressure than that of the solution within the protoplasm, the granular or coloured cell contents are seen to shrink away from the cell wall owing to the loss of water and contraction in volume which they experience. By diluting the external solution, it is easy to find a concentration which just ceases to produce this contraction; then the cell contents are isotonic with this solution. In the same way, a solution of another substance may be found which is isotonic with the same cell. These two solutions are then isotonic with each other. This last statement is proved by experiments which show that two solutions which have been found to be isotonic with respect to one kind of cell are also isotonic with regard to other kinds of cell. In this again we have an indication that the nature of the membrane has no influence on the osmotic pressure, if only it is impermeable to the dissolved substance.

In what follows it will practically always be assumed that the osmotic pressure of a solution is strictly proportional to its concentration. This is by no means always an exact relation, and really holds good only for somewhat dilute solutions. The reason is of course not far to seek. As has been already stated above, some of the ordinary laboratory solutions have osmotic pressures of nearly 100 atmospheres. Now, concentration of a solution corresponds to absolute density in the case of a gas. Boyle's law for gases states that the pressure of a gas is proportional to its absolute density, or inversely proportional to its volume, which is the same thing. But this by no means necessarily holds good for pressures as high as 100 atmospheres. We cannot expect, then, that the corresponding law for solutions—that the osmotic pressure is proportional to the concentration—will be exactly true at similar high osmotic pressures. In general, we can expect no exact proportionality between osmotic pressure and concentration at strengths above normal, and we very often find that much more dilute solutions have to be considered in order to get the simple laws to apply in strictness.

An account of the preparation of osmotic cells for exact measurements will be found in the following papers:—

R. H. ADIE, "On the Osmotic Pressure of Salts in Solution," *Journal of the Chemical Society*, 1891, **59**, p. 344; H. N. MORSE and J. C. W. FRAZER, *American Chemical Journal*, 1902, **28**, p. 1.

CHAPTER XVII

DEDUCTIONS FROM THE GAS LAWS FOR DILUTE SOLUTIONS

In discussing the evaporation and solidification of solutions in Chapters VIII. and IX., we have met with empirical laws which find a theoretical basis in the conception of osmotic pressure. Such are the law that the vapour pressure of a solution is less than the vapour pressure of the pure solvent by an amount proportional to the strength of the solution (p. 84); that the boiling point of a solution is higher than the boiling point of the solvent by an amount proportional to the strength of the solution; and that the freezing point of a solution is slower that the freezing point of the solvent by an amount proportional to the strength of the solution.

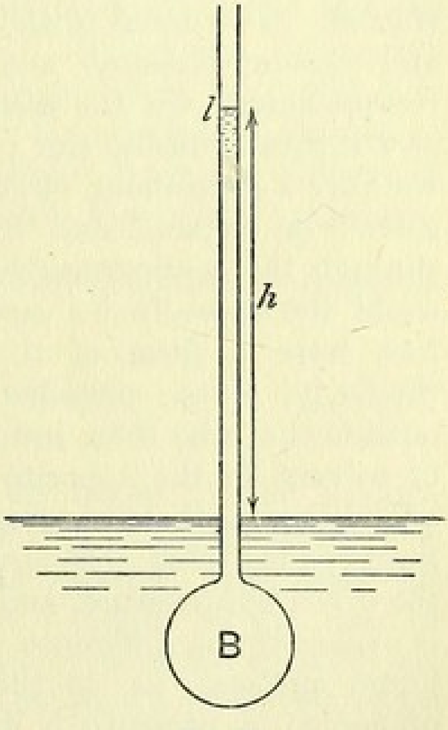


Fig. 27.

The more strict thermodynamical deduction of these relations from the gas laws for dilute solutions is given in Chapter XXVIII., but in this chapter we can show, at least approximately, the relations of the various magnitudes. In the first place, we shall consider the connection between osmotic pressure and the relative lowering of the vapour pressure.

In the figure (Fig. 27) B represents a porous bulb with a semi-permeable membrane deposited within the wall (p. 167). It is filled with a known solution and immersed in the pure solvent. The solvent will enter the bulb until the solution in the tube rises to a height where the difference of level of the liquids inside and outside the bulb causes a pressure equal to the osmotic pressure of the solution. Let this equilibrium be reached in an atmosphere which consists only of the vapour of the solvent, and let the difference in level be represented by *h*. The temperature throughout is supposed to remain at the constant value T on the absolute scale.

In the first place, we note that the pressure of vapour at the level l of the surface of the solution must be the same inside and outside the tube. If it were not, being, let us assume, greater inside than outside, vapour would pass from the region of higher to the region of lower pressure. This would lower the pressure of vapour immediately over the surface of the solution, and some of the solvent would therefore evaporate in order that the pressure should regain its former value, which is the value in equilibrium with the solution. The original value outside the tube is the value corresponding to the vapour pressure of the pure solvent, so that the accession of vapour from the inner tube would increase the pressure of vapour above its equilibrium value, and consequently some of the vapour would condense at the surface of the pure solvent. The process would be then, in short, that some of the liquid inside the tube would distil over and condense to liquid outside the tube. This would evidently increase the concentration of the solution within the bulb, and so we should no longer have osmotic equilibrium between the solution and the solvent. To restore the osmotic equilibrium, some of the solvent would pass inwards through the membrane and dilute the solution to its original concentration. The liquid in the tube would then regain its original height and vapour pressure, and the whole process of distillation would recommence. On the assumption, then, that the pressure of vapour at l is greater inside the pressure tube than outside at the same level, we have a continuous circulation of solvent from the solution to the solvent as vapour, and from the solvent to the solution as liquid through the semipermeable membrane. The current thus generated could theoretically be used to perform work, and we should therefore have a form of the perpetual motion, which is impossible. Similarly, if the pressure at the level l is supposed to be greater outside the tube than inside, we should have a continuous circulation of solvent in the opposite direction. The conclusion which we must adopt, then, is that the pressure within and without the tube at the same level l is the same. If now f is the vapour pressure of the solvent at the given temperature, and f' that of the solution, the difference $f-f'$ is evidently the difference of pressure between the levels at the two liquid surfaces, *i.e.* at the top and bottom of the height h. This difference in pressure is due to the weight of the column of vapour between the two levels on a surface of one square centimetre, and is equal to the product of the height and absolute density of the column of vapour, *i.e.* to hd, if d is the density expressed in grams per cubic centimetre.

Let us now consider a gram-molecular weight of this vapour. For it we have

$$pv = RT,$$

where R is the ordinary gas constant. But the density d is the weight divided by the volume, *i.e.* $d = M/v$, where M is the molecular weight of the solvent in the gaseous state. The pressure of the gaseous solvent is f, so that we obtain $v = RT/f$, and

$$d = \frac{fM}{RT}.$$

We have seen above that $f - f' = hd$, or, substituting the value of d here found, $f - f' = h \cdot \frac{fM}{RT}$, whence

$$\frac{f - f'}{f} = h \cdot \frac{M}{RT}.$$

Now $f - f'$ is the lowering of the vapour pressure of the solvent, and $\frac{f - f'}{f}$ is therefore the proportional or **relative lowering**, with which we are alone concerned. We have thus obtained an expression for the relative lowering of the vapour pressure in terms of the "osmotic height" h, and constants for the gaseous solvent. It is now an easy matter to express h in terms of the osmotic pressure of the solution, and another constant for the solvent.

The osmotic pressure, *i.e.* the excess of pressure inside the cell over that outside, is equal to the height of the column h into the absolute density of the liquid. This we may denote by s, which is the absolute density of the pure solvent, for if the solution considered is very dilute, its density will not greatly differ from the density of the solvent. We have, then, if p represents the osmotic pressure, $p = hs$, or $h = \frac{p}{s}$. Substituting this value of h in the previous equation, we obtain

$$\frac{f - f'}{f} = p \cdot \frac{M}{sRT}. \qquad (1)$$

Here the relative lowering is expressed in terms of the osmotic pressure of the solution and magnitudes referring to the solvent, which for constant temperature are constant. It appears, then, that the relative lowering of the vapour pressure of a liquid by the solution in it of some foreign substance is at any one temperature proportional to the osmotic pressure of the solution and independent of the nature of the dissolved substance.

By making use of the gas laws for solutions we can eliminate temperature from the above expression, and put it in a simpler form. If we express the concentration of the solution in the form that n gram molecules of the solute are contained in W grams of the solvent, then we have for n gram molecules the equation

$$pv = nRT.$$

Now the volume in which these n gram molecules are contained is equal to W, the weight of solvent, divided by s, the density of the solvent, *i.e.* $v = W/s$, so that

$$p = \frac{nsRT}{W}.$$

Substituting this value in the former equation, we obtain

$$\frac{f-f'}{f} = \frac{nsRT}{W} \cdot \frac{M}{sRT},$$

or

$$\frac{f-f'}{f} = \frac{n}{W} \cdot M. \tag{2}$$

The relative lowering is now expressed in terms of the concentration of the solution and the molecular weight of the solvent in the gaseous state, which is constant. The temperature has, according to this result, no influence on the value of the relative lowering—a conclusion which is in accordance with the experimental data. For a given weight of any one solvent, the relative lowering is proportional to the number of molecules of dissolved substance in solution. Consequently, if we find that for certain quantities of different substances, dissolved in the same weight of the same solvent, the relative lowering of the vapour pressure of the solvent is the same, we conclude that these quantities contain the same number of dissolved molecules, and thus we obtain a method for determining the molecular weights of substances in solution. The molecular weight of a dissolved substance might also be calculated in terms of the relative lowering of the vapour pressure by finding the numerical value of p from equation (1), and introducing the osmotic pressure thus obtained into the gas equation.

For a given amount of the same substance dissolved in the same weight of different solvents, we find from equation (2) that the relative lowering is proportional to the molecular weight of the solvent in the gaseous state, provided that the molecular weight of the dissolved substance remains the same in the different solvents.

The expression for the relative lowering receives a still simpler form if, instead of the actual weight of the solvent, we introduce the number of gram molecules of the solvent. The weight of solvent may be expressed as the product of the number of molecules into the gram-molecular weight of the substance in the gaseous state, *i.e.* as MN, if N represents the number of gram molecules of the solvent as gas. We have therefore

$$\frac{f-f'}{f} = \frac{n}{MN} \cdot M,$$

or

$$\frac{f-f'}{f} = \frac{n}{N}. \tag{3}$$

The relative lowering is here given as the ratio of the number of dissolved molecules to the number of molecules which the solvent would produce if it were converted into vapour.

It must be emphasised that the number of molecules N in the above equation does not denote the number of liquid molecules in the solvent, but only the number of *gaseous* molecules derivable from the liquid. This caution is necessary, because it has frequently been supposed that the equation enables us to determine the molecular weight of the *liquid* solvent, which is not the case. As we shall see, methods exist for determining the molecular weights of liquids, but this is not one of them.

In deriving the above equations, we have assumed that the specific gravities of the solutions considered are the same as the specific gravities of the respective solvents. This assumption only holds good for very dilute solutions, but it gives serviceable approximations in practical work, as the following numerical examples will show:—

A solution of 2·47 g. of ethyl benzoate in 100 g. of benzene showed a relative lowering of vapour pressure equal to 0·0123, *i.e.* if the vapour pressure of pure benzene is 1, the vapour pressure of the solution is $1 - 0·0123$. The temperature at which the determination was made was 80° C., and at this temperature the density of benzene is 0·812. The molecular weight of gaseous benzene is 78. If we substitute these values in equation (1), we obtain

$$0·0123 = p \cdot \frac{78}{0·812 \times 84{,}700 \times (273 + 80)},$$

whence $p = 3830$ g. per square centimetre, or over 3·7 atmospheres.

If we wish to calculate the molecular weight of ethyl benzoate from these data by means of equation (2), we get by substitution

$$0·0123 = \frac{n}{100} 78,$$

whence $n = 0·0158$, *i.e.* in 2·47 g. of benzoate of ethyl there are 0·0158 gram molecules. There is therefore one gram molecule of dissolved ethyl benzoate in $2·47/0·0158 = 156$ g., or 156 is the molecular weight of ethyl benzoate when it is dissolved in benzene. It must be remembered that this number is only approximate, but still it is sufficient to show that the molecular weight of the dissolved substance is practically that of the gaseous substance, which is 150. Equation (3) leads to the same result, for in order to get the number of molecules N we have to divide the number of grams taken, viz. 100, by the molecular weight, viz. 78.

The determination of the lowering of vapour pressure is somewhat too difficult and tedious to be of much use in fixing the molecular weights of dissolved substances, and it is therefore preferable to ascertain in its stead the **elevation of the boiling point**, which is for dilute solutions nearly proportional to it, and susceptible of easy and rapid determination. As a solution of a non-volatile substance at a given temperature has a lower vapour pressure than the pure solvent, it is evident that in order that the solution and solvent may have the same vapour pressure, *e.g.* equal to the standard atmospheric pressure, it is necessary to heat the solution to a higher temperature than the solvent. The boiling point of the solution is therefore always higher than the boiling point of the solvent. A consideration of the accompanying diagram (Fig. 28) will show that for small changes, the lowering of the vapour pressure and the elevation of the boiling point are nearly proportional.

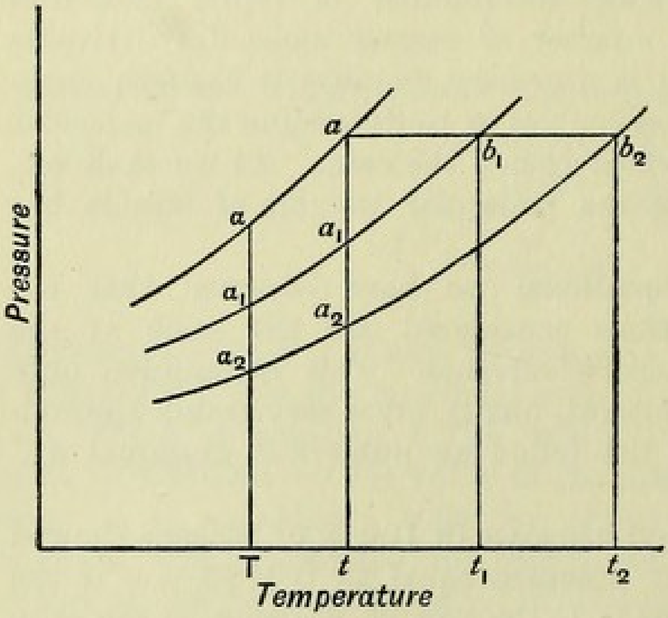


FIG. 28.

In the figure the three curved lines represent the vapour pressure curves of a pure solvent and of two solutions of different concentrations. At the temperature t, the intercept aa_1 represents the actual lowering of the vapour pressure of the solution 1, and the ratio $aa_1 : ta$ the relative lowering. For the temperature T we have the corresponding magnitudes $\alpha\alpha_1$ and $\alpha\alpha_1 : \mathrm{T}\alpha$. Since for any one solution the relative lowering is independent of the temperature, we have $aa_1 : ta = \alpha\alpha_1 : \mathrm{T}\alpha$. Similarly for the second solution $aa_2 : ta = \alpha\alpha_2 : \mathrm{T}\alpha$, so that $aa_1 : aa_2 = \alpha\alpha_1 : \alpha\alpha_2$, or $aa_1 : a_1a_2 = \alpha\alpha_1 : \alpha_1\alpha_2$. If the curves were straight lines, they would in virtue of these proportions meet in one point, but if we only consider the very small lowerings observed in dilute solutions, their directions are so nearly the same that they may in small intervals be treated as parallel straight lines. Consider the line ab_2 parallel to the temperature axis. This is a line of constant vapour pressure, and cuts the curves at points corresponding to the temperature t_1 and t_2. The intercepts ab_1 and ab_2 represent the elevations of the boiling point, if the boiling point at the atmospheric pressure is t. Now if the curves were parallel straight lines we should have $aa_1 : aa_2 = ab_1 : ab_2$, *i.e.* the elevation of the boiling point would be proportional to the lowering of the vapour pressure, and thus also to the osmotic pressure.

Another easily determinable magnitude which is proportional to the osmotic pressure is the **depression of the freezing point** in dilute solutions. By means of a diagram similar to the above we can show that this depression is approximately proportional to the lowering of the vapour pressure, and thus indirectly establish the connection with osmotic pressure. In the figure (Fig. 29) $a0$ represents the vapour pressure curve of the liquid solvent, say water, and $a0'$ that of the solid solvent, ice. The temperature t, where these two curves intersect, is the freezing point of the pure solvent (cp. p. 104). The curves 1 and 2 represent as before the vapour-pressure curves of two solutions. These cut the ice curve at two points, b_1 and b_2, the corresponding temperatures t_1 and t_2 representing the freezing points of the two solutions, *i.e.* the temperatures at which ice and the solutions are in equilibrium, and at which, therefore, they have the same vapour pressure. Now as before we may treat the curves 0, 1, and 2 as three parallel straight lines if we only consider small intervals. We have then $aa_1 : aa_2 = ab_1 : ab_2 = tt_1 : tt_2$. But tt_1 is the depression of the freezing point for the solution 1, and tt_2 the depression for the solution 2. Consequently, we have the depressions of the freezing point proportional to the lowerings of the vapour pressure, aa_1 and aa_2. The freezing-point depressions are thus proportional in dilute solutions to the osmotic pressures of the solutions, and can therefore be substituted for the latter in ascertaining molecular weights.

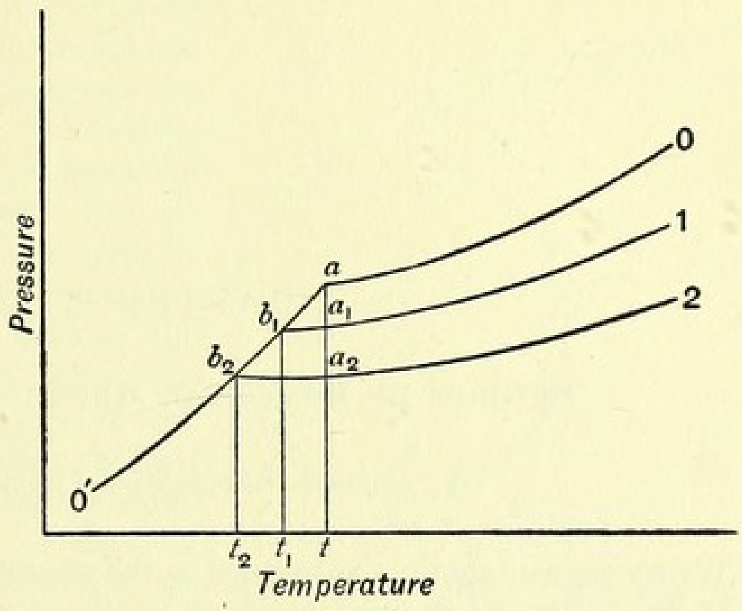


FIG. 29.

It has now been shown on approximate assumptions that

$$\text{Elevation of boiling point} = cP,$$

and

$$\text{Depression of freezing point} = c'P,$$

where P is the osmotic pressure, and c and c' constants. These constants remain in each case the same for a given solvent, and are valid for all dissolved substances. They correspond in their nature to the constant factor on the right-hand side of equation (1) in this chapter. They depend on the properties of the solvent, and their derivation from these properties will be shown in Chapter XXVIII.

CHAPTER XVIII

METHODS OF MOLECULAR WEIGHT DETERMINATION

1. *Gaseous Substances—Vapour Density*

WHEN we can obtain a substance in the gaseous state, the determination of its molecular weight resolves itself, as we have seen in Chapter II., into ascertaining what weight of the vapour in grams will occupy 22·4 litres at 0° and 760 mm., or, if we deal with smaller quantities, what weight in milligrams will occupy 22·4 cc. In general, we cannot weigh these volumes of the vapour under the standard conditions. In the case of water, for example, it is impossible to get a pressure of 760 mm. of vapour at 0°, the vapour pressure of water at that temperature being only a few millimetres of mercury. We can, however, make the actual determination under any conditions we please, and then reduce to the standard conditions by means of the gas laws.

The practical problem to be solved, then, in vapour-density determinations for the purpose of finding molecular weights is to measure the weight, volume, temperature, and pressure of a given amount of substance in the gaseous state. This may be done in various ways, as the following short description of the principal methods will show.

Dumas's Method.—In this method the weight of a known volume of gas or vapour is determined, a globe of known capacity being filled with the gas at atmospheric pressure and known temperature, sealed off, cooled, and weighed. The volume of the globe is ascertained by weighing it when empty and when filled with water. Its weight when filled with air minus the weight of air contained in it (which can be calculated from the volume and the known density of air) gives the weight of the empty globe. This, when subtracted from the weight of the globe filled with the gas under investigation, gives the weight of that gas which fills the given volume at the given pressure and temperature. The method, when applied to the vapours of substances liquid at the ordinary temperature, usually assumes the following form: The bulb is of 50 to 100 cc. capacity and has the shape shown in the figure (Fig. 30). Several grams of the liquid substance are placed in the bulb, which is then immersed in a bath of constant temperature about 20° higher than the boiling point of the liquid. The liquid in the bulb boils and expels the air with which the bulb was originally filled. After the vapour ceases to escape from the narrow neck of the bulb, this is sealed off near the end with a small blowpipe flame. There is then in the bulb a known volume of vapour at a known temperature and pressure, so that all that has now to be done is to ascertain the weight of the vapour. This method is somewhat troublesome, and is usually applied to substances which are only volatile with difficulty.

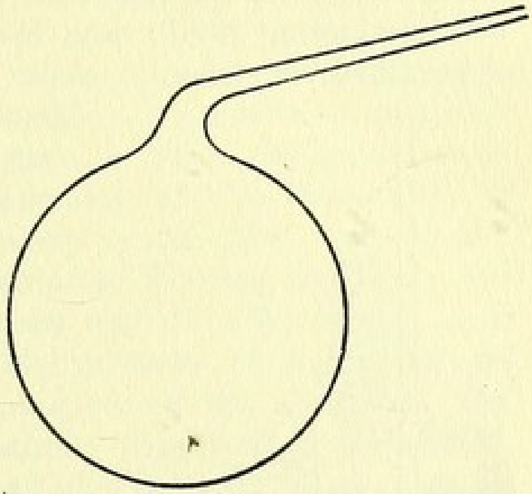


FIG. 30.

Hofmann's Method.—Here, instead of taking a known volume of vapour and measuring its weight, we take a known weight of substance and measure the volume which it occupies as vapour, and the pressure which the vapour exerts. The apparatus employed for the purpose is shown in Fig. 31. It consists of an inner tube about a yard long and half an inch in bore, which is graduated in cubic centimetres. This is filled with mercury, and inverted in a mercury trough so that at the top of the tube a Toricellian vacuum is formed. Outside this tube is a wider tube which acts as a vapour jacket, the vapour of a boiling liquid passing in through the narrow tube *d*, and issuing, together with the condensed liquid, through the side tube just above the mercury. A weighed quantity of the liquid, the density of whose vapour is to be determined, is introduced into the inner tube in a bulb or very small stoppered bottle made for the purpose, and containing only about a tenth of a cubic centimetre. The inner tube is then heated by the vapour from a liquid boiling in a suitable vessel attached to *d*, the boiling being continued until the vapour issues freely from the lower tube and the level of the mercury in the inner tube no longer alters. The weighed quantity of substance has now been converted into vapour, and occupies the volume

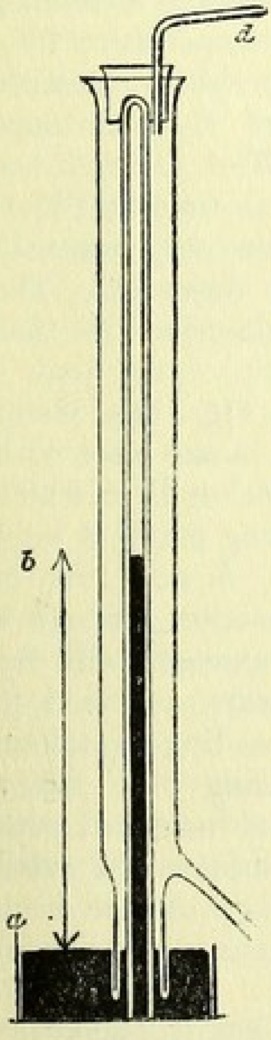


FIG. 31.

above the mercury at the top of the graduated tube, at the boiling point of the liquid used for heating, and under a pressure equal to the atmospheric pressure minus the height of the column of mercury *ab*.

The external liquid used for heating the inner tube to a constant temperature is usually water. This evidently will vaporise any liquid with a boiling point under 100°, but in reality it can be used for liquids with much higher boiling points, for the vaporisation takes place in the inner tube under reduced pressure. Thus a liquid such as aniline, with a boiling point of 180°, is easily vaporised in the Hofmann apparatus by boiling water, if the quantity taken is such that the vapour only occupies a small proportion of the total volume of the graduated tube.

Variable Pressure Method.—In this method a known weight of substance is vaporised at known temperature in a constant volume, and the rise in pressure due to the conversion of the substance into vapour is noted. The method has been proposed from time to time by different investigators, but has only recently received the attention it deserves. The form of apparatus here described is that employed by Lumsden.

The vaporising bulb A (Fig. 32), of about 100 cc. capacity, is blown in one piece with the surrounding vapour jacket B, in which a liquid of suitable boiling point is kept in a state of ebullition. A side tube of narrow bore makes connection through a three-way tap with the manometer CE, the mercury of which is always adjusted to the mark E before a reading is taken. The neck of the vaporising bulb has a diameter of 8 mm., and is furnished with a short side-tube for the insertion of a glass rod to support the small bottle containing the weighed substance. The neck is protected from undue heating by a shield of asbestos paper (not shown in the figure) which rests on the top of the vapour jacket.

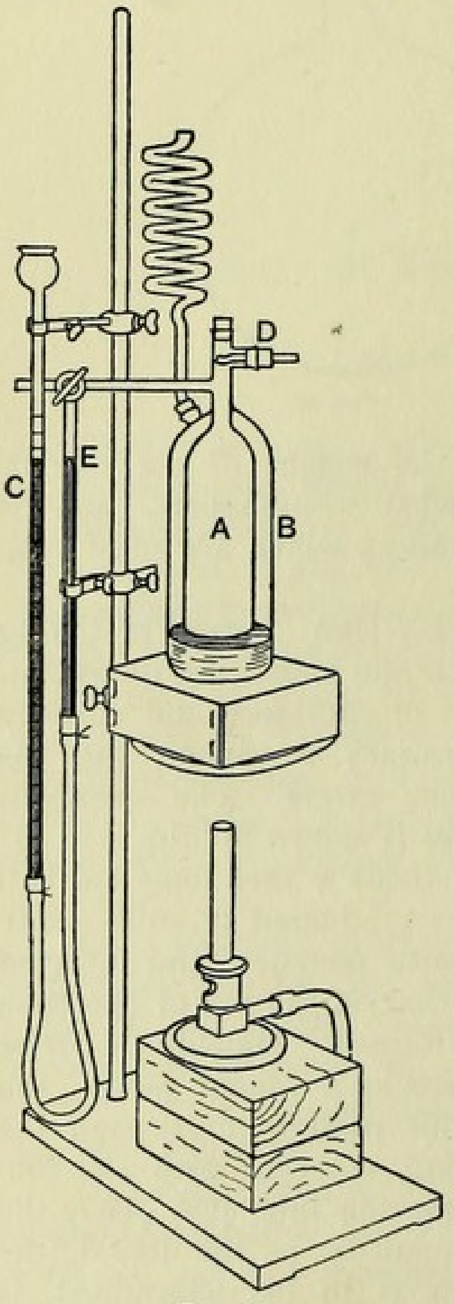


Fig. 32.

To perform an experiment the liquid in the jacket is boiled for fifteen minutes by means of a bunsen flame, which plays on the wire-gauze bottom of the asbestos box in a hole in the top of which the vapour-jacket rests. The temperature is then constant and the mercury is adjusted to the mark E, all parts of the apparatus having free connection with the air through the three-way tap. The capsule containing the substance is then placed on the support at D, a rubber stopper inserted into the neck of the flask, and the tap turned so as to retain connection with the manometer but to shut off connection with the air. By turning the support the capsule is released and falls into the bulb, where vaporisation at once begins. While the substance is being vaporised the movable graduated limb of the manometer is gradually raised so as to keep the mercury in the other limb at the mark E. After a minute the pressure has become constant, the mercury is accurately adjusted to the mark, and the difference in level read off. This difference is due to the pressure of the vaporised substance. If we therefore know the volume of the apparatus, the boiling point of the liquid in the jacket, the weight of the substance, and the pressure due to it, we have all the data for calculating its molecular weight. It is true that the vapour is not distributed uniformly through the bulb, but since no change in pressure would result if diffusion proceeded until uniformity of composition had been attained, the increase in pressure immediately after vaporisation is the pressure which the vapour would exert if it uniformly filled the whole apparatus.

A principle may be here adopted which is often available for simplifying molecular weight and other similar calculations. If in this case the temperature and volume are kept constant, *i.e.* if the same apparatus and the same liquid in the jacket are used, the molecular weights of two substances are proportional to the weights of them taken and inversely proportional to the pressures produced, *i.e.*

$$\frac{M_1}{M_2} = \frac{w_1}{w_2} \cdot \frac{p_2}{p_1},$$

or

$$M_1 = \frac{M_2 p_2}{w_2} \cdot \frac{w_1}{p_1} = c \cdot \frac{w_1}{p_1}.$$

If therefore we take a substance of known molecular weight M_2 and determine the pressure p_2 caused by the vaporisation of a weight w_2 of it, we can then by means of the above formula find a "constant" c for the apparatus which includes both the volume and the temperature, neither of which needs to be known, if only both be kept at the former values when the measurements for the substance of unknown molecular weight M_1 are made. This mode of working is especially convenient for high temperatures, where it is much easier to keep a temperature constant for a time than to determine exactly what the temperature is. It also eliminates volume corrections for expansion of the bulb by rise of temperature and for the difference in temperature between the bulb proper and its connections.

Victor Meyer's Method.—This method is akin to Hofmann's inasmuch as a weighed amount of liquid is vaporised, but it differs from the other methods on account of the gas whose volume, temperature, and pressure are actually determined not being the vapour under investigation, but an equal volume of air which has been displaced by the vapour. On account of the simplicity of the apparatus and the convenience in manipulation, this method is widely adopted in practical work where great accuracy is not required.

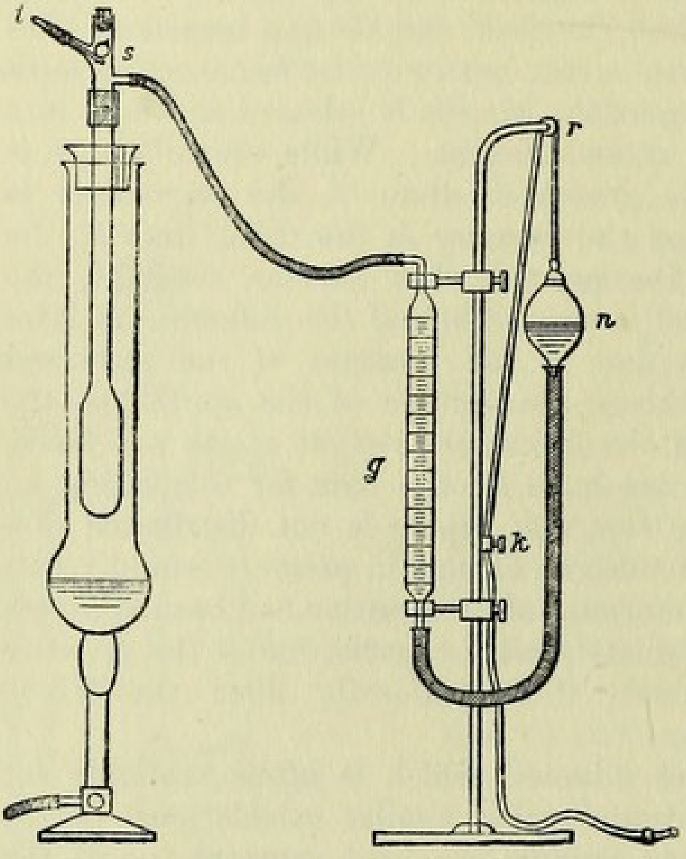


Fig. 33.

The apparatus consists of a cylindrical vessel of about 100 cc. capacity with a long narrow neck, having a top piece furnished with two side tubes. One of these side tubes acts as a delivery tube, and is connected by means of a piece of thick-walled, narrow-bored rubber tubing with the gas-measuring tube *g*, which at the beginning of the experiment is filled with water. Through the other side tube a glass rod projects into the neck, connection being made by means of a short piece of rubber tube, permitting a good deal of play. A weighed quantity of the liquid whose vapour density is to be determined is contained in the small bulb *s*, which is held in place by the rod *t*. The principal tube is closed at the top by a cork, and contains a little asbestos at the bottom, in order to protect the glass from the fall of the bulb. The wide cylindrical portion and a large part of the neck are heated by means of a liquid boiling in an external cylinder with a bulb-shaped end. To perform an experiment, the level of water in the measuring tube is adjusted to zero by moving the reservoir *n*, the bulb is put into position, and the heating started while the tube is still open at the top. When the temperature of the whole apparatus has become steady, the tube is corked, and the level of the water in the measuring tube is observed for some minutes. If it has altered slightly, it is readjusted to zero, and the bulb is let drop by drawing back the rod *t* for a moment. The liquid at once begins to vaporise, and air passes over into the measuring tube. To keep the gases in the apparatus at the atmospheric pressure, and thus prevent leakage, the water in the reservoir is kept at the same level as the water in the measuring tube by continually lowering the reservoir. The vaporisation is complete in about a minute, as a rule, and if after two or three minutes the level of water in the measuring tube does not change, the volume is read off, the barometric pressure and the temperature on a thermometer near the measuring tube being noted at the same time.

The distribution of temperature throughout the whole apparatus is the same before and after the volatilisation of the substance, and therefore the volume of air collected is the same as the volume of vapour formed, after reduction to the temperature and pressure at which the collected air is measured. The temperature is the temperature of the water, the pressure that of the atmosphere minus the vapour pressure of water; for the vapour pressure of the water over which the gas is collected and the pressure of the gas itself together make up the total pressure, which is equal to that registered by the barometer.

In the simplest form of apparatus the gas is collected in a graduated tube over water contained in a shallow dish, the side tube being in this case long, of narrow bore, and bent to the appropriate form for delivery.

It will be seen that this method of vapour-density determination does not involve a knowledge of the temperature at which the vaporisation takes place, for since all gases are equally affected by changes of temperature, the contraction in volume of the hot air on cooling is the same as the contraction which the vapour itself would experience. We thus, instead of measuring the volume at the temperature of vaporisation, measure the reduced volume at the atmospheric temperature. The liquid used for heating should have in general a boiling point at least as high as that of the experimental substance, and the ebullition should be so brisk as to make the vapour condense two-thirds of the way up the outer tube.

The mode of calculation of a molecular weight from the observed data for the vapour density may be seen from the following example. The bulb contained 0·1008 g. of chloroform, boiling point 61°, and was dropped into a tube heated by the vapour from boiling water. The air collected measured 22·0 cc., the temperature being 16·5°, and the height of the barometer 707 mm. Now the vapour pressure of water at 16·5° is 14 mm., so that the actual pressure of the gas was $707 - 14 = 693$ mm. We have only now to solve the following proportion: If 100·8 mg. of chloroform vapour occupies 22·0 cc. at 16·5° and 693 mm., what number of milligrams will occupy 22·4 cc. at 0° and 760 mm.?—*i.e.* to evaluate the expression

$$\frac{100{\cdot}8 \times 22{\cdot}4 \times (273 + 16{\cdot}5) \times 760}{22{\cdot}0 \times 273 \times 693}.$$

The result we obtain is 119, the actual molecular weight of chloroform as calulated from its formula being a little over 118.

It should be borne in mind that in the determination of molecular weights from vapour densities only approximate results are obtained, for we assume that the vapours obey the simple gas laws exactly, which is by no means the case when the vapour is at a temperature only a little removed from the boiling point of the liquid from which it is produced. As, however, the vapour density is used in conjunction with the results of analysis in fixing the accurate value of the molecular weight, an error amounting to 5 or even 10 per cent of the value is unimportant, the number obtained from the vapour density merely determining the choice between the simplest formula weight and a multiple of it. The molecular weight of chloroform in the above example can from the formula be only 118 or a multiple of 118; and the vapour-density estimation shows conclusively that the simplest formula is here the molecular formula.

2. *Dissolved Substances—Osmotic Pressure*

Assuming the complete similarity in pressure, temperature, and volume relations of substances in dilute solution and of gases, we can evidently determine the molecular weight of a dissolved substance by simultaneous observations of its weight, temperature, volume, and osmotic pressure.

Pfeffer found, for example, that a one per cent solution of cane sugar at 32° had an osmotic pressure of 544 mm. One gram, or 1000 mg., of cane sugar here occupied approximately 100 cc. We have then as before the proportion: If 1000 mg. of sugar occupy 100 cc. at 32° and 544 mm., what number of milligrams will occupy 22·4 cc. at 0° and 760 mm.? The answer is

$$\frac{1000 \times 22{\cdot}4 \times (273 + 30) \times 760}{100 \times 273 \times 544} = 347.$$

The molecular weight of cane sugar calculated from the formula $C_{12}H_{22}O_{11}$ is 342. It is evident, then, that the molecular formula of cane sugar in aqueous solution is the simplest that will express the results of analysis.

Were it not for the extreme difficulty of obtaining a membrane perfectly impermeable to the dissolved substance, this method would be the most suitable and the most accurate for determining molecular weights of substances in very dilute solution.

3. *Dissolved Substances—Lowering of Vapour Pressure*

An example of how a molecular weight of a dissolved substance may be estimated by this method has been given in the preceding chapter (p. 179). The method has little practical importance, and is scarcely ever employed.

4. *Dissolved Substances—Elevation of Boiling Point*

This is a practical method for determining the molecular weights of substances in solution, and is coming more and more into general use. An essential condition for its success is that the dissolved substance should not itself give off an appreciable amount of vapour at the boiling point of the solvent. It is only applicable, therefore, to substances of comparatively high boiling point, say over 200°, and cannot be employed with success for liquids such as alcohol, benzene, or water. Two forms of apparatus may be described, which differ principally in the mode of heating.

Beckmann's Apparatus.—In this form of apparatus the solution is raised to its boiling point by the indirect heat from a burner. Now in ascertaining the boiling point of a liquid, it is customary to place the thermometer, not in the boiling liquid itself, but in the vapour coming from it. In this way superheating is avoided. The liquid itself may be at a temperature considerably above its true boiling point, but a thermometer placed in the vapour will show very little sign of this superheating. The plan, however, cannot be adopted in ascertaining the boiling point of a solution. The vapour which comes from the solution of a non-volatile substance is the vapour of the solvent, a part of which condenses to liquid on the bulb of the thermometer. Now the temperature at which the condensed and vaporous solvents are in equilibrium on the bulb of the thermometer is the boiling point of the solvent and not that of the solution, so that the temperature registered by a thermometer placed in the vapour from a boiling solution is the boiling point of the solvent, slightly raised perhaps by radiation from the hotter solution. It is necessary then to immerse the bulb of the thermometer directly in the boiling solution if the boiling point of the latter is to be determined, *i.e.* the temperature at which the solution and the vapour of the solvent are

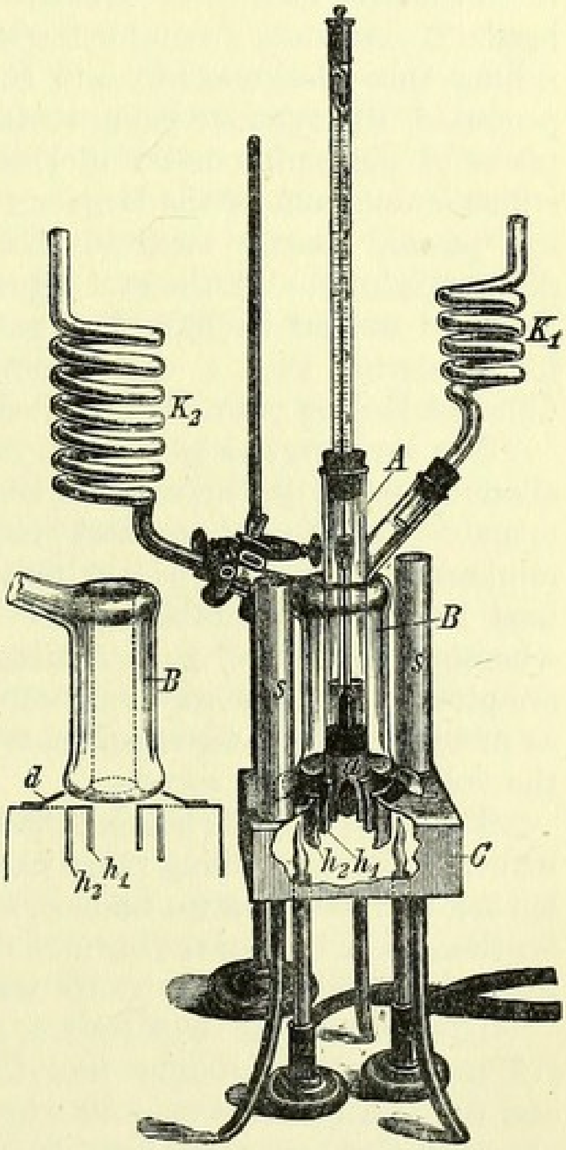


Fig. 34.

in equilibrium. When, therefore, the source of heat is external and necessarily of a higher temperature than the boiling point which has to be measured, precautions of the most rigorous kind have to be adopted in order to prevent superheating of the liquid whose boiling point is in question. In Beckmann's apparatus this is done as follows. The boiling tube A (Fig. 34) is about 2·5 cm. in diameter, provided with a stout platinum wire fused through its end, and filled for about 4 cm. with glass beads. The platinum wire is for the purpose of conducting the external heat into the solution so as to get the bubbles of vapour to form chiefly at one place and prevent superheating. The glass beads are used in order to split up the large bubbles of vapour into smaller bubbles, so that more intimate mixture of the solution and the vapour of the solvent may be secured. A more effective method of preventing superheating is to use instead of beads Beckmann's platinum tetrahedra. These are made by tightly rolling thin platinum foil, and cutting off pieces of the cylinder thus produced, the cylinder being rotated through 90° after each cut. The pieces of platinum cut off in this way are in the form of tetrahedra, which, on account of the large surface, sharp edges, and good conducting power, greatly facilitate boiling. The thermometer, which is divided into hundredths of a degree, and may be read to thousandths, is placed so that its bulb dips partly into the glass beads. A device for rendering such a thermometer available for solvents of widely different boiling points is described on p. 194.

The inner vessel is surrounded by a vapour jacket, charged with about 20 cc. of the solvent, which is kept boiling during the experiment. This jacket reduces radiation towards the exterior to a minimum, and consequently only a comparatively small amount of heat has to be afforded to the solution in order to make it boil, whereby the risk of superheating is greatly reduced. Both vessels are provided with reflux condensers, which may either be air condensers, as in the figure, or water condensers of the ordinary type, according to the volatility of the solvent.

The small asbestos heating chamber C has two asbestos rings, *h* and *h'*, which protect the boiling vessel from the direct action of the flame of the burner, and two asbestos funnels, *ss*, which carry off the products of combustion. The heat of the burners reaches the liquid in the vapour jacket through the ring of wire gauze visible in section at *d* as a dotted line.

To perform the experiment, a weighed quantity of the solvent (15 or 20 g.) is brought into the boiling tube, the heating begun, and the thermometer read off when it has become steady, which may not be before an hour has elapsed. The condensed solvent should only drop back very slowly from the condenser, so that the boiling must not be hastened by using a large flame. The condenser K_1 is then removed, and a weighed quantity of the experimental substance added, best in the form of a pastille if a solid, or from a specially shaped pipette if a liquid. The boiling point will now be found to rise, and the thermometer will after a short time again become stationary. The difference between the first and second readings of the thermometer is the elevation of the boiling point. Another weighed quantity of the substance may now be added, and the temperature of equilibrium again read off. This will give a second value for the molecular weight.

Landsberger's Apparatus. — Since the boiling point of a solution of a non-volatile substance is the temperature at which the solution is in equilibrium with the vapour of the solvent, we can bring a solution to its boiling point by continually passing into it a stream of vapour from the boiling solvent. As long as the solution is under its boiling point, some of the vapour will condense, and the latent heat of condensation will go to heat the solution until finally the boiling point is reached, when the vapour will pass through the solution without further condensation if no heat is lost to the exterior. Here there is little risk of superheating, since the vapour which heats the solution is originally at a lower temperature than the solution itself; so that if we surround the solution with a jacket of the vaporous solvent, we have all the conditions for real equilibrium, at least so far as the determination of molecular weights is concerned. Landsberger's apparatus secures these conditions in a very simple manner, and a slight modification of it is shown in Fig. 35.

The apparatus consists of a flask F, a bulbed inner tube N, which contains the solution, and a wider tube E, which is connected with a Liebig's condenser C. The vapour is generated in F (which contains the boiling solvent), passes through the solution in N, from which it issues through the hole H, to form a vapour jacket between the two tubes, and finally passes into the condenser. The lower end of the delivery tube R, where the vapour passes into the solution, is perforated with a rose of small holes, so that the vapour is well distributed through the liquid. The bulb prevents portions of the liquid being projected through H if the boiling is vigorous.

The boiling point of the solvent is first determined by placing enough of the pure solvent in N to ensure that the bulb of the thermometer is just covered by the liquid when equilibrium has been attained. This quantity usually amounts to from 5 to 7 cc. The parts of the apparatus are then put together, and the boiling of the solvent in F begun. To ensure regular ebullition, it is necessary to place in F a few fragments of porous tile, which must be renewed every time the boiling is interrupted. If the ebullition is brisk, the vapour heats the liquid in N to the boiling point in the course of a few minutes, as is evidenced by the reading of the thermometer rapidly becoming constant. The boiling is now interrupted, the tube emptied, and the whole process repeated, with the addition of a weighed quantity of the substance under investigation to 5–7 cc. of solvent in N. The difference between the temperature now observed and the former temperature is the elevation of the boiling point, and it only remains to determine the weight of solvent employed. This is done by detaching the inner tube N, with thermometer and delivery tube, and weighing to centigrams. If from this weight we subtract the weight of the substance taken, and the tare of the tubes, etc., we obtain the weight of the solvent present when the temperature of equilibrium was reached.

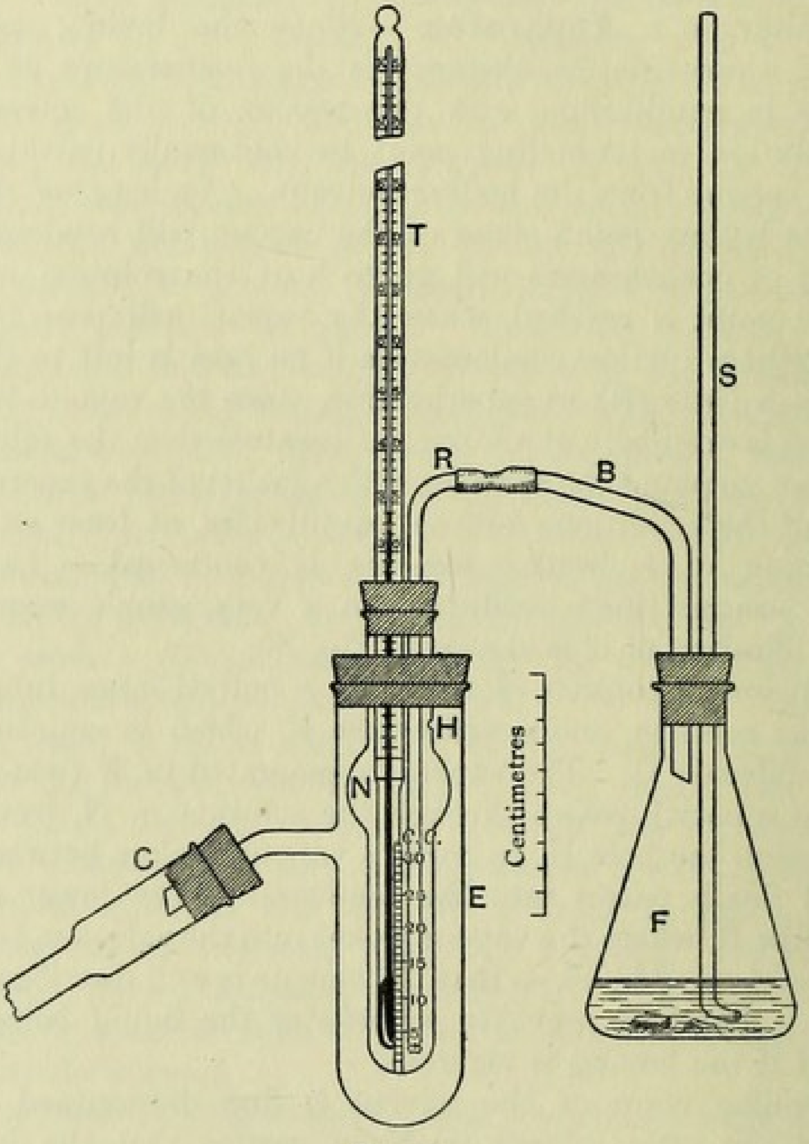


Fig. 35.

If great accuracy is not desired, several successive determinations with the same quantity of substance may be made by replacing the tube with its charge and continuing the passage of vapour, interrupting the boiling from time to time to ascertain the amount of solvent present at the moment of reading the temperature. In this case, instead of determining the weight of solution, it is more convenient to read off its volume in cubic centimetres by having the tube N appropriately graduated, as shown in the figure, and removing the thermometer and delivery tube at each interruption in order to read the volume. The successive determinations are less accurate on account of the boiling points being observed under somewhat different conditions, the pressure of the column of solution increasing, for example, as the solvent condenses in N. For ordinary rough laboratory work a thermometer graduated into fifths of a degree is sufficiently accurate.

The calculation of the molecular weight is carried out as follows. For each solvent we have a constant, which is the elevation produced if a gram-molecular weight of any substance were dissolved in a gram of the solvent. Of course such an elevation is purely fictitious as it stands, but it has a real physical meaning if we take it to be a thousand times the elevation which would be produced if a gram-molecular weight of the substance were dissolved in 1000 g. of the solvent. The hundredth part of this constant, *i.e.* the elevation caused by dissolving 1 g. molecular weight in 100 g. of solvent, is often spoken of as the **molecular elevation.** For the solvents ordinarily employed the constants are as follows:—

Solvent.	k	k'
Alcohol	1150	1560
Ether	2110	3030
Water	520	540
Acetone	1670	2220
Chloroform	3660	2600
Benzene	2670	3280

The constants in the first column refer to 1 g. of solvent; those in the second column refer to 1 cc. of solvent at its own boiling point, and are useful if we measure the volume of the solution instead of ascertaining its weight.

In the calculation we assume exact proportionality between the concentration of the solution and the elevation of the boiling point. We thus obtain for the molecular weight the expression

$$M=\frac{s}{L}\cdot\frac{k}{\Delta},$$

where Δ is the elevation, s the weight of substance, and L the weight of solvent, both expressed in grams, or

$$M=\frac{s}{V}\cdot\frac{k'}{\Delta},$$

where V is the volume of solution in cubic centimetres.

As an example of the calculation we may take the elevation produced by camphor in acetone. An elevation of 1·09° was produced by 0·674 g. camphor dissolved in 6·81 g. acetone. We have, therefore,

$$M=\frac{0{\cdot}674\times 1670}{6{\cdot}81\times 1{\cdot}09}=151.$$

The molecular weight of camphor, according to the formula $C_{10}H_{16}O$, is 152. An estimation by volume resulted as follows. An elevation of 1·47° was found for 8·1 cc. of an acetone solution containing 0·829 g. camphor. This gives

$$M = \frac{0{\cdot}829 \times 2220}{8{\cdot}1 \times 1{\cdot}47} = 154.$$

The molecular weight of camphor in acetone solution is thus in accordance with the simplest formula that expresses its composition.

5. *Dissolved Substances—Depression of Freezing Point—Raoult's Method*

The apparatus chiefly used for determining molecular weights by the freezing-point, or cryoscopic, method is that devised by Beckmann, and figured in the accompanying illustration (Fig. 36). It consists of a stout test-tube A, provided with a side tube, and sunk into a wider test-tube B, so as to be surrounded by an air space. The whole is fixed in the cover of a strong glass cylinder, which is filled with a substance at a temperature of several degrees below the freezing point of the solvent. The inner tube is closed by a cork, through which pass a stirrer and a thermometer of the Beckmann type. This thermometer has a scale comprising 6° and divided into hundredths of a degree, but the quantity of mercury in the bulb can be varied by means of the mercury in the small reservoir at the top of the scale, and thus the instrument can be adjusted for use with solvents having widely different freezing points.

To perform an experiment, a weighed quantity (15 to 20 g.) of the solvent is placed in A, and the external bath is regulated to a few degrees below the freezing point of the solvent. Thus if the solvent is water, a freezing mixture at about $-5°$ should be placed in the external cylinder C. The temperature of A is lowered by taking it out of the air jacket and immersing it in the freezing mixture directly until a little ice appears. It is then replaced in the air jacket, and the liquid in it is stirred vigorously. As there is invariably overcooling before the ice and water are thoroughly mixed, the thermometer rises during the stirring until it reaches the freezing point, after which it remains constant. This constant temperature is then read off.

The tube A is now taken out of the cooling mixture, and a weighed quantity of the substance under investigation is introduced and dissolved by stirring, the ice being allowed to melt save a small residue. The tube is replaced in the air jacket and the temperature allowed to fall in order that the liquid may become slightly overcooled. Stirring is then recommenced. The thermometer rises, remains constant for a very short time, and then slowly sinks. The maximum temperature is read off, and taken as the freezing point of the solution. The reason for the subsequent sinking of the temperature of equilibrium is plain.

As long as the solution remains in the cooling mixture, ice continues to separate. This results in making the remaining solution more concentrated than the original solution, so that its temperature of equilibrium with the solidified solvent will sink (cp. p. 67). The highest temperature registered corresponds therefore most closely to the freezing point of the solution whose concentration is expressed by the weights of substance and solvent taken, although even this is evidently not high enough, for some of the solvent has necessarily separated out as ice before equilibrium can be attained at all.

The calculation is precisely the same as that for the elevation of the boiling point. Each solvent has a constant of its own, representing the fictitious lowering of the freezing point caused by dissolving one gram molecule of substance in one gram of solvent. The hundredth part of this constant, *i.e.* the depression caused by dissolving 1 gram molecule of substance in 100 grams of solvent, is usually termed the **molecular depression**. The constants for the most common solvents are as follows:—

Solvent	K
Water	1870
Acetic acid	3880
Benzene	4900
Phenol	7500

The formula for calculation is

$$M = \frac{s}{L} \cdot \frac{K}{\Delta},$$

where M is the molecular weight of the dissolved substance, s its weight in grams, L the weight of the solvent in grams, and Δ the observed depression. A solution of 1·458 g. acetone in 100 g. benzene showed a depression of 1·220 degrees, whence we have the molecular weight

$$\frac{1{\cdot}458 \times 4900}{100 \times 1{\cdot}220} = 58{\cdot}6.$$

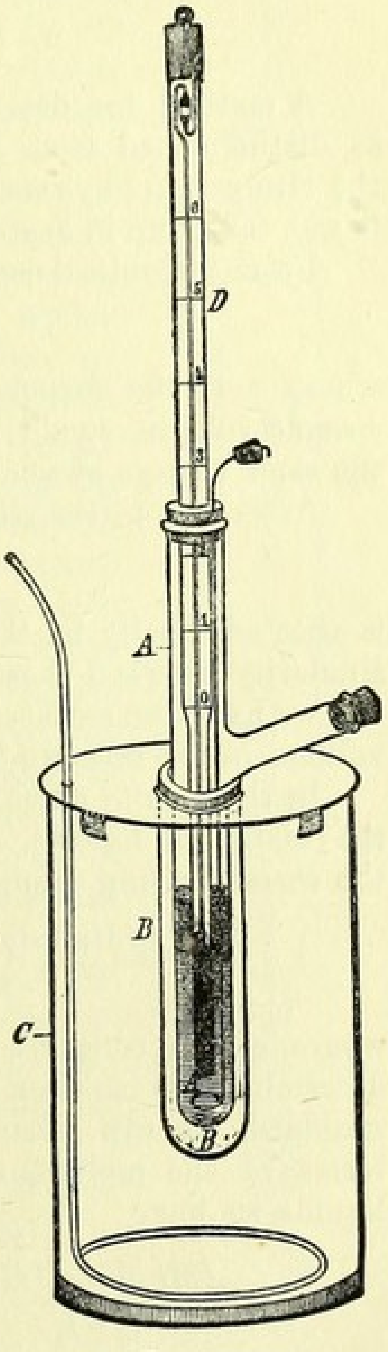


FIG. 36

The formula C_3H_6O requires 58.

An indispensable requirement of this method is that the solvent should separate out in the pure state without admixture of the solid dissolved substance. If this does not occur, the method is worthless as a practical means of ascertaining molecular weights.

6. *Pure Liquids—Surface Tension*

A method for determining the molecular weight of pure liquids, as distinguished from substances in liquid solution, was indicated by the Hungarian physicist Eötvös in 1886, but received no attention until it was taken up in a practical manner by Ramsay and Shields in 1893.

From theoretical considerations Eötvös reasoned that the expression

$$\gamma(Mv)^{\frac{2}{3}},$$

where γ is the surface tension, M the molecular weight, and v the specific volume, would in the case of all liquids be affected equally by the same change of temperature.

According to the simple gas laws, the expression

$$p(Mv)$$

is affected equally by temperature for all gases. There is an obvious similarity between these two expressions. For the pressure p in the one we have the surface tension γ in the other. For Mv, the molecular volume in the one, we have $(Mv)^{\frac{2}{3}}$, the molecular surface in the other.

In the case of gases we might calculate the molecular weight from the relation as follows. The ratio of the change in the expression to the corresponding change of temperature is

$$\frac{p_0(Mv_0) - p_1(Mv_1)}{t_0 - t_1} = c, \text{ whence } M = \frac{c(t_0 - t_1)}{p_0v_0 - p_1v_1},$$

where c is a constant having the same value for all gases. If we determine this constant once for all in the case of one gas taken as standard, we can calculate the molecular weights of other gases in terms of the molecular weight of the standard gas. Similarly for liquids we have

$$\frac{\gamma_0(Mv_0)^{\frac{2}{3}} - \gamma_1(Mv_1)^{\frac{2}{3}}}{t_0 - t_1} = k, \text{ whence } M = \left\{ \frac{k(t_0 - t_1)}{\gamma_0v_0^{\frac{2}{3}} - \gamma_1v_1^{\frac{2}{3}}} \right\}^{\frac{3}{2}},$$

where k is a constant having the same value for all liquids. If then we determine the numerical value of this constant for one standard liquid, we can calculate the molecular weight of other liquids in terms of the molecular weight of this standard liquid. It should be mentioned that both the above expressions hold good only when the molecular weight does not change with the temperature, and are not applicable to gases like nitrogen peroxide in the one case, or liquids like water in the other, where there is such a change.

The method for determining the surface tension adopted by Ramsay and Shields was to measure the capillary rise of the liquid in a narrow tube. The simplest form of apparatus they used is shown in Fig. 37. FG is the capillary tube, open at the top and blown out to a small bulb at the bottom, in which there is a minute opening to admit the liquid contained in the wider tube A. D is a closed cylinder of very thin glass, which contains a spiral of iron wire and is connected with the capillary by means of a fine glass rod. The capillary tube and liquid under investigation are introduced into A through the tube C before it is drawn out and sealed. After being drawn out at I, the open end of C is connected with the air pump, and the liquid within the tube boiled under diminished pressure, with application of heat if necessary. While the vapour is still issuing from the tube the narrow portion is rapidly sealed off at I. The tube now contains nothing but the liquid and its vapour, and is ready for the experiment. In order to maintain the liquid at a constant temperature, the tube is surrounded from L upwards by a mantle through which flows a stream of water heated to the desired point. HH represents the section of a magnet which by its attraction for the iron spiral is made to adjust the level of the capillary so that the liquid within it is always at the same place G, a few millimetres from the end, where the bore of the capillary has been previously determined by means of a microscope and micrometer scale. The difference of level between the liquid within and without the capillary is read off by a telescope and scale attached to the apparatus. The temperature is then changed and a fresh reading made, in order to ascertain the temperature-variation.

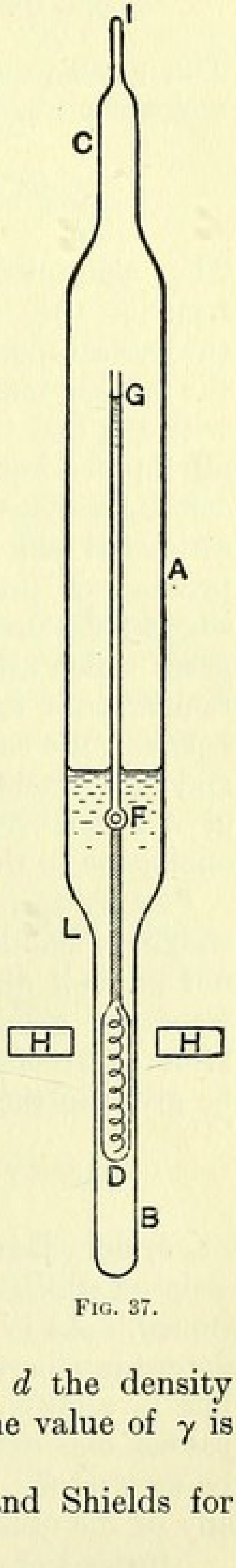


FIG. 37.

To obtain the surface tension γ from the observed capillary rise, we have the approximate formula

$$\tfrac{1}{2}grdh = \gamma,$$

where g is 981, the gravitational acceleration in cm. ÷ sec.^{2}, h the capillary height in centimetres, r the radius of the capillary tube at G in centimetres, and d the density of the liquid at the temperature of observation. The value of γ is then obtained in dynes per centimetre.

The following values were observed by Ramsay and Shields for carbon bisulphide :—

Radius of capillary	0·0129 cm.	
Temperature	$19{\cdot}4^\circ = t_0$	$46{\cdot}1^\circ = t_1$
Capillary height	4·20 cm.	3·80 cm.
Density	1·264	1·223

From these numbers we have the surface tensions

$$\begin{aligned}\gamma_0 &= 0{\cdot}5 \times 981 \times 0{\cdot}0129 \times 1{\cdot}264 \times 4{\cdot}20 = 33{\cdot}58 \text{ at } 19{\cdot}4^\circ\\ \gamma_1 &= 0{\cdot}5 \times 981 \times 0{\cdot}0129 \times 1{\cdot}223 \times 3{\cdot}80 = 29{\cdot}41 \text{ at } 46{\cdot}1^\circ.\end{aligned}$$

The mean value of k for various liquids is $-2{\cdot}12$, so that for the molecular weight we have, remembering that $v = 1/d$,

$$M = \left\{ \frac{-2{\cdot}12(19{\cdot}4 - 46{\cdot}1)}{33{\cdot}58/1{\cdot}264^{\frac{2}{3}} - 29{\cdot}41/1{\cdot}223^{\frac{2}{3}}} \right\}^{\frac{3}{2}} = 81{\cdot}5.$$

The molecular weight of carbon bisulphide corresponding to the formula CS_2 is 76. The divergence here found between the theoretical molecular weight and that calculated from the variation of the surface tension with temperature is considerable, and is connected with the fact that the constant k has not precisely the same value for all liquids, but varies nearly 20 per cent, although most liquids give constants not far removed from the mean value $-2{\cdot}12$. If we estimated the molecular weights of gases from the change in the product of pressure and molecular volume with the temperature as suggested above we should find similar variations, as it is only for the gases which are liquefied with difficulty that we have nearly the same temperature coefficient. Thus there is a difference of 6 per cent between the coefficients of expansion of hydrogen and sulphur dioxide, and this would lead to a corresponding error in the molecular weight of the one referred to that of the other if we used the method analogous to that here used for liquids.

As we see, the surface-tension method only gives us the molecular weight of one liquid as compared with that of another liquid, and does not in itself afford us evidence of the relation between the molecular weight of a substance in the liquid state compared with that of the same substance in the gaseous state. A discussion of this point will be given in the next chapter.

7. *Traube's Volume Method*

Isidor Traube has devised a method for determining molecular weights which differs in principle from any of those previously mentioned. As in the former cases the method depends on the numerical determination of the value of a physical property, namely, the density, but in addition Traube's method presupposes a *knowledge of the composition and constitution* of the substance whose molecular weight is to be ascertained. No such knowledge is required for the application of any of the other methods.

Instead of considering with Kopp the molecular volumes of liquids at their respective boiling points (cp. p. 136), Traube works up the density data of liquids at constant temperature and arrives at the following system. As before the molecular volume of a liquid is constituted of the sum of the atomic volumes of the atoms contained in it, but (and herein consists the peculiarity of Traube's method) there is always to be added to the sum of the atomic volumes a constant magnitude termed the **molecular co-volume.** The following table contains the values of some of Traube's atomic volumes at 15°, Kopp's numbers for the temperatures of ebullition being added for the sake of comparison.

	Atomic Volumes.	
	Traube at 15°.	Kopp at b.p.
C	9·9	11·0
H	3·1	5·5
O (in first hydroxyl group)	2·3	7·8
O (in subsequent hydroxyls)	0·4	7·8
O (in CO group)	5·5	12·2
O (attached to different C's)	5·5	7·8
S (not attached to O)	15·5	22·6
Molecular co-volume	25·9	0

It is apparent that there is little parallelism between the two sets of numbers, and that a knowledge of the constitution is even more necessary for Traube's treatment than for Kopp's.

From Kopp's equation for the molecular volume it is impossible to calculate a molecular weight, since all the terms depend on the values for atoms only. It is possible to make the calculation from Traube's equation, because there, in addition to the atomic values, we have a term—the co-volume—which depends, not on the atoms, but on the molecule, having the constant value of 25·9 cc. for each molecular quantity in grams.

Traube's mode of calculation may best be shown by means of a concrete example. A liquid is known to have the empirical formula $C_8H_{14}O_3 = 158$, and it is also known that all the oxygen is combined with carbon only. Its density at 15° is 0·957. The molecular formula must be $(C_8H_{14}O_3)_n$ and the molecular weight $158n$; the problem is to find n. According to Traube we have the equation

$$\frac{158n}{0{\cdot}957} = n\{(8 \times 9{\cdot}9) + (14 \times 3{\cdot}1) + (3 \times 5{\cdot}5)\} + 25{\cdot}9,$$

whence $n = 0{\cdot}995$. Since n is here practically equal to 1, the molecular weight of the liquid is the same as the empirical formula weight.

In general if E is the empirical formula weight of a liquid, d the density at 15°, and Σv the sum of the atomic volumes in the empirical formula, then

$$\frac{n\mathrm{E}}{d} = n\Sigma v + 25{\cdot}9,$$

or

$$n = \frac{25{\cdot}9}{\mathrm{E}/d - \Sigma v}.$$

Traube applies his method to solutions as follows. A quantity S of the solution is considered which contains the empirical formula weight E of the dissolved substance in grams. If d is the density of the solution, then S/d is the volume which it occupies. If, further, D is the density of the solvent, then $\frac{S-E}{D}$ is the volume which would be occupied by the quantity of solvent which is contained in S of the solution. The difference between the volume of the solution and of the solvent which it contains

$$V = \frac{S}{d} - \frac{S-E}{D}$$

may be called the "formula solution volume" of the dissolved substance, and corresponds to E/d, the "formula volume" in the equation for a pure liquid. The calculation is then made exactly as before. For non-aqueous solutions at 15° we have

$$n = \frac{25{\cdot}9}{V - \Sigma v}.$$

When water is the solvent, the value of the molecular co-volume in dilute solution is not 25·9 but 12·4, so that for dilute aqueous solutions

$$n = \frac{12{\cdot}4}{V - \Sigma v}.$$

Traube's method gives results both for solutions and liquids which generally accord fairly well with the molecular weights obtained by other methods, but sometimes the results are quite discordant. It must be borne in mind that in Traube's equation the essential term is the co-volume, which is a comparatively small residue derived from a complex system of atomic volumes more or less arbitrarily fixed. When the method, therefore, gives an abnormal value of n, the abnormality may be real, or it may arise from some constitutional influence not being taken into account, and is, therefore, correspondingly uncertain.

8. *Other Methods*

Besides the methods already mentioned, there are other methods of determining molecular weights of substances in solution based on the osmotic-pressure theory. These methods are not in general use, but occasionally they afford valuable information where the usual means are unavailable. If we take a liquid such as ether, which is only partially miscible with water, and determine its solubility in the water, we find that this solubility is diminished if we dissolve in the ether a substance which is at the same time insoluble in the water. Just as the solution of a substance in ether diminishes the vapour pressure of the ether, so also it diminishes its solubility in any liquid with which it is partially miscible; and the diminution of solubility gives us a means of ascertaining the molecular weight of the substance dissolved in the ether just as the diminution of the vapour pressure does. In the case of liquids the method is of no special value, but in the case of "solid solutions" the results obtained are of some importance.

The so-called solid solutions with which we have chiefly to deal are isomorphous mixtures, *i.e.* crystals which are uniformly composed of two crystalline substances which present similarity in crystalline form as well as of chemical composition (cp. p. 74). Such mixed crystals are in a sense comparable with liquid solutions, and one crystalline substance may be said to be dissolved in the other. The method of diminished solubility can be applied to find the molecular weight of the dissolved substance. If the mixed crystal consists of a large quantity of the substance A, in which a small quantity of the substance B is dissolved, the molecular weight of B may be determined by finding the diminution of the solubility of A in any solvent which it occasions. In the practical investigation the difficulty is encountered that both A and B are usually soluble in the same solvents on account of their chemical analogy, without which there can be no isomorphous mixture. The calculation in such a case becomes more complex, and the results are of doubtful significance.

For a more detailed description of the methods see—

OSTWALD, *Physico-Chemical Measurements*, London, 1894.

RAMSAY AND SHIELDS, *Journal of the Chemical Society*, **63** (1893), p. 1089 : "The Molecular Complexity of Liquids."

WALKER AND LUMSDEN, *ibid.* **73** (1898), p. 502 : "Determination of Molecular Weights—Modification of Landsberger's Boiling-Point Method" ; also H. N. MACCOY, *American Chemical Journal*, **23** (1900), 353.

J. S. LUMSDEN, *Journal of the Chemical Society*, **83** (1903), 342 : "A New Vapour Density Apparatus."

TRAUBE, *Raum der Atome*, Stuttgart, 1899.

CHAPTER XIX

MOLECULAR COMPLEXITY

THE molecular weights as determined by any of the methods of the preceding chapter are average molecular weights. Indeed, the methods do not directly give molecular weights at all, but rather the number of gram-molecules in a given number of grams of the substance considered (cp. calculation, p. 179). As a rule, the molecules of any one substance under given conditions are all of the same size, so that in most cases the molecular weight as determined is perfectly definite. But even with gases we have sometimes to deal with molecules of a single substance which are not of the same magnitude, with the result that the molecular weight determined from observation is not the weight of any one kind of molecule, but a weight intermediate between real extreme values. Thus the molecular weight of nitrogen peroxide deduced from its vapour density under atmospheric pressure at 4° is 74·8, while under atmospheric pressure at 98° it is 52. Now these molecular weights cannot belong to molecules all of one kind, for the molecular weight corresponding to the simplest formula NO_2 is 46, while for the next simplest, N_2O_4, it is double this, or 92. It is evident, therefore, that under the given conditions we must be dealing with a mixture of simple and complex molecules, and that the observed molecular weights are merely average molecular weights of all the molecules present. We have here, then, a case of a substance existing in at least two different states of molecular complexity under the same conditions. Experiment shows that raising the temperature or lowering the pressure favours the existence of the simple molecules, whilst lowering the temperature or raising the pressure favours the existence of the complex molecules.

The formation of complex, usually double, molecules is frequently encountered with vapours at temperatures near the boiling points of the liquids from which they are derived. The vapours of the fatty acids, for example, have in the neighbourhood of the boiling points of the liquids, molecular weights considerably above those found when the density of the vapour is taken at a higher temperature. It should be remarked, however, that this is by no means the case for all liquids, and is on the whole exceptional, although it is true that we very seldom get numbers for the vapour density exactly equal to the theoretical value when the vapour is near its point of condensation.

The thorough-going analogy between substances in the gaseous and dissolved states furnishes us with a means of comparing their molecular weights in these two conditions. As a rule, we may say that the molecular weight in dilute solution is the same as the molecular weight of the substance in the state of vapour. Since, however, even for vaporous substances we find variations in the molecular weight under different conditions, we cannot expect in every case that there should be identity of the gaseous and dissolved molecules. In general, we may say that substances which tend to form complex molecules in the gaseous state exhibit the same tendency in solutions, the extent to which the formation of complex molecules proceeds depending largely on the nature of the solvent, as well as on the temperature and osmotic pressure (concentration) of the solution.

The numbers in the following table give the percentage of nitrogen peroxide existing as double molecules in various solvents, the concentration in each case corresponding to an osmotic pressure of about seven atmospheres. At this pressure, and at the temperatures given in the table, the gaseous substance would exist almost entirely as double molecules; as a matter of fact, the substance is liquid under these conditions, with the molecular formula N_2O_4 as judged by the method of Ramsay and Shields.

Solvent.	Double Molecules at 20°.	Double Molecules at 90°.
Acetic acid	97·7	95·4
Ethylene chloride	95·8	91·3
Chloroform	92·3	85·5
Carbon bisulphide	87·8	77·5
Silicon tetrachloride	84·3	74·0

This question of the influence of the solvent on the molecular weight of the dissolved substance is one of practical importance in the selection of a solvent in which to determine the molecular weight of a given substance by means of the freezing- or boiling-point method. As a rule, what we wish to obtain is the *smallest* molecular weight, and it is therefore expedient to select a solvent in which the tendency to the formation of complex molecules is as little marked as possible. Of the ordinary solvents, water and alcohol are those in which the formation of complex molecules is least apparent; so that the former would be preferably chosen for the cryoscopic method, and the last mentioned for the boiling-point method. Acetone and ether come next in order, and are suitable for determining the elevation of the boiling point; acetic acid is a similar solvent for the cryoscopic method. In benzene and chloroform the tendency to association of the simple molecules is often considerable, so these solvents should not be used if it is suspected that the substance tends to form complex molecules.

Of the substances which show a tendency to the formation of complex molecules, organic bodies containing the groups hydroxyl (OH) and cyanogen (CN) are of the most frequent occurrence. Thus the alcohols and the carboxyl acids almost invariably tend to form complex molecules in a solvent such as benzene. The subjoined tables serve to show this behaviour, the freezing-point method with benzene as solvent being employed. In the first column is given the number of grams of substance dissolved in 100 g. of benzene.

ETHYL ALCOHOL, $C_2H_5(OH)=46$

Concentration.	Molecular Weight.
0·494	50
1·088	61
2·290	82
3·483	100
8·843	159
14·63	208

PHENOL, $C_6H_5(OH)=94$

Concentration.	Molecular Weight.
0·337	144
1·199	153
2·481	161
3·970	168
7·980	188
17·29	223

ACETIC ACID, $CH_3(COOH)=60$

Concentration.	Molecular Weight.
0·465	110
1·195	115
2·321	117
4·470	122
8·159	129

BENZOIC ACID, $C_6H_5(COOH)=122$

Concentration.	Molecular Weight.
0·567	223
1·444	228
2·603	232
4·725	236

It will be noticed that except in the case of ethyl alcohol the molecular weight does not even in the strongest solutions rise much above twice the value for the simplest molecule corresponding to the generally accepted formula. With ethyl alcohol the formation of complex molecules proceeds much further than this, if we assume the simple gas laws to hold good for the solutions of the strengths investigated.

To give an idea of the behaviour of a substance which shows no tendency to molecular complexity, the numbers for phenetol in benzene solution are subjoined. This substance is derived from phenol, and has the formula $C_6H_5(OC_2H_5)$ and the molecular weight 122. The solvent was again benzene, and with the removal of the hydroxyl group the substance has lost the power to form associated molecules.

PHENETOL, $C_6H_5(OC_2H_5)=122$

Concentration.	Molecular Weight.
0·651	120
2·589	119
7·255	121
10·85	122
16·55	125
23·30	128

Even in what must be accounted a very strong solution the molecular weight does not here greatly depart from the normal value corresponding to the formula.

Colloidal solutions, such as those of gelatine, gum arabic, starch, silicic acid, or tungstic acid, exhibit very small osmotic pressures, and correspondingly small rates of diffusion, depression of freezing point, etc. This would indicate a very high molecular weight of the dissolved substance, and indeed if the molecular weights are calculated in the ordinary way from such observations, values are found ranging from 1000 for dextrine to 50,000 for silicic acid. It is extremely doubtful, however, if the ordinary conceptions of solution are applicable to such "colloidal solutions" at all, and the tendency now is to treat them as being for the most part *pseudo-solutions*, *i.e.* apparently homogeneous fluids which are not in reality solutions but rather suspensions of very fine undissolved particles. It is possible, for example, by establishing an electric arc between platinum points under pure water to obtain a brown "colloidal solution" of platinum, the particles of which are so fine as to be undetected by the most powerful microscope. That the fluid is not in reality homogeneous, however, can be shown by its power of scattering and polarising a beam of light passed through it. Owing to the difficulty of obtaining colloidal substances in a state of purity, it is somewhat uncertain if the properties of real solutions which they undoubtedly exhibit to some extent are not due to small quantities of some impurity which passes into true solution whilst the bulk of the substance remains in a state of "pseudo-solution." Such pseudo-solutions are characterised by their power of coagulating or gelatinising under the influence of temperature or some suitable chemical agent.

Soluble salts, strong acids, and strong bases in dilute aqueous solution invariably exhibit too small a molecular weight, whether this is determined by the osmotic-pressure, vapour-pressure, freezing-point, or boiling-point methods. The normal molecular weight of sodium chloride, corresponding to the formula NaCl, should be 58·5, but all the above methods give for its molecular weight when dissolved in water numbers approximating to 30, *i.e.* about half the normal value. Here we are dealing with a **dissociation** instead of an association of the simplest molecules. It is evident that unless we halve the atomic weights of sodium and chlorine, and write the formula na cl, where na and cl represent the half atomic weights, the two molecules into which the normal molecule of sodium chloride dissociates cannot be the same. The most probable assumption to make is that the atomic weights retain their ordinary value, and that the normal molecule splits up into two different molecules, Na and Cl. The average molecular weight of the sodium chloride in solution would then, if the dissociation were complete, be half the normal molecular weight corresponding to the simplest formula. It is preferable to make this assumption of dissociation into atoms rather than the assumption that our ordinary atomic weights are twice what they should be, because we find that in other cases the last assumption would not account for the molecular weight observed. Thus in very dilute solutions of sulphuric acid or sodium sulphate, the atomic weight deduced from the boiling-point or freezing-point methods is considerably less than half the normal molecular weight, so that halving the atomic weights of the constituent atoms would be insufficient to produce the low molecular weight actually observed. The assumption that the dissociation is into products of different kinds receives support from what we learnt of the properties of salt solutions. It will be remembered that very frequently the properties of salt solutions were such that the positive and negative radicals appeared to be independent of each other (cp. p. 161). Now if we assume that the independence is caused by the salt actually splitting up into these radicals, each of which then acts, as far as osmotic pressure and the derived magnitudes are concerned, as a separate molecule, we have an explanation both of the peculiarities of the physical properties of aqueous salt solutions and of the low molecular weights exhibited by the dissolved salts. In a subsequent chapter the subject of dissociation in salt solutions will be treated in greater detail.

This dissociation is not confined to aqueous solutions alone, although it is exhibited by them to the greatest extent, but is found also, for example, in alcoholic and acetone solutions. The following numbers were obtained by the boiling-point method, and show the abnormally small molecular weight in aqueous and alcoholic salt solutions :—

SODIUM ACETATE IN WATER, $C_2H_3O_2Na = 82$

Concentration.	Molecular Weight.
1·01	46
4·19	48
6·32	46
10·69	45

SODIUM IODIDE IN ALCOHOL, $NaI = 150$

Concentration.	Molecular Weight.
1·56	109
5·00	118
8·22	115
14·35	108

In the chapter on solutions we found that a substance distributed itself between two immiscible solvents in such a way that there was a constant ratio of the concentrations of the substance in the two solutions, depending on the solubility of the substance in the solvents separately. This constant partition coefficient is observed, however, only when the dissolved substance has the same molecular weight in both solvents. If, for example, we shake up acetic acid in small quantity with benzene and water, we do not get a constant partition coefficient of the acid between the two solvents independent of the quantity of acetic acid present, as we should if the molecular weight were the same in both solvents; but we get a ratio of concentrations which varies as the values of the concentrations themselves change. This is due to acetic acid in benzene solution consisting practically of double molecules, whereas in aqueous solution it consists of practically single molecules. In such a case we have the following rule for the concentrations in the two solvents. Let the solvents be A and B, and let the concentrations of the dissolved substance in these two solvents be C_A and C_B respectively. Then if the dissolved substance in the solvent A has a molecular weight n times greater than the molecular weight of the substance when dissolved in B, the ratios

$$\sqrt[n]{C_A}/C_B \text{ or } C_A/C_B{}^n$$

are constant. It will be seen that when the molecular weight in both solvents is the same, we get the partition coefficient as a particular case of the general rule. In the above-mentioned instance of the distribution of acetic acid between benzene and water, where the molecular weight in benzene is approximately twice that in water, the ratio $C_W{}^2/C_B$ should be approximately constant. The following experiments show that this is indeed the case. In the first column we have the concentration of the acetic acid in the benzene, in the second the concentration in the water, in the third the ratio of these concentrations, and in the fourth the expression which should be nearly constant:—

C_B	C_W	C_W/C_B	$C^2{}_W/C_B$
0·043	0·245	5·7	1·40
0·071	0·314	4·4	1·39
0·094	0·375	4·0	1·49
0·149	0·500	3·4	1·69

As the third column shows, there is no constant partition coefficient.

It has already been pointed out (p. 62) that there is a great analogy between the partition co-efficient of a substance between two solvents and the solubility coefficient (or, shortly, solubility) of a gas in a liquid according to Henry's Law, and the mere existence of this law is sufficient to indicate that for the substances to which it applies the molecular complexity in the dissolved and gaseous states is the same. If the molecular complexity of a substance in the gaseous state is different from what it is when dissolved in a given solvent, Henry's Law, that the amount of gas dissolved is proportional to the pressure, *i.e.* that the ratio of the concentrations of the substance in the two states is constant, no longer holds good. Thus the solubility of carbon dioxide in water is not exactly proportional to the pressure, varying by as much as a hundred per cent, between 1 atm. and 30 atm. This is no doubt due to the formation of gaseous C_2O_4 molecules under great pressures, as may be deduced from vapour-density determinations. If we make allowance for this increase of molecular complexity of the gaseous phase, as compared with the dissolved phase, on increase of pressure, we find that the theoretical expression, where n now varies with the pressure, gives a fair approximation to constancy.

When we come to compare many properties of substances in the liquid state with each other, we find that liquids containing the hydroxyl group, such as the alcohols, water, and the fatty acids, are quite exceptional in their behaviour. In the first place, it must be noted that the boiling points of such compounds are exceptionally high, and this alone might lead us to suspect an exceptionally high molecular weight in the liquid state. As a rule, we find that on comparing the boiling points of similar compounds, the compound with highest molecular weight has the highest boiling point. If we substitute a CH_3 group for a C_2H_5 group we have, in accordance with the general rule, a fall in the boiling point, and similarly if we substitute H for CH_3. But if these groups are attached to an oxygen atom, we find that though the substitution of CH_3 for C_2H_5 lowers the boiling point, the substitution of H for CH_3 raises it greatly. The following substances afford examples of this behaviour :—

		Boiling Point.	Difference.
Ethyl methyl ether	$C_2H_5 . O . CH_3$	11°	
			− 35
Dimethyl ether	$CH_3 . O . CH_3$	− 24°	
			+ 90
Methyl alcohol	$CH_3 . O . H$	+ 66°	
			+ 34
Water	$H . O . H$	100°	
Propyl acetate	$CH_3 . COOC_3H_7$	102°	
			− 25
Ethyl acetate	$CH_3 . COOC_2H_5$	77°	
			− 20
Methyl acetate	$CH_3 . COOCH_3$	57°	
			+ 61
Hydrogen acetate	$CH_3 . COOH$	118°	

Another point in which organic hydroxyl compounds differ from most other liquids is the following. If a substance obeyed the gas laws exactly, its density at the critical temperature and pressure could easily be calculated from Avogadro's Law. Now all liquids have a much greater critical density than the calculated value, and for most of them the actual critical density is 3·77 times the theoretical. With hydroxyl compounds, however, the factor is greater than this normal value, varying from 4 to 5. This points to association of simple molecules under the critical conditions.

Again, the vapour-pressure curves of most liquids do not cut each other when tabulated on the same diagram, but the curves of the hydroxyl compounds often cut each other and sometimes those of the "normal" liquids. This exceptional behaviour once more points to the existence of complex molecules in the liquids, which are progressively decomposed as the temperature rises.

As we have seen in the preceding chapter, the surface-tension method for determining molecular weights gives a constant approximately equal to − 2·1 for most liquids. The constants for the following substances are much lower than this mean value, and vary with the temperature—alcohols, fatty acids, water, acetone, propionitrile, and nitroethane. It is impossible to calculate the molecular weight of such substances by means of the formula given on p. 196, for that formula assumes that the molecular weight remains constant through the range of temperature examined. By suitably altering the formula, however, probable values may be obtained for substances whose molecular weight changes with the temperature, and a few of these are exhibited in the subjoined table, in which *t* is the temperature and *n* the association factor, *i.e.* the number of times the molecular weight of the liquid is greater than that corresponding to the ordinary formula:—

WATER		ACETIC ACID	
t	*n*	*t*	*n*
0°	1·71	20°	2·13
20	1·64	60	1·99
60	1·52	100	1·86
100	1·40	140	1·72
140	1·29	280	1·30

METHYL ALCOHOL		ETHYL ALCOHOL	
t	*n*	*t*	*n*
− 90°	2·65	− 90°	2·03
+ 20	2·32	+ 20	1·65
110	2·06	100	1·39
180	1·86	180	1·15
220	1·75	220	1·03

In each case a diminution of *n* with increasing temperature is observable, indicating that the associated molecules decompose as the temperature is raised. In all the above instances, except water, the association factor is greater than 2, so that we are probably dealing with molecules more complex than double molecules.

Traube's method also leads to the conclusion that the molecules of these substances are complex, although his values of *n* are generally lower than those obtained by the method of Ramsay and Shields.

Reviewing the facts regarding the associative tendency of the common solvents, we find first that hydroxylic solvents such as water and alcohol of themselves tend to form complex molecules, whilst as solvents they are characterised by their dissociative power—that is, they not only prevent the association of molecules dissolved in them, but even in the case of salts dissociate the normal molecules into still simpler molecules. Hydrocarbon solvents such as benzene, on the other hand, which themselves form no complex molecules, promote the association of molecules dissolved in them, and in no case exhibit a dissociative action comparable with that shown by the other class of solvents. These facts may be harmonised to some extent by the following general consideration. Self-associating liquids have molecules which possess a certain power of combination with each other; it is not improbable, therefore, that this power of combination may be exerted on the molecules of substances dissolved in the liquid, counteracting any power of self-association which these molecules may themselves possess. This would be in harmony, for example, with the normal molecular weight which alcohol shows when dissolved in water. On the other hand the molecule of a solvent such as benzene, which shows no tendency to unite with other like molecules, may be supposed to be without action on the molecules of substances dissolved in the liquid, thus permitting these substances still to display any self-associative tendency they may exhibit in the undissolved state. The behaviour of alcohol and phenol in benzene solution would in this way be intelligible.

It might be objected that as we compare the molecular weights of liquids only amongst themselves, we have no right to compare the molecular weight of a substance in the liquid state with that of the same substance in the dissolved or gaseous state. The mere fact of the continuity of the gaseous and liquid states (Chap. IX.) is not in itself sufficient to indicate that the molecular condition is the same in the two cases; but where the surface-tension method shows the liquid to have a molecular weight corresponding to a complex molecule, there we have behaviour amenable to much less simple laws than those which hold good for the bulk of liquids. We should be disposed, therefore, to assume that the origin of the comparatively simple laws is to be sought in the molecular condition in the liquid and vaporous states being the same. For if the moleular conditions in the two states were different, even in the case of normal liquids, it would be difficult to explain the abnormalities shown by liquids such as alcohol. That the normal molecular weight in solution is identical with the normal molecular weight in the gaseous state is practically certain from the existence of Henry's Law, and from the perfect analogy in pressure, volume, and temperature relations exhibited by dissolved and gaseous substances (cp. Chap. XXVIII.).

CHAPTER XX

ELECTROLYTES AND ELECTROLYSIS

If we take platinum wires from the terminals of a battery and join their free ends by another metallic wire, we find that a current of electricity flows through the system without being accompanied by any motion of ponderable matter. If we dip the free ends of the wires from the terminals into water acidulated with sulphuric acid, we find that an electric current again flows through the system, but that now the passage of the current is accompanied by chemical phenomena and motion of matter. Oxygen appears at one wire where it dips into the solution, and hydrogen at the other; and if we continue the passage of the current, taking measures to prevent mechanical mixing in the solution, we shall find that the sulphuric acid will accumulate round the wire at which the oxygen is evolved.

We distinguish, therefore, between two kinds of electrical conduction, viz. metallic conduction, which is unaccompanied by material change, and electrolytic conduction, which is essentially bound up with movement, and usually chemical change, in matter. In this chapter we are concerned with electrolytic conduction and the accompanying phenomena, and have first to ascertain what substances are conductors in this sense.

Comparatively few pure substances act as electrolytic conductors, the chief exceptions being fused salts and bases. Fused silver chloride conducts electricity freely, and is itself decomposed during the process, and there is even a perceptible electrolytic conduction in the substance in the solid state at temperatures not far removed from its melting point. It was by the electrolysis of fused salts that many of the metals were first prepared. Lithium and magnesium, for example, may be easily obtained by the passage of an electric current through their fused anhydrous chlorides; and Davy first discovered the metals of the alkalies by electrolysing the fused bases, potassium and sodium hydroxides. At present, aluminium is manufactured on the large scale by the electrolysis of fused aluminium oxide, and many other technical applications of similar processes are being developed.

Electrolysis of pure fused substances has as yet offered little of a regular character adapted to theoretical treatment from the chemical point of view, and the subject has not hitherto been systematically worked out. The result is that our systematic knowledge of electrolysis is confined almost entirely to the second class of electrolytes, namely solutions, and, in particular, aqueous solutions.

Pure water can scarcely be called an electrolyte, its conductivity being extremely small. Dry liquid hydrochloric acid in the same way cannot be called an electrolyte; yet if we bring these two substances together, the resulting solution of hydrochloric acid is an excellent conductor of electricity, and undergoes decomposition when electrolysed. The conductivity, therefore, is not a property of either constituent of the solution, but of the aqueous solution itself. It is not every solvent that acquires the conducting property when a substance such as hydrogen chloride is dissolved in it. Chloroform, for example, does not conduct electricity itself, neither does a chloroform solution of hydrochloric acid. The nature of the solvent, therefore, plays an important part in determining whether the resulting solution will conduct or not. If a substance is such that its aqueous solution is an electrolyte, then its solution in ethyl and methyl alcohol will also conduct electricity, but not so well as the aqueous solution. Acetone ranks with the alcohols in this respect. Ether follows next, and solutions in chloroform or benzene and other hydrocarbons scarcely conduct at all. Solvents, then, which tend to associate substances dissolved in them (cp. p. 203) do not yield conducting solutions, while substances with no such tendency form solutions which conduct to a greater or less extent.

The conductive property does not depend only on the nature of the solvent, however, but also on the nature of the dissolved substance. In general, it may be said that the only substances which exhibit conductivity in aqueous solution in any marked degree are salts, acids, and bases, of which the salts and bases also conduct electrolytically at high temperatures when fused. An aqueous solution of sugar or alcohol, for example, does not conduct much better than water itself, and cannot in the ordinary sense be called an electrolyte. It should be noted that the conducting solution is, properly speaking, the electrolyte, but by a convenient transference the term is often applied to the dissolved substance, the solvent in such a case being usually understood to be water. We therefore speak of acids, bases, and salts as electrolytes, meaning thereby that their aqueous solutions conduct electricity.

It is often expedient to make a distinction between electrolytes, half-electrolytes, and non-electrolytes. In the first class are included practically all salts, together with the strong acids and bases, *e.g.* hydrochloric and sulphuric acids, potassium and sodium hydroxides. The half-electrolytes comprise the weak acids and bases, *e.g.* acetic and benzoic acids, ammonia and hydrazine. Non-electrolytes are neutral substances which are not salts, *e.g.* sugar, alcohol, urea. There is, strictly speaking, no sharp line of demarcation between these classes, intermediate substances existing which cannot be definitely classified within any one set. The distinction is based on degree of conductivity, in which there is no sudden break; but we may say that normal aqueous solutions of the electrolytes conduct electricity well, those of half-electrolytes conduct rather poorly, and those of non-electrolytes very feebly, or practically not at all. Thus normal hydrochloric acid has a conductivity two hundred times greater than normal acetic acid, and this again a conductivity many hundred times greater than a normal aqueous solution of alcohol. It should be noted at once by the student that although weak acids and bases are only half-electrolytes, their salts are good electrolytes. Normal potassium acetate, for example, has a conductivity fifty times that of acetic acid; and normal ammonium chloride a conductivity more than a hundred times as great as the conductivity of normal ammonia. Neglect or forgetfulness of this relation has often led to serious error, and it should therefore be impressed firmly in the memory.

When a solution of sulphuric acid in water is electrolysed, the electrodes being of platinum or other resistant material, oxygen, as we have said, comes off at one of the electrodes and hydrogen at the other. The electrode at which the oxygen appears is called the **positive electrode** or **anode**, and is connected with the positive pole of the battery which generates the current; that at which the hydrogen is evolved is termed the **negative electrode** or **kathode**, and is connected with the negative or zinc pole of the battery. It was observed by Faraday that the amount of decomposition in such an electrolyte is proportional to the amount of electricity which flows through it. We have here, then, a direct proportionality between quantity of matter and quantity of electricity. For example, each gram of hydrogen liberated by an electric current corresponds to the passage through the electrolyte of 96,500 coulombs. It is of no moment whether the current which liberates the hydrogen is strong or weak, whether much or little time is occupied in the decomposition, whether the sulphuric acid solution is more or less concentrated, so long as hydrogen alone is evolved; the result is always the same—a given quantity of electricity liberates in each case the same amount of * hydrogen. What here holds good for hydrogen also holds good for other elements or groups of elements. A given quantity of electricity passed through a solution of copper sulphate always deposits the same quantity of copper on the kathode. On this depends the use of the hydrogen or copper voltameter, by means of which a quantity of electricity is measured by finding the amount of hydrogen or copper which it has liberated.

Not only is the quantity of hydrogen liberated by a given amount of electricity unaffected by the concentration, temperature, etc., of the electrolytic solution: it is even unaffected by the nature of the dissolved substance, provided that this substance is of such a kind as to permit of the evolution of hydrogen at all. Thus if the same current is passed successively through dilute solutions of sulphuric acid, hydrochloric acid, and sodium sulphate, it will be found that the same amount of hydrogen is liberated by the current in each solution.

When we compare the volumes of oxygen and hydrogen evolved simultaneously at the anode and kathode from a solution of sulphuric acid, we find that if the solution is dilute and the current has been passed for some time before the measurement is begun, in order to get rid of the effect of initial subsidiary reactions, the volume of hydrogen is double that of the oxygen. The gases are thus liberated in the proportions in which they combine, *i.e.* in chemically equivalent proportions. The same thing may be observed if we take other solutions. The quantity of copper deposited on the kathode from a solution of copper sulphate is exactly equivalent to the oxygen liberated at the anode by the same current. An indirect consequence of this is that if we send the same amount of electricity through solutions of sulphuric acid and copper sulphate, the amount of copper deposited by the current in the one solution will be equivalent to the amount of hydrogen liberated by the same current in the other. A quantity of electricity equal to 96,500 coulombs will therefore deposit 31·5 g. of copper from the solution of a cupric salt, as this is the amount equivalent in these salts to 1 g. of hydrogen.

In general, we may say that the electrochemical equivalents of substances are identical with their chemical equivalents, if we define electrochemical equivalent as the amount of substance liberated by the same current as liberates 1 g. of hydrogen. This relation, together with the proportionality established between the amount of electricity and the amount of chemical action, gives the most general expression of **Faraday's Law**.

If we inquire as to what happens within the electrolytic solution during electrolysis, we must assume that matter travels along with electricity, in order to explain the changes of concentration that occur round the electrodes. Faraday introduced the term **ion** to denote the matter which travels in the electrolyte, and as in each solution matter travels towards both electrodes, the term **anion** was used to denote the matter travelling towards the anode, and **kation** the matter travelling towards the kathode. It is not an easy matter to determine in any given case what the ions really are, and the views now held are not entirely in accordance with those of Faraday. The following system, however, is self-consistent and involves no contradiction, while it affords a satisfactory explanation of most of the phenomena. In the aqueous solution of an acid the kation is hydrogen, and the anion the acid radical. In the solution of a base, the kation is the metal or metallic radical, *e.g.* ammonium, NH_4, and the anion hydroxyl, OH. In the solution of a salt the kation is the metal or metallic radical and the anion the acid radical. The kations carry the positive electricity, and therefore move towards the negative electrode or kathode. The anions carry the negative electricity, and therefore move towards the positive electrode or anode. Certain facts relating to the speed of the ions are best accounted for on the assumption that the ions in aqueous solution are "hydrated," or enclosed in a "water atmosphere" different from the rest of the solvent water. For most purposes, however, we may look upon the ions as being the simple positive and negative radicals.

The quantitative phenomena of electrolysis are accounted for if we assume that for monobasic acids, monacid bases, and their salts, each gram ion is charged with 96,500 coulombs of electricity, which it loses when it reaches the oppositely-charged electrode. Take, for example, a dilute aqueous solution of hydrochloric acid. The positive ion in this case is assumed to be hydrogen, and the negative ion chlorine, the water being supposed to play no part in the conductivity. Each gram of hydrogen ion is charged with 96,500 coulombs of positive electricity, and moves towards the negative electrode. There it is discharged and becomes ordinary hydrogen, which is liberated at the electrode. Now while this is going on at the negative electrode, an equal quantity of negative electricity must be neutralised at the positive electrode, as the same current flows through the whole circuit. This quantity of negative electricity is supplied by the gram equivalent of the negative radical, viz. 35·5 g. of chlorine. The chlorine when discharged of its electricity does not in general appear at the positive pole as such entirely. If the solution of hydrochloric acid is concentrated, the bulk of the discharged chlorine is liberated, but in dilute solutions it rather attacks the water of the solvent, combining with the hydrogen and liberating an equivalent quantity of oxygen. As a rule both oxygen and chlorine are produced, but if both be accurately estimated they are found to be together equivalent to the hydrogen evolved at the negative pole.

If the solution electrolysed is one of sodium sulphate, the positive ion is sodium, and the negative ion SO_4. From the formula of sodium sulphate it is evident that one SO_4 ion is equivalent to two sodium ions. Thus for every 23 g. of sodium ion which loses its 96,500 coulombs of positive electricity, half of 96 g. of sulphate ion will lose 96,500 coulombs of negative electricity. In dealing with electrolytes we shall often find it convenient to give the charges of the ions in the formulæ. A charge of 96,500 coulombs of positive electricity will be indicated by a dot attached to the gram-symbol of the positive ion, a charge of 96,500 coulombs of negative electricity will be indicated by a dash attached to the gram-symbol of the negative ion. Thus sodium sulphate will be written $Na_2{}^{\cdot}SO_4{}''$, and sodium chloride $Na^{\cdot}Cl'$.

Neither sodium nor the sulphate radical is capable of independent existence in presence of water, so that they are not obtained as products of the electrolysis, the products of their action on water appearing in their stead. The sodium acts on water with production of hydrogen and sodium hydroxide, according to the equation

$$2Na + 2H_2O = 2NaOH + H_2,$$

while the sulphate radical acts on water with production of sulphuric acid and oxygen:—

$$SO_4 + H_2O = H_2SO_4 + O.$$

The equations represent the action on water of equivalent quantities of the discharged ions, the amounts of hydrogen and oxygen formed by the action being therefore also equivalent. According to this view, the liquid round the anode should become acid, and the solution round the kathode alkaline. This can easily be shown to be the case, and if proper precautions be taken to prevent diffusion within the liquid, the quantity of sulphuric acid formed at the anode is found to be exactly equivalent to the quantity of caustic soda formed at the kathode.

It is convenient to have a system of names for the ions derived from acids, bases, and salts, which shall represent not so much the ions as particles, but rather the ionic substances. The following system has been proposed, in which the names are derived directly from the names of the ionised salts. The positive ions receive their names from the names of the positive radicals of the salts, acids, or bases by replacement of the terminations by the suffix *-ion*, *e.g. hydrion* $H^{\cdot}$, *sodion* (or *natrion*) $Na^{\cdot}$, *calcion* $Ca^{\cdot\cdot}$, *argention* $Ag^{\cdot}$, *ammonion* $NH_4^{\cdot}$, etc. When one radical, *e.g.* iron, Fe, exists in two sets of salts, the positive ions of these salts may be distinguished from each other by a prefix indicating the electro-valency, thus *diferrion* $Fe^{\cdot\cdot}$, *triferrion* $Fe^{\cdot\cdot\cdot}$. The names of all negative radicals terminate in *ate*, *ite*, or *ide*. Corresponding to these we have the terminations for the negative ions *-anion*, *-osion*, and *-idion* respectively. Thus we obtain the names *sulphanion* SO_4'', *sulphosion* SO_3'', *sulphidion* S'', *hydrosulphidion* HS', *carbanion* CO_3'', *hydroxidion* OH', etc. Using these names we can say that a solution of sodium chloride contains so many grams of unionised sodium chloride, so many grams of natrion, and so many grams of chloridion, thus treating the products of ionisation as ordinary substances—a method of treatment which has many advantages.

It has been supposed in what has been said above that the material of the electrodes is not attacked by the discharged ions, a condition which is practically secured if the electrodes are constructed of platinum, or, as often occurs in practice, of gas carbon. If we electrolyse the solution of a silver salt, say silver nitrate, between two silver electrodes, we find that the argention is discharged and deposited as silver on the negative pole. At the same time, an equivalent quantity of the negative nitranion NO_3' is discharged at the positive silver electrode. The nitrate radical in this case is neither liberated as such, nor does it attack the water. It combines with the silver to form silver nitrate, so that the whole electrolytic process has here consisted in the transference of silver from the anode to the kathode, and a change in the concentration of silver nitrate round the electrodes. Such a process is made use of in electroplating, the anode consisting of silver and the kathode of the object to be silver-plated. The silver salt is chosen of such a type as to ensure a coherent film of silver on the surface of the plated object, and is usually a double cyanide of potassium and silver.

In the formation of hydrogen gas from the hydrogen ions of hydrochloric acid it is evident that we have union of the discharged atoms, as each molecule of hydrochloric acid can contribute only one atom of hydrogen. Here then there is, strictly speaking, action of the discharged ions on each other. This is not uncommon, and is most evident in the actions of the discharged negative ions of carboxylic acids. If we take, for instance, potassium propionate, and subject it to electrolysis, the positive ion $K^{\cdot}$ goes to the kathode, and the negative ion $CH_3 . CH_2 . COO'$ to the anode. The discharged potassion as usual acts on the water with formation of potassium hydroxide and evolution of hydrogen. The discharged negative ion acts in a variety of ways. A portion of it acts on the water with production of the acid and liberation of oxygen.

$$2CH_3 . CH_2 . COO + H_2O = 2CH_3 . CH_2 . COOH + O.$$

Under favourable conditions, however, the discharged anions react with each other according to the following equations :—

$$2CH_3 . CH_2 . COO = \underset{\text{(Butane)}}{CH_3 . CH_2 . CH_2 . CH_3} + 2CO_2,$$

$$2CH_3 . CH_2 . COO = CH_3 . CH_2 . COOH + \underset{\text{(Ethylene)}}{CH_2 : CH_2} + CO_2,$$

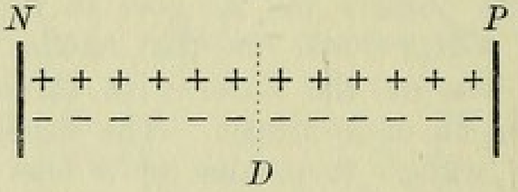
$$2CH_3 . CH_2 . COO = \underset{\text{(Ethyl propionate)}}{CH_3 . CH_2 . COO . CH_2 . CH_3} + CO_2.$$

The amount of ethyl propionate produced is not great, but in other cases the corresponding compound is formed in considerable quantity. Butane, also, is only a subsidiary product, the chief substances formed being carbon dioxide and ethylene. With other acids the compounds corresponding to butane may form the bulk of the product of the interaction of the anions.

The laws concerning the **migration of the ions** in opposite directions towards the electrodes were ascertained experimentally by Hittorf. It has been said that in a solution of silver nitrate electrolysed between silver electrodes, the only change is a transference of silver from the anode to the kathode, and a change in the concentration of the silver salt round the two electrodes. By properly constructing the apparatus so that mechanical convection of the dissolved salt between the two electrodes is prevented, the exact change in concentration in the neighbourhood of the electrodes can be measured, and from this change the relative speeds of the two ions can be calculated.

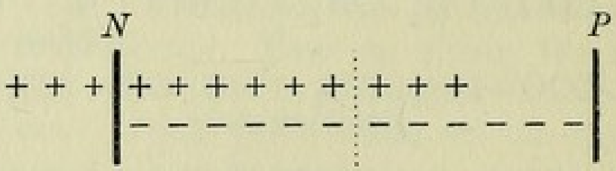
It might be thought on a superficial consideration that the anion and kation must move at the same rate since they are liberated in equivalent proportions at the opposite electrodes. In silver nitrate solution, for instance, there is one nitrate ion discharged at the anode for each silver ion discharged at the kathode. The equivalence of discharge would, however, be retained for *any* relative rate of motion of the two ions, as the following scheme will show. In it the positive ions are represented by + and the negative ions by −. *P* is the positive electrode or anode, *N* is the negative electrode or kathode. *D* is a porous diaphragm to prevent convection currents. To begin with, let there be 6 molecules on each side of the diaphragm, as represented in Scheme I.

I



The concentration in each compartment before any current has passed may thus be represented by 6. Let a current now be passed, and let the kations alone be capable of movement, the anions remaining in their original compartments. The state after 3 kations have passed through the partition from the anodic to the kathodic compartment is represented in II.

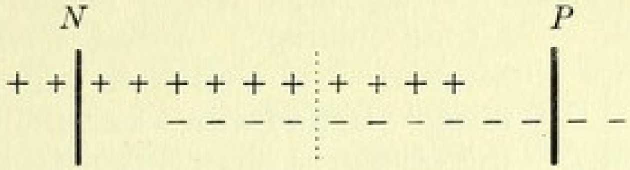
II



Each ion without a partner is supposed to be discharged and liberated, and it will be seen that although the negative ion has not moved at all, the number of liberated positive and negative ions is the same. The number of complete molecules in the kathodic compartment has not altered; the number of complete molecules in the anodic compartment has been reduced to 3.

Let now both ions move at the same rate, *i.e.* let one negative ion cross the diaphragm to the right for each positive ion that crosses it to the left. If four ions of each kind are discharged, we shall have the state shown in III.

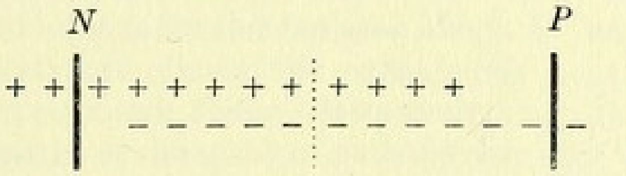
III



Here the concentration in both compartments has been reduced to the same extent, namely from 6 to 4.

Let, finally, the positive ion move at twice the rate of the negative ion, *i.e.* let one negative ion cross the partition to the right in the same time as two positive ions cross it to the left. After three ions of each kind have been discharged, we have the scheme—

IV



The concentration has here fallen off from 6 to 5 in the kathodic compartment, and from 6 to 4 in the anodic compartment.

It is obvious from the diagrams that the loss of concentration in any of the compartments is proportional to the speed of the ion leaving the compartment. Thus in the last example the anodic compartment loses kations twice as fast as the kathodic compartment loses anions, so that the fall of concentration round the anode is twice as great as the fall of concentration round the kathode in the same time. If both ions move at the same rate, the concentrations in the two compartments fall off at the same rate, as in III. We therefore get the ratio of the speeds of the two ions from the observed falls in concentration round the two electrodes as follows:—

$$\frac{\text{Fall round anode}}{\text{Fall round kathode}} = \frac{\text{Speed of kation}}{\text{Speed of anion}}.$$

It must be borne in mind that it is the kation which leaves the anode, and produces the fall of concentration round that electrode.

In actual practice the conditions are usually somewhat different from those indicated above. For example, the relative speeds of the ions of silver nitrate may be conveniently determined in an apparatus of the form shown in Fig. 38. In this form a diaphragm is dispensed with, the construction of the vessel itself preventing diffusion to a sufficient extent. The vessel has two limbs connected by a short, wide tube, the longer limb being furnished at the lower end with a tap. The kathode C in the short limb consists of a piece of silver foil connected to the battery wire by a piece of silver wire. The anode A consists of silver wire which is bent in the form of a flat spiral. The portion which forms the stem is protected by being enclosed in a narrow glass capillary throughout the entire length immersed in the silver nitrate solution. A feeble current is passed between the electrodes through the silver nitrate solution with which the vessel is charged, the amount of electricity passed being registered by means of a voltameter or other suitable instrument. At the expiration of some hours, half the solution is carefully withdrawn by opening the tap at the anode, and the amount of silver held in solution determined by analysis, the original concentration of the silver nitrate solution having been previously ascertained.

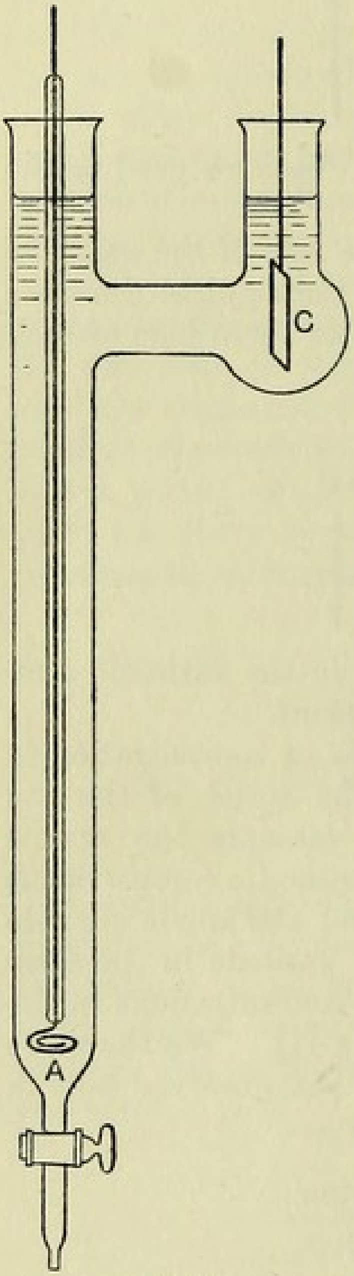
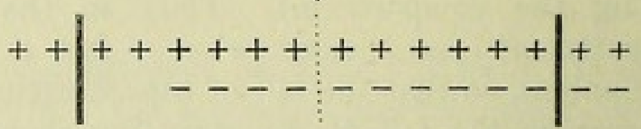


Fig. 38.

In this case the concentration round the anode does not fall off at all; for although silver ions leave the anodic limb, each nitrion that arrives at the anode dissolves from it one ion of silver so as to form silver nitrate. On the supposition that the ions move at the same rate, the state of the solution may be represented by Scheme V., which is comparable with Scheme III.

V



The concentration at the kathode has fallen off as before from 6 to 4, but the concentration at the anode has increased from 6 to 8, the total number of complete molecules remaining the same before and after the passage of the current. It is easy, however, to ascertain how many kations have crossed the diaphragm to the left, and thus find what the fall in concentration round the anode would have been had no silver been dissolved from the electrode. The reading of the voltameter tells us the quantity of electricity which has passed through the solution, *i.e.* the number of negative ions which have been discharged at the anode. In the above case it is 4. Now a molecule of silver nitrate appears at the anode for each negative ion discharged. If no kations had left the anodic compartment, there would thus be an increase in the concentration equal to 4; but the actual increase is only 2: therefore had no silver been dissolved from the anode there would have been a fall of concentration equal to 2, or 2 kations have crossed the diaphragm to the left in the same time as 2 anions have crossed it to the right.

In an actual experiment a current which deposited 32·2 mg. of silver in a silver voltameter was passed through a solution of silver nitrate contained in an apparatus similar to that of Fig. 38. The fall of concentration at the kathode corresponded to 16·8 mg. of silver as silver nitrate, and the rise in concentration round the anode to the same, since the total quantity of silver nitrate in solution necessarily remained unaltered. Had no silver ions migrated from the anode, the rise in concentration would have been 32·2, so that the fall due to migration of the kations is $32·2 - 16·8 = 15·4$. We have therefore

$$\frac{\text{Speed of kation, Ag}}{\text{Speed of anion, NO}_3} = \frac{\text{Fall round anode}}{\text{Fall round kathode}} = \frac{15·4}{16·8} = 0·917.$$

From the speed ratios for any substance it is easy to calculate what Hittorf called the **transport numbers** of the ions of the substance. If only the positive ion of a substance moves, as in Scheme II., this ion is responsible for the total electricity carried, the negative ion having no share in the transport. If both ions move, they share the transport between them, and as each equivalent of the ions has the same charge, the share of each in the transport is evidently proportional to the speed at which it moves. If u and v are the speeds of migration of the positive and negative ions respectively, $\frac{u}{u+v}$ represents the share taken by the kation in the transport, and $\frac{v}{u+v}$ the share taken by the anion. These are the transport numbers of Hittorf. It is customary to denote the transport number of the anion by n. The transport number of the kation is therefore $1 - n$, since the sum of the two transport numbers $\frac{u}{u+v}$ and $\frac{v}{u+v}$ is equal to 1. As has been indicated above, the ratio of the transport numbers of the ions is the ratio of their speeds, so that we have

$$\frac{u}{v} = \frac{1-n}{n}.$$

If we wish to express n in terms of the ratio of the speeds $u/v = r$, we have, from the above equation,

$$n = \frac{1}{1+r}.$$

As a numerical example, we may again take silver nitrate. For this salt we have

$$n = \frac{1}{1 + 0·917} = 0·522.$$

This may also, of course, be got directly from the fall of concentration round the electrodes, which are proportional to the speeds of the ions. We have

$$n = \frac{v}{u+v} = \frac{16{\cdot}8}{15{\cdot}4 + 16{\cdot}8} = 0{\cdot}522.$$

From his researches on the conductivity of dilute salt solutions, Kohlrausch established a very simple relation connecting the transport numbers and the molecular conductivity of the dissolved substance. By the **molecular conductivity** of a solution is meant its specific conductivity in the ordinary electrical units multiplied by the volume of the solution in litres which contains one gram molecular weight of the dissolved substance. In very dilute salt solutions the value of the molecular conductivity is independent of the concentration of the solution, and Kohlrausch found that this constant value was for different salts additively made up of two terms, one depending on the positive and the other on the negative radical, *i.e.* on the positive and negative ions. On considering any one salt, he found that the ratio of the terms for the two ions was the ratio of the speeds of migration of the ions. By properly choosing the units it was therefore possible to state for very dilute salt solutions, which exhibit a molecular conductivity independent of further dilution, the simple relation

$$\mu = u + v,$$

when μ is the molecular conductivity, and u and v numbers proportional to the relative speeds of the positive and negative ions. The numbers u and v do not of course represent the actual speeds of the ions, if the ordinary electrical units are employed for the molecular conductivity; but it is easy to calculate the absolute value of the velocities in any given case, and the following table contains the speeds of the principal univalent ions in dilute aqueous solution at 18°, when the difference of potential between the electrodes 1 cm. apart is 1 volt. The velocities of migration are given in centimetres per hour.

Kations.		Anions.	
H	10·8	OH	5·6
K	2·05	Cl	2·12
NH_4	1·98	I	2·19
Na	1·26	NO_3	1·91
Ag	1·66	$C_2H_3O_2$	1·04

The movement of the ions through practically pure water is seen, therefore, to be a very slow one. If we calculate the force required to drive 1 g. of hydrion through water at the rate of 1 cm. per second, it is found to be equal to about 320,000 tons weight. On reference to p. 171, it will be found that this number is of the same order of magnitude as the corresponding number calculated from the rate of diffusion of urea by means of the osmotic-pressure theory, viz. 40,000 tons.

It is somewhat curious that when the rates of migration of a series of ions such as those afforded by the metals of the alkalies are compared with each other, the metals with the greatest atomic weights move with the greatest speed. Thus potassion has a greater velocity of migration than sodion, and this again than lithion, whilst caesion moves at the greatest rate of all. This is usually accounted for by the assumption that the degree of hydration of lithion is greater than that of sodion, which is in its turn greater than that of potassion, and so on. On this view the positive ion of lithium salts is not lithium itself, but lithium plus a comparatively large amount of water which travels with it, and therefore reduces its rate.

The coincidence in the magnitudes of the driving forces would lead us to suspect that the resistance offered to the diffusion of substances in water and to the passage of ions through water under the influence of electric forces is of the same kind, and further inquiry serves to bear out the supposition. The resistance is connected with the viscosity or internal friction of the liquid, which may be measured by the time the liquid takes to flow through a narrow tube under given conditions. When the fluid friction increases, the resistance to the passage of substances through the liquid increases, and the rate of diffusion and rate of ionic migration diminish in consequence of the increased resistance which the particles in motion through the fluid experience. The addition of a small quantity of a substance such as alcohol to water increases the viscosity of the water. Corresponding to this increase we find that the rate of diffusion is less when a substance is dissolved in water containing a little alcohol than the rate of diffusion when water alone is the solvent, no matter what the dissolved substance may be. Similarly the speed of ions in water containing alcohol is less than their speed in pure water.

Again, when the temperature of water is raised, its fluidity increases. Corresponding to this we have increased rate of diffusion and ionic migration as the temperature increases. There is even a rough proportionality between the different magnitudes. Thus at the ordinary temperature the fluidity of water increases at the rate of about 2 per cent per degree. In close accordance with this, the rate of migration of ions through water increases about 2 per cent at 15° for a degree rise in temperature. Indeed, if slow-moving ions alone are considered, the influence of temperature on the conductivity of aqueous solutions and on the fluidity of water is almost exactly the same within wide limits, both conductivity and fluidity disappearing at a temperature of about $-35°$. The assumption that the ions are hydrated is again of service in enabling us to understand this exact accordance, for the sluggish ions are supposed to be most highly hydrated, so that the resistance they experience in passing through water is practically the resistance of their "water atmosphere" against water, *i.e.* precisely what determines the viscosity of pure water.

In connection with resistance, a word must be said as to the nature of that offered by **jellies.** If we make a 5 per cent solution of gelatine in hot water, it will set on cooling to a firm, stiff jelly, which we should be inclined to classify with solids rather than liquids. The jelly has very great internal friction, yet it offers little more resistance to the passage of diffusing substances or to moving ions than pure water does, so that the rate of diffusion or ionic migration is practically the same in an aqueous jelly as in water. The water in a jelly must therefore be supposed to retain its properties unchanged, and practically to remain fluid. The comparative rigidity of the jelly as a whole we must therefore attribute to the gelatine. The only reasonable conception of a jelly then that we can make is, that the gelatine on setting forms a sort of fine spongy network in which the liquid water is held immeshed by capillary forces, *i.e.* we must compare the state of the water in a jelly to the state of the water soaked up in a sponge or the water in the interstices of a porous cell. The porous pots used in galvanic elements prevent the mixing of the different liquids by convection, but they do not greatly hinder liquid diffusion proper or the passage of ions with their charges from one compartment to the other. The porous pot with the absorbed liquid is rigid, but the liquid in the wall retains its fluid properties unchanged.

The actual **determination of the molecular conductivity** as usually carried out in chemical laboratories proceeds as follows:—The principle adopted is to determine the resistance of the given solution by the arrangement known as Wheatstone's bridge, shown in the diagram, Fig. 39. R is a resistance box, by means of which resistances of known value can be introduced. W is the resistance to be measured—that of a piece of wire, for example. G is a galvanometer, and B a battery to produce current. MM′ is a platinum wire of uniform resistance stretched along a metre scale subdivided into millimetres. Connection is made between the galvanometer and any point on this wire by means of the sliding contact C. In general, a current flows through the galvanometer, but in the special case when the resistance of R is to that of W as the resistance of *a* is to that of *b*, no current flows through G, and the galvanometer exhibits no deflection. To determine the resistance of

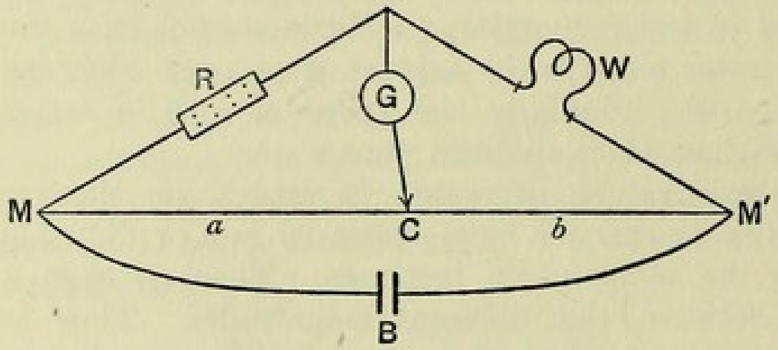


FIG. 39.

W we place a known resistance in the box R, and move the contact C along the platinum wire until the galvanometer shows no deflection. We know then that

$$R : W = a : b.$$

But the platinum wire is of uniform resistance, so that the resistance of a is to the resistance of b as the length of a is to the length of b, and these lengths may be read off directly on the scale along which the wire is stretched.

When the resistance to be measured is that of an electrolyte, it is generally impossible to use a galvanometer owing to the polarisation at the electrodes when a steady current flows through the electrolyte. This polarisation may be avoided by the use of an alternating current instead of a direct current, but then the galvanometer is useless to indicate the alternating current. Its place, however, may be taken, as Kohlrausch has shown, by the telephone, which is silent when no current passes through it, but sounds when it is traversed by alternating currents. The alternating current is got from the secondary coil of a small inductorium, worked by the battery B, which is usually a single bichromate cell. The modified arrangement is shown in Fig. 40, where S is the electrolytic solution, T the telephone, and I the induction coil.

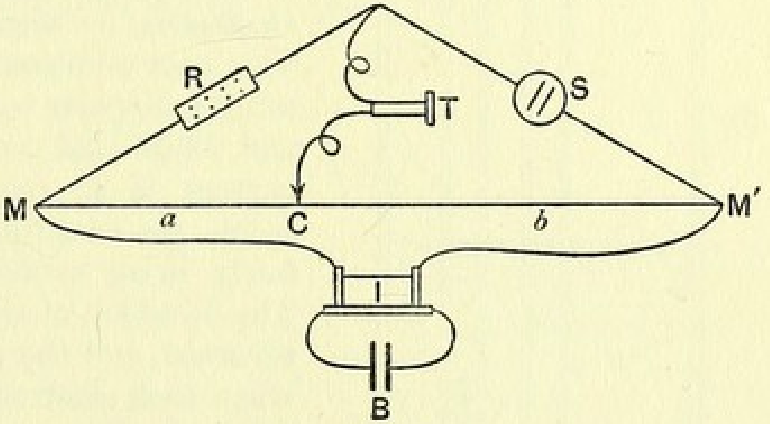


FIG. 40.

The vessel which contains the solution is generally of the type proposed by Arrhenius, and shown in Fig. 41 in natural size. The electrodes are made of stout platinum discs, fitting closely to the cylindrical vessel. A short platinum stem from each is sealed into a glass tube, held firmly in the ebonite cover C. The connecting wires are passed down the glass tubes till they make contact with the platinum wires by means of a drop of mercury introduced into each tube. This form is most suitable for very small conductivities. For solutions which have greater conductivity, a modified type with a narrower end may be employed, which has the advantage of being considerably cheaper on account of the much smaller size of the platinum electrodes used in its construction. If the platinum electrodes are bright, there is no sharp minimum of sound in the telephone at any position of the sliding contact. It is therefore necessary to cover the surface of the platinum with a coating of finely-divided platinum, and the success of the method largely depends on how the platinisation of the electrodes is effected. If a fine velvety coating of platinum black does not entirely cover the inner surfaces of the electrodes, the sound minimum is more or less indistinct owing to the polarisations of the make and break induction currents not exactly neutralising each other, and the measurements of resistance in consequence are more or less doubtful. The platinisation is carried out by electrolysing a solution of platinum chloride (chloroplatinic acid) between the electrodes by means of a direct current. The best solution to employ is one containing 30 parts water, 1 platinum chloride, and 0·008 lead acetate. The electrolysing current is so regulated that there is a feeble gas evolution from the anode and a fairly brisk evolution from the kathode. The direction of the current is occasionally reversed, and the platinisation is complete when each electrode has served as kathode for about fifteen minutes.

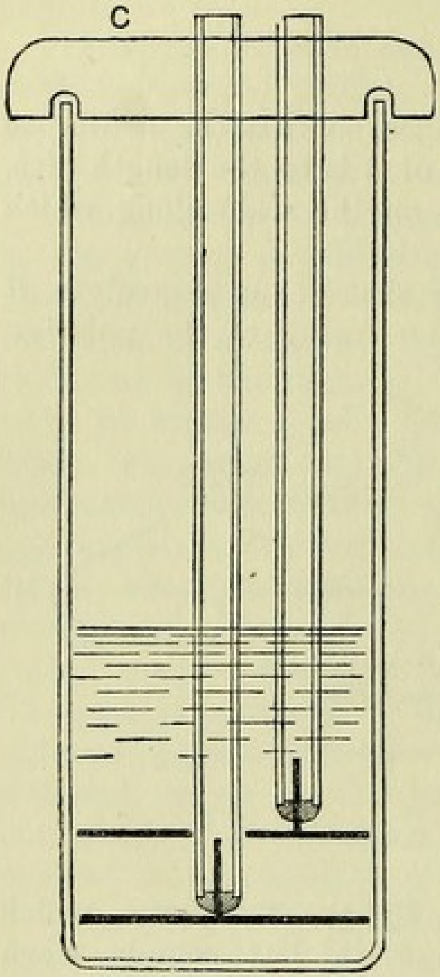


FIG. 41.

A large induction coil is not necessary for the success of the method; in fact, a small toy coil with a high rate of alternation works best in the chemical laboratory. It should be some six feet distant from the measuring wire, and enclosed in a box so that the sound from the make and break of the coil itself does not interfere with the sound in the telephone.

The cell containing the electrolytic solution is immersed in a bath of constant temperature, usually 25°, fluctuations of more than a tenth of a degree from the mean being inadmissible, owing to the great variation of the conductivity with the temperature.

For chemical purposes the dilutions generally are made to increase in powers of 2. If the substance under investigation is sufficiently soluble, a solution containing a gram equivalent, or a gram molecule, in 16 litres is first prepared, and 20 cc. of this solution introduced into the electrolytic cell by means of a 10 cc. pipette twice filled. Another 10 cc. pipette is marked by direct experiment so as to remove exactly as much water as the first pipette delivers. After the first reading of the conductivity has been taken, 10 cc. of the solution are removed by the second pipette and 10 cc. of water added by means of the first pipette, after which the diluted solution is well mixed by motion of the electrodes. The solution is now twice as dilute as formerly, *i.e.* its dilution is 32. The reading is repeated after the solution has attained the temperature of the bath, and the dilution process is gone through anew. When the dilution has reached 1024 the process is usually stopped, except in the case of strongly-dissociated salts, for the conductivity caused by impurities in the distilled water renders the values uncertain.

For further information concerning methods for the determination of electric conductivity in solutions, see OSTWALD, *Physico-Chemical Measurements* (1894); KOHLRAUSCH AND HOLBORN, *Leitvermögen der Elektrolyte* (1898).

F. KOHLRAUSCH, "The Resistance of the Ions and the Mechanical Friction of the Solvent," *Proc. Roy. Soc.* 71 (1903), p. 338.

CHAPTER XXI

ELECTROLYTIC DISSOCIATION

In the preceding chapter we have become acquainted with some of the fundamental facts of electrolysis; in the present chapter we proceed to the consideration of a mechanical scheme which affords a simple mode of representing them, as well as many other peculiarities of electrolytic solutions. Before entering on the discussion of this scheme, however, it is necessary to draw attention to two further facts which must be accounted for by any satisfactory theory of electrolysis.

In the first place, it has been ascertained by careful experiment that electrolytic solutions obey Ohm's Law as strictly as do metallic conductors, the current being proportional to the electromotive force for all values of the force. A direct consequence of this is that no electrical energy is expended in splitting up the dissolved salt molecules into their constituent ions, as was first indicated by Clausius.

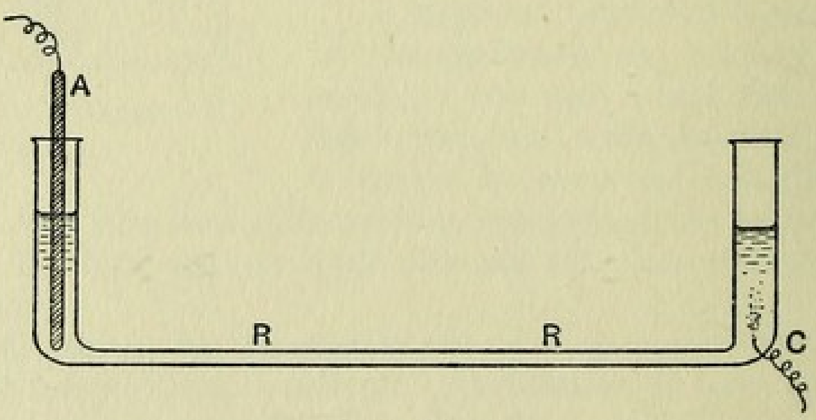
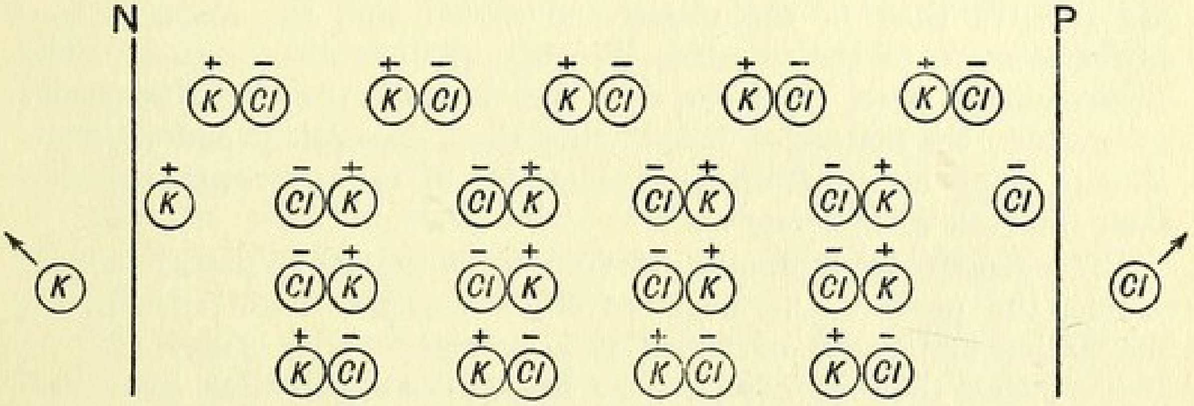


Fig. 42.

In the second place, when the circuit is completed between two electrodes, the products of electrolysis appear simultaneously at both, no matter how far apart they may be. Thus if we have, as in Fig. 42, a narrow glass tube RR, 1 cm. in bore and 40 cm. long, connected at the ends with wide tubes containing the two electrodes A and C, and filled with sulphuric acid, the products of the electrolysis of the sulphuric acid will make their appearance at the electrodes as soon as connection is made through a powerful battery. If the anode A is of copper and the kathode a piece of platinum wire, the blue colour of copper sulphate and the bubbles of hydrogen at C will be observed simultaneously. Now the first hydrogen ions cannot therefore come from the same molecules of sulphuric acid as the first sulphite ions, which unite with the copper to form copper sulphate, for the ions, in whatever way they might be supposed to move, could not traverse a distance of 40 cm. in a few seconds, as may be seen from the table of rates of migration given in the preceding chapter.

In the schemes for the representation of the migration of the ions, we have assumed that there is a constant change of partners going on as the ions travel to the opposite electrodes. This idea was introduced by Grotthus, who conceived that the molecules at the two electrodes were split up into their positive and negative constituents under the influence of the electric charges on the electrodes, and that the intermediate molecules changed partners according to a scheme like the following, the first action of the electric charges being to direct all the positive ends of the molecules towards the negative electrode and the negative ends towards the positive electrode :—



This, however, does not get over the difficulty indicated by Clausius, an account of whose views may be given in the words of Clerk Maxwell.

"Clausius has pointed out that on the old theory of electrolysis, according to which the electromotive force was supposed to be the sole agent in tearing asunder the components of the molecules of the electrolyte, there ought to be no decomposition and no current as long as the electromotive force is below a certain value, but that as soon as it has reached this value a vigorous decomposition ought to commence, accompanied by a strong current. This, however, is by no means the case, for the current is strictly proportional to the electromotive force for all values of that force.

"Clausius explains this in the following way :—According to the theory of molecular motion, of which he has himself been the chief founder, every molecule of the fluid is moving in an exceedingly irregular manner, being driven first one way and then another by the impacts of other molecules which are also in a state of agitation.

"This molecular agitation goes on at all times independently of the action of electromotive force. The diffusion of one fluid through another is brought about by this molecular agitation, which increases in velocity as the temperature rises. The agitation being exceedingly irregular, the encounters of the molecules take place with various degrees of violence, and it is probable that even at low temperatures some of the encounters are so violent that one or both of the compound molecules are split up into their constituents. Each of these constituent molecules then knocks about among the rest till it meets with another molecule of the opposite kind, and unites with it to form a new molecule of the compound. In every compound, therefore, a certain proportion of the molecules at any instant are broken up into their constituent atoms. At high temperatures the proportion becomes so large as to produce the phenomenon of dissociation studied by M. Ste. Claire Deville.

"Now Clausius supposes that it is on the constituent molecules in their intervals of freedom that the electromotive force acts, deflecting them slightly from the paths they would otherwise have followed, and causing the positive constituents to travel, on the whole, more in the positive than in the negative direction, and the negative constituents more in the negative direction than in the positive. The electromotive force, therefore, does not produce the disruptions and reunions of the molecules, but, finding these disruptions and reunions already going on, it influences the motion of the constituents during their intervals of freedom."

The constituent molecules referred to in the above passage are, of course, the positive and negative radicals of the dissolved salt, *i.e.* the kation and anion of which it is assumed to be composed. At any one time then we have, on the hypothesis of Clausius, some proportion of the salt molecules split up into their constituent ions, which, with their electric charges, move towards the appropriate electrodes. It must be observed that this state of partial dissociation of the dissolved substance is the normal condition of the liquid, and exists whether there is an electric current passing through the solution or not. All that the electric forces do is to direct the dissociated charged products to the electrodes and there discharge them. Nothing has been said as to the proportion of dissolved substance which is thus dissociated into ions. For the purpose of accounting for the validity of Ohm's Law in electrolytic solutions, any proportion, however small, will suffice, provided that the small quantity is always regenerated by the action of the molecules themselves without any interference of the electrical forces. In proportion as the free ions are removed from the solution at the electrodes, Clausius supposes them to be regenerated by the collisions of the undissociated molecules, so that the process of conduction and electrolysis goes on. If we are to give the hypothesis definiteness and precision, however, we must take account of the relative quantities of the electrolyte in the dissociated and undissociated states. The manner of doing this was first pointed out by Arrhenius, and it is to his hypothesis of **electrolytic dissociation** that we must resort if we wish to explain quantitatively the phenomena exhibited by electrolytic solutions, whether during electrolysis or in their ordinary state.

Arrhenius supposes substances which give solutions that conduct electricity freely to be almost entirely split up into their constituent ions, while substances which yield solutions of feeble conductivity are supposed by him to be split up only to a very small extent. In fact, he proposes to measure the degree of dissociation of a substance by the conductivity of its solutions. On his hypothesis, only those molecules which are split up into their constituent ions play any part in the conduction of electricity, the undissociated molecules remaining idle. It is obvious, therefore, that the conductivity of any given solution depends on two factors—the number of ions in the solution, and the rate at which these ions move. To simplify matters we will, in what follows, only consider univalent ions, *i.e.* those derived from monacid bases, monobasic acids, and the salts which they form by mutual neutralisation. Every ion derived from these substances has the same charge of electricity, *i.e.* 96,500 coulombs per gram-ion. Since each carrier of electricity has the same load, the quantity carried can depend only on the number of carriers and the speed at which they move. Now the rate at which the ions move may, as we have seen, be determined from the work of Hittorf and Kohlrausch. It only remains, therefore, to find the number or proportion of ions in any given solution.

Kohlrausch ascertained experimentally that the molecular conductivity of a salt increases as the dilution of the solution increases, and that the rate of increase of conductivity gets smaller and smaller as the dilution gets greater, until finally the molecular conductivity remains constant, although the addition of water to the solution is continued. This may best be figured as follows. Consider a cell of practically infinite height and of rectangular horizontal section, two parallel sides of which are of platinum, and are placed at a distance of 1 cm. from each other. These platinum sides may be used as electrodes. Let there now be introduced into the cell a gram molecular weight of common salt (58·5 g.) dissolved in a litre of water. If the resistance offered to the passage of the current through the liquid is measured in Siemens' mercury units (p. 6), the reciprocal of the number obtained represents the molecular conductivity as ordinarily expressed. We thus obtain the molecular conductivity of sodium chloride at the dilution 1. If we add water so as to make up the volume to 2 litres, and again determine the molecular conductivity, we find that the value for the dilution 2 is greater than before. As we add more water so as to increase the volume in which the gram-molecular weight of the salt is contained, the molecular conductivity will also increase, finally to reach a limit when the dilution amounts to about 10,000 litres. The numbers obtained by Kohlrausch for sodium chloride at 18° are given in the following table:—

Dilution $= v$	Mol. Cond. $= \mu$	Dissociation $= m$
1 lit.	69·5	0·675
2 ,,	75·7	0·736
10 ,,	86·5	0·841
20 ,,	89·7	0·872
100 ,,	96·2	0·935
500 ,,	99·8	0·970
1,000 ,,	100·8	0·980
5,000 ,,	101·8	0·989
10,000 ,,	102·9	...
50,000 ,,	102·8	...
100,000 ,,	102·4	...

From this table it will be seen that the rate of increase of the molecular conductivity is much greater when the dilution is small than when it is great. Doubling the quantity of water when the dilution is 1 adds more than 6 units to the conductivity; doubling the quantity when the dilution is 500 only adds 1 unit to the conductivity. Increasing the dilution tenfold when it is already 10,000 has no further effect, the small variations observed in the last three values being due to experimental error.

The molecular conductivity, as has been said, depends only on the number of ions and the rate at which they move. We have therefore to determine to which of these causes the increase of molecular conductivity on dilution is due. The rate of the ions depends on the resistance to their motion offered by the liquid. Now at a dilution of 10 we have 58·5 g. of salt dissolved in 10,000 g. of water. So far as viscosity is concerned, this is practically pure water, and further additions of water should have no appreciable effect in changing the resistance offered to the passage of the ions. We may suppose therefore that the rate at which the ions travel is practically unaltered after a dilution of about 10 is reached, so that the increase of conductivity with further dilution is not due to any increase of speed of the ions, but to an increase in their number. In the imaginary cell considered above we have always the same amount of salt between the electrodes, but evidently as we add water we obtain a greater proportion of ions. With increasing dilution the salt then must split up more and more into ions capable of conveying the electricity, if we are to account for the increase of molecular conductivity which the salt exhibits. When all the salt has been split up into its ions the increase of molecular conductivity with dilution must cease, for further dilution can neither increase the speed of the ions nor augment their number. In the case of sodium chloride the salt is entirely ionised at a dilution of 10,000, and we find that salts in general exhibit this behaviour. The limiting value of the molecular conductivity corresponding to complete ionisation is called the **molecular conductivity at infinite dilution**, and is usually denoted by μ_∞.

Since in dilute solutions the addition of more water is assumed not to affect the speed of the ions, it is obvious that in a cell such as we considered above, the conductivity of the solution is directly proportional to the amount of ionised substance in it. Now we know that at infinite dilution all the sodium chloride is ionised. At finite dilutions, therefore, the degree of dissociation, *i.e.* the proportion of the whole which exists in the state of ions, is equal to the quotient of the molecular conductivity at the dilution considered by the molecular conductivity at infinite dilution. The degree of dissociation or ionisation is generally denoted by m, so we have the equation

$$m = \frac{\mu_v}{\mu_\infty}.$$

For example, if we wish to ascertain the degree of ionisation of sodium chloride at a dilution of 1 litre, *i.e.* in normal solution, we divide the molecular conductivity, 69·5, by the molecular conductivity at infinite dilution, viz. 102·9, and obtain as quotient 0·675. In a normal solution of sodium chloride then at 18°, a little over two-thirds of the salt is split up into its constituent ions.

It must be very specially emphasised that the molecular conductivity itself is no measure of the degree of ionisation of a dissolved substance; the true measure is the ratio of this conductivity to the molecular conductivity at infinite dilution. The degree of ionisation is *not* proportional to the molecular conductivity unless under certain conditions which must be carefully specified. For example, the molecular conductivity of a normal solution of sodium chloride at 50° is 120. This is nearly twice as great as the molecular conductivity at 18°, but the increase cannot come from a duplication of the number of ions, as the salt at 18° is already more than half ionised. The great increase in the molecular conductivity is due to the increase in the other factor, namely, the speed of the ions. The fluid friction of the solution is greatly diminished by the rise in temperature, and consequently the ions move much faster, thus in a given time conveying more electricity. At 50° the molecular conductivity at infinite dilution is 185. If we therefore divide 120 by this number we obtain an ionisation approximately equal to 0·65, which is practically the same value as we got for 18°. In general, we find with salts that rise of temperature, while greatly augmenting the molecular conductivity, has very little effect on the degree of ionisation, the increase in the conductivity being almost wholly due to the increased speed of the ions.

In a similar way the addition of non-conducting substances to salt solutions lowers the conductivity without appreciably altering the ionisation as measured by the ratio of the molecular conductivity at the dilution considered to that at infinite dilution. Thus diethylammonium chloride dissolved in water and in mixtures of water and ethyl alcohol gave the following values at 25° for decinormal solutions, and for infinite dilution :—

Percentage of Alcohol by Volume.	μ_{10}	μ_{∞}	$m = \frac{\mu_{10}}{\mu_{\infty}}$
0	84·7	107·5	0·788
10·1	64·9	83·5	0·778
30·7	40·5	53·9	0·751
49·2	30·0	42·9	0·699
72·0	23·9	39·4	0·607
90·3	17·0	38·8	0·438

The column headed μ_{∞} gives the effect of the alcohol in reducing the speed of the ions, since at infinite dilution the salt is entirely ionised in each case, the ionised amount being therefore the same throughout. In the last column we have the degree of ionisation as measured by the ratio of the molecular conductivity at 10 litres to μ_{∞}. The addition of alcohol diminishes both the speed of the ions and the ionisation, so that the molecular conductivity in decinormal solution is reduced from both these causes. It will be noticed, however, that these two effects of the addition of alcohol do not go hand in hand. The degree of ionisation is scarcely affected by the first substitutions of alcohol for water (up to 30 per cent), while the speed of the ions, and consequently the molecular conductivity, is reduced to one-half. On the other hand, when nearly all the water has been replaced by alcohol, the effect of further additions is scarcely noticeable on the speed of the ions, but very marked on the degree of ionisation, and consequently on the molecular conductivity, in decinormal solution. On the whole the molecular conductivity in decinormal solution in 90 per cent alcohol is only about a fifth of what it is in pure water: if the speed of the ions alone had been affected, the reduction would have been to a value a little more than a third of the value for water; the balance of the reduction is due to diminution in the degree of ionisation.

The student is particularly recommended to a close study of the above examples, in order that he may become familiar with the two factors on which the molecular conductivity depends, as beginners almost invariably neglect to take account of the change in speed of the ions under different conditions, and thus from the values of the molecular conductivity draw utterly erroneous conclusions regarding the degree of ionisation. Degree of ionisation is never proportional to molecular conductivity unless the speed of the ions is the same in the two solutions compared. If two dilute solutions contain the same salt dissolved in the same solvent at the same temperature, then the degree of ionisation of the substance in the two solutions *is* proportional to the molecular conductivity, for the maximum molecular conductivity is the same in both cases. But if in the solutions compared the dissolved substance is different, the solvent is different, or the temperature is different, then the molecular conductivity is no longer a measure of the degree of ionisation, for the maximum molecular conductivity will no longer be the same.

If we investigate the influence of dilution on the molecular conductivity of dilute solutions, we find that the weak acids and bases which form the group of half-electrolytes obey a law which was deduced by Ostwald from theoretical considerations, as will be shown in a subsequent chapter. Since other conditions are the same, and increase in dilution does not affect the speed of the ions, the change in the molecular conductivity observed is due entirely to change in the degree of ionisation. If we represent the degree of ionisation by m and the dilution by v, the following relation holds good :—

$$\frac{m^2}{(1-m)v} = \text{constant.}$$

The constant is usually denoted by k, and is called the **dissociation constant.** In the subjoined tables are given the values obtained at 25° for acetic acid and ammonia respectively.

Acetic Acid, CH_3COOH

$\mu_\infty = 364$

v	μ	$100m$	$100k$
8	4·34	1·193	0·00180
16	6·10	1·673	0·00179
32	8·65	2·380	0·00182
64	12·09	3·33	0·00179
128	16·99	4·68	0·00179
256	23·82	6·56	0·00180
512	32·20	9·14	0·00180
1024	46·00	12·66	0·00177
		Mean .	. 0·00180

Ammonia, $NH_4(OH)$

$\mu_\infty = 237$

v	μ	$100m$	$100k$
8	3·20	1·35	0·0023
16	4·45	1·88	0·0023
32	6·28	2·65	0·0023
64	8·90	3·76	0·0023
128	12·63	5·33	0·0023
256	17·88	7·54	0·0024
		Mean .	. 0·0023

In the third column of the tables is given the percentage ionisation, *i.e.* the degree of ionisation multiplied by 100 ; and in the fourth column is one hundred times the value of the dissociation constant derived from the above formula. This centuple constant is often used instead of the smaller number on account of its leading for all substances to more convenient figures. The values of the constant at particular dilutions vary as a rule only 1 or 2 per cent from the mean, and this variation is due to errors of observation, which are greatly magnified in the calculation of the constant.

In the first place, it is evident from the tables that acetic acid and ammonia in equivalent solutions are about equally ionised, the former into hydrion, $H^{\cdot}$, and acetanion, CH_3COO', the latter into ammonion, $NH^{\cdot}_4$, and hydroxidion, OH'. If we compare these tables with that given on p. 232 for a good electrolyte, it will be seen that dilution has a far greater influence on the molecular conductivity in the former case than the latter. For sodium chloride an increase of the dilution from 1 to 100,000 only increases the molecular conductivity by about half its value; while an increase in the dilution from 8 to 1024 increases the molecular conductivity of acetic acid more than tenfold. Although the molecular conductivity thus increases much more rapidly with the dilution than is the case for good electrolytes, yet the increase is not nearly proportional to the increase in the dilution. When the degree of ionisation is small the molecular conductivity is roughly proportional to the square root of the dilution, as may be seen from a consideration of the general formula

$$\frac{m^2}{(1-m)v} = k.$$

For small degrees of ionisation, $1 - m$ is not greatly different from 1, so that the formula becomes

$$m^2 = kv, \text{ or } m = k'\sqrt{v}.$$

If in the general formula we put $m = 0{\cdot}5$, *i.e.* if we assume that the electrolyte is half ionised, we obtain a conception of the physical dimensions of the constant k. The expression becomes

$$\frac{0{\cdot}5^2}{(1-0{\cdot}5)v} = k,$$

whence $$\frac{1}{2v} = k, \text{ or } \frac{1}{2}c = k, \text{ if } c = \frac{1}{v}.$$

In words, the dissociation constant k is numerically equal to half the concentration at which the substance is half dissociated, the concentration being expressed in gram molecules per litre. Thus for acetic acid we have $k = 0{\cdot}000018$, whence $c = 0{\cdot}000036$, *i.e.* acetic acid is half ionised when the concentration of its aqueous solution is 0·000036 normal.

It is obvious that if in such a solution, which contains only about 2 parts of acetic acid per million, the acid is only half ionised, the direct determination of the molecular conductivity for solutions in which the acid is wholly ionised is an impossibility. Yet the value of the molecular conductivity must be known in order that the degree of ionisation may be calculated. It has therefore to be determined indirectly by means of Kohlrausch's Law. Although weak acids and weak bases are but half-electrolytes, their salts are good electrolytes, and as much dissociated in solution as the corresponding salts of strong acids and bases. Thus for sodium acetate at 25° we have the following numbers:—

v	μ	m
32	75·5	0·858
64	77·6	0·882
128	79·8	0·907
256	81·6	0·927
512	83·5	0·949
1024	85·0	0·966
∞	88·0	...

For ammonium chloride, Kohlrausch found at 18° numbers much the same as those for sodium chloride, p. 232, viz.—

v	μ	m
1	90·7	0·750
2	94·8	0·784
10	103·5	0·856
20	107·8	0·892
100	114·2	0·945
500	118·0	0·976
1,000	119·0	0·985
5,000	120·4	...
10,000	120·9	...
50,000	120·9	...

It is an easy matter, then, to find numbers for the molecular conductivity at infinite dilution in the case of *salts* of weak acids or bases. Now, according to Kohlrausch's Law, there is a constant difference between the maximum molecular conductivities of all acids and their sodium salts—a difference due to the difference in speed of hydrion and sodion. But strong acids like hydrochloric acid are at equivalent dilutions quite as much ionised as their sodium salts, so that their maximum molecular conductivities may be determined experimentally. For these acids we can thus get directly the difference between their maximum molecular conductivity and that of their sodium salts. This difference, amounting at 25° to about 275 in the customary units, when added to the maximum molecular conductivity of the sodium salt of an acid, which can always be directly determined, gives the molecular conductivity of the acid itself at infinite dilution, and this enables us to give the degree of ionisation of the acid at any other dilution.

It is a curious fact, of which no adequate explanation has as yet been given, that good electrolytes do not obey Ostwald's dilution law, which holds so accurately for the half-electrolytes. Certain empirical relations have, however, been found connecting the degree of ionisation and the dilution, and these have a form similar to that of Ostwald's dilution formula, although they have not the theoretical foundation possessed by the latter. The first of these relations is called **Rudolphi's dilution formula,** and differs from Ostwald's by the square root of the dilution being introduced instead of the dilution itself. It has thus the form

$$\frac{m^2}{(1-m)\sqrt{v}} = \text{constant},$$

and agrees fairly well with the observed values. Thus for ammonium chloride at 18° we have the following numbers :—

v	m	$\frac{m^2}{(1-m)\sqrt{v}}$
10	0·852	1·55
20	0·887	1·56
33·3	0·906	1·52
100	0·940	1·47
166·7	0·952	1·47
500	0·971	1·46
1000	0·979	1·47
1667	0·985	1·60
5000	0·991	1·53
	Mean . .	1·51

The second empirical dilution formula is that of van 't Hoff, which in some respects is simpler than Rudolphi's, and accords quite as closely with the facts. We may write Ostwald's dilution formula in the form

$$\frac{\left(\frac{m}{v}\right)^2}{\frac{1-m}{v}} = \text{constant},$$

where $\frac{m}{v}$ is the concentration of the ionised portion of the electrolyte, and $\frac{1-m}{v}$ the concentration of the unionised part. If C_d and C_u represent these concentrations, we have the simple expression

$$\frac{C_d^2}{C_u} = \text{constant}.$$

Rudolphi's formula gives no such simple relation of the concentrations of the ionised and unionised portions. Van 't Hoff proposes the expression

$$\frac{m^{\frac{3}{2}}}{(1-m)\sqrt{v}} = \text{constant},$$

which may be written in the form

$$\frac{\left(\frac{m}{v}\right)^3}{\left(\frac{1-m}{v}\right)^2} = \frac{C_d{}^3}{C_u{}^2} = \text{constant.}$$

Here again we have a simple relation between the concentration of the ionised and unionised portions, and the constancy of the expression is at least equal to that obtained with Rudolphi's formula, as is shown by the subjoined table for ammonium chloride :—

v	m	$\frac{m^{\frac{3}{2}}}{(1-m)\sqrt{v}}$
10	0·852	1·68
20	0·887	1·66
33·3	0·906	1·60
100	0·940	1·52
166·7	0·952	1·51
500	0·971	1·48
1000	0·979	1·49
1667	0·985	1·61
5000	0·991	1·54
	Mean . .	1·56

According to the foregoing hypothesis of electrolytic dissociation, aqueous solutions of salts, strong acids, and strong bases have a certain proportion of the dissolved molecules split up into charged ions, and the amount in any given case is determinable from measurements of electrical conductivity. The ions are supposed to be independent of each other, and ought to act as separate molecules if the independence is complete. We should therefore expect that salt solutions, when investigated by the customary method of molecular-weight determination, should exhibit exceptional behaviour, and give for the molecular weights of the dissolved substances, values smaller than those which we should deduce from the ordinary molecular formulæ. As has already been indicated, such abnormal values are frequently observed. When the molecular weight of sodium chloride and other similar salts is determined from the freezing or boiling points of their aqueous solutions, the numbers obtained are only equal to little more than half the values given by the formula NaCl, *i.e.* the depressions of the freezing point and the elevations of the boiling point have almost twice the normal value. A normal solution of cane sugar freezes at − 1·87° ; a normal solution of sodium chloride freezes at − 3·46°. Such an abnormally high value for the depression indicates that there are more dissolved molecules in the normal solution of common salt than there are in the normal solution of sugar, although each solution in the usual system of calculation is supposed to contain 1 gram molecule per litre. It should be noted at once that it is only electrolytic solutions which show these abnormally high values, the values given by non-electrolytic solutions being almost invariably equal to, or less than, the normal values. Abnormally small values we have already attributed to molecular association (cp. p. 202), so that we ought, by parity of reasoning, to attribute the abnormally large values for salt solutions to a dissociation of the molecules.

Van 't Hoff introduced for salt solutions a coefficient i which represents the number by which the normal value of the freezing point, etc., must be multiplied in order to give the value actually found. Thus for the solution of sodium chloride we have the depression 3·46°, instead of the "normal" value 1·87 shown by solutions of non-electrolytes containing 1 gram molecule per litre. In this case $i = 3{\cdot}46/1{\cdot}87 = 1{\cdot}85$, *i.e.* the normal value 1·87 has to be multiplied by 1·85 in order to bring it up to the observed value 3·46.

In the first place, it is to be noticed that for salts, acids, and bases which, according to the theory of electrolytic dissociation, split up into two ions, the coefficient i is never greater than 2. If dissociation into two ions were complete, the value for the depression of freezing point, etc., would be twice the normal value, since each molecule represented by the ordinary chemical formula becomes two independent molecules by dissociation. Now at common dilutions the ionisation is never complete, so that the value of the depression should be something less than 2, as is actually found by observation. When the dissociation hypothesis admits of a dissociation into more than two charged molecules, the depressions of the freezing point give values of i greater than 2. Thus strontium chloride, according to the dissociation hypothesis, splits up at infinite dilution into the three ions, $Sr^{\cdot\cdot}$, Cl', and Cl', the first of which has two charges of positive electricity, and the others a charge each of negative electricity. At moderate dilutions, therefore, we ought to expect a value of i less than 3, but probably greater than 2, as the dissociation of salts is generally high. We find in accordance with this that strontium chloride in decinormal solution gives the depression 0·489, instead of the value 0·187 obtained for non-electrolytes. The value of i is therefore $0{\cdot}489 \div 0{\cdot}187 = 2{\cdot}6$.

It is obvious from the above examples that there is a direct numerical relation between the degree of ionisation in any given case and van 't Hoff's coefficient i, so that if one is given the other can be calculated. If the degree of ionisation of a binary salt in solution is m, then there will be present in the solution $1 - m$ undissociated molecules and $2m$ dissociated molecules, in all $1 + m$ molecules for each molecule represented by the chemical formula. The depression of the freezing point, etc., will therefore have $1 + m$ times the normal value, *i.e.*

$$i = 1 + m.$$

Should the original molecule split up into n ions when the ionisation is complete, m again representing the ionised proportion, there will be present $1 - m$ undissociated molecules, and nm dissociated molecules, in all $1 + (n - 1)m$ molecules for each original molecule, *i.e.* we shall have

$$i = 1 + (n - 1)m.$$

Giving m in terms of i, we have

$$m = i - 1$$

for dissociation into two ions, and

$$m = \frac{i - 1}{n - 1}$$

for dissociation into n ions.

A comparison of the values of i deduced for the same solution directly from the freezing point, and indirectly from determinations of m by means of the electric conductivity, shows very fair accordance between the two methods. In the first place, it is found that in the case of non-electrolytes where $m = 0$, we have $i = 1$, *i.e.* we obtain the normal value for the freezing-point depression, etc.; and Arrhenius showed from his own freezing-point determinations that the values obtained for i with electrolytes differ from the corresponding values calculated from the electric conductivity by not more than 5 per cent on the average. Although this difference is comparatively great, better accordance was scarcely to be expected owing to the difficulty in effecting the comparison. It must be borne in mind that the molecular conductivity can only give accurate figures for the degree of ionisation when the solutions are so dilute that further dilution does not sensibly change the speed of the ions. Now this condition necessitates a dilution of at least 10 litres, *i.e.* the solution must not be more concentrated than decinormal, even in the most favourable case. But the normal depression for a decinormal solution is only 0·187°, so that to obtain an accuracy of 1 per cent on the value of i, as measured by the freezing-point depression, we must be able to determine depressions with an accuracy of about a thousandth of a degree centigrade. It is by no means easy to attain this degree of accuracy, the error in ordinary careful work with Beckmann's apparatus being nearer a hundredth of a degree than a thousandth. For more dilute solutions the relative error on the depression is of course still greater, and extraordinary precautions have to be taken if the freezing points are to be of any value in calculating van 't Hoff's coefficient i, or the degree of ionisation m. The following table gives a comparison of the degree of ionisation of solutions of potassium chloride as calculated from Whetham's determinations of the conductivity at 0°, and from the mean value of the best series of observations on the freezing point by different investigators. In the first column we have the dilution in litres, in the second the percentage dissociation deduced from the freezing points, and in the third the same magnitude calculated by means of the dissociation hypothesis from the conductivity :—

Dilution.	Percentage Ionisation = 100 m.	
v	From Freezing Point.	From Conductivity.
10	86·0	89·6
20	88·8	91·7
33·3	90·8	93·2
100	95·3	96·2

This is a typical example of the numerical agreement attained by the two methods of calculation, which, it must be remembered, are entirely independent of each other. As a rule the divergencies amount to about 2 per cent of the actual values, the numbers deduced from the conductivity being generally the greater, but the parallelism between the series is always close. In normal solutions the differences are much larger, as the student may see in the case of sodium chloride, the numbers for which have been given above; but this of course arises from the conditions for the comparison not being fulfilled.

The cause of the absence of exact agreement between the electrical and freezing-point methods of estimating ionisation, and also of the want of obedience to Ostwald's dilution law in the case of good electrolytes, has given rise to much discussion. At present the general tendency seems to be to question the validity of the assumption that the speed of all ions remains uninfluenced by increasing dilution after the value $v = 10$. If this assumption is not strictly valid in all cases, it follows that the conductivity method of estimating the degree of ionisation may give slightly incorrect values. Much experimental work still remains to be done, however, before the question can be regarded as definitely settled.

From what has been stated above, it is obvious that the hypothesis of electrolytic dissociation affords a satisfactory explanation of the anomalous behaviour of the solutions of salts, strong acids, and strong bases with regard to freezing point, boiling point, and in general all magnitudes directly derivable from the osmotic pressure. Not only does it do this, but it explains also very directly the additive character of most of the properties of salt solutions. In a previous chapter it has been shown that the properties of salts in aqueous solution are most simply explained when we assume that they are additively composed of two terms, one depending on the basic or positive portion of the salt, and the other on the acidic or negative portion. According to the theory of electrolytic dissociation, the salt is actually decomposed on dissolution in water into its positive and negative ions, which then lead an independent existence, each conferring therefore on the solution its own properties undisturbed by the properties of the other ion. The total numerical value of any given property in a salt solution will consequently be made up of the value for the positive ion plus the value for the negative ion, at least when the solutions considered are dilute, and so the additive character of the properties of salt solutions is satisfactorily accounted for.

The theory of electrolytic dissociation offers, too, a simple explanation of a set of facts that are so familiar that we generally accept them without any attempt at accounting for them. It is well known that salts in aqueous solution enter into double decomposition with the greatest readiness. If we add a soluble silver salt to a soluble chloride, a precipitate of silver chloride is at once produced. The positive and negative radicals here exchange partners, and they do so readily because the positive and negative for the most part exist free in the solution as ions, so that the whole action practically consists of the union of the silver ions with the chloride ions to produce the insoluble silver chloride. If alcohol is used as solvent, the action takes place with equal readiness. If we take now a solution in alcohol of an organic chloride, such as phenyl chloride, we find that it is a non-electrolyte, and corresponding with this, it may be mixed with an alcoholic solution of silver nitrate without any double decomposition taking place. Even after boiling for a considerable time there is little or no silver chloride produced. In this case there are no free chloride ions in the solution to unite directly with the silver ions, and consequently the action is much slower. Other organic halogen compounds act much more rapidly than phenyl chloride when in alcoholic solution, but it is very doubtful if any act with a speed even approximately comparable with that of the inorganic chlorides. Reactions between salts in aqueous solution, which do not proceed by a simple rearrangement of the ions, are much slower than the double decompositions where the ions undergo no change except rearrangement. We have instances of this type of reaction in the oxidations and reductions occurring in aqueous solution, such as the conversion of ferrous into ferric salts, or stannous into stannic salts, and *vice versa.* Although one may find exceptions to these rules, they are yet of a general character such as we should expect on the theory of electrolytic dissociation.

It has occasionally been urged that the existence of chlorine in a solution of sodium chloride cannot be accepted even hypothetically, as the solution shows none of the properties of a solution of chlorine. This, of course, rests on a misunderstanding. What we suppose to exist in the solution is not chlorine, but chloridion. The molecule of the former consists of two uncharged atoms of chlorine, the molecule of the latter consists of one atom of chlorine, possibly hydrated, charged with negative electricity according to Faraday's Law, *i.e.* every 35·5 g. of chlorine as ion has 96,500 coulombs of electricity associated with it. But we know that a charge of electricity profoundly affects the chemical properties of substances. The mere fact of the chemical changes accompanying electrolysis is evidence of this, and other instances exist in plenty. Neither aluminium nor mercury decomposes water at the ordinary temperature, but if the aluminium is coated with mercury the amalgam formed has this power, hydrogen being evolved and aluminium hydroxide produced. The action of the copper-zinc couple is similar. These metals separately are unable to perform chemical reactions which are easily brought about by zinc coated with copper. Another familiar instance is the behaviour of zinc towards sulphuric acid. Commercial zinc readily decomposes sulphuric acid with evolution of hydrogen, whilst pure zinc is almost without action on the dilute acid. This is due to the fact that the commercial metal contains other metals as impurities, and these increase the action of the zinc. If to the solution of sulphuric acid in contact with pure zinc we add a small quantity of a platinum or a cobalt salt, these metals are deposited on the surface of the zinc and vigorous action ensues. In each of these cases the two metals on coming into contact assume electrical charges which greatly modify their ordinary chemical character.

Within the past few years considerable attention has been paid to the electrolytic behaviour of non-aqueous solutions. In general it may be said of them that the relations they exhibit are much less simple in character than those shown by solutions in which water is the solvent. Thus Ostwald's dilution law for binary electrolytes is scarcely ever obeyed, and even the expressions of Rudolphi and van 't Hoff have a very limited application. Besides organic solvents such as the alcohols, which have been already mentioned, solvents like liquid ammonia, liquid hydrocyanic acid, and liquid sulphur dioxide have been employed, and many interesting results obtained. For example, bromine, which is scarcely a conductor when dissolved in ordinary solvents, gives a molecular conductivity when dissolved in liquid sulphur dioxide greater than that of many weak acids in aqueous solution. Again, triphenylmethyl chloride $(C_6H_5)_3CCl$ in liquid sulphur dioxide is as good a conductor as methylammonium chloride $N(CH_3)H_3Cl$, which is universally accepted as a true salt. What the ions are in such cases is somewhat difficult to determine, but these examples make it plain that our views as to ionogenic substances must be widened so as to include many other substances than the ordinary acids, bases, and salts.

The student who wishes to pursue the subject of Electrolysis and Electrochemistry from the dissociation point of view may be referred to S. ARRHENIUS, *Electrochemistry* (1902); and R. LÜPKE, *Electrochemistry* (1903).

Tables of Conductivity Data are given in KOHLRAUSCH AND HOLBORN'S book *Leitvermögen der Elektrolyte, insbesondere der Lösungen*, Leipzig, 1898.

The fundamental paper of ARRHENIUS "On the Dissociation of Substances dissolved in Water" appeared in *Zeitschrift für physikalische Chemie*, **1** (1887), p. 631.

References to the literature for non-aqueous solutions are given by P. WALDEN in a paper "On abnormal Electrolytes," *ibid.* **43** (1903), p. 385.

CHAPTER XXII

BALANCED ACTIONS

Many of the chemical actions familiar to the student in his laboratory experience are reversible, *i.e.* under one set of conditions they proceed in one direction, under another set of conditions they proceed in the opposite direction. Thus if we pass a current of hydrogen sulphide into a solution of cadmium chloride, double decomposition occurs, according to the equation

$$CdCl_2 + H_2S = CdS + 2HCl.$$

If the precipitate is now filtered off and treated with a solution of hydrochloric acid of the requisite strength, the action proceeds in the reverse direction, the equation being

$$CdS + 2HCl = CdCl_2 + H_2S.$$

What determines the direction of the action in this case is apparently the relative quantities of hydrogen sulphide and hydrogen chloride present in the solution. If hydrogen sulphide solution is added to a solution of a cadmium salt which contains a considerable quantity of free hydrochloric acid, a part only of the cadmium will be precipitated as sulphide, part remaining as soluble cadmium salt. We are here dealing with a **balanced action,** and we shall find it convenient to formulate actions of this type by means of the ordinary chemical equation for the action with oppositely-directed arrows instead of the sign of equality, thus :—

$$CdCl_2 + H_2S \rightleftarrows CdS + 2HCl.$$

As a rule, in analytical work we do not wish to stop half-way in a chemical action, and therefore choose such conditions for the action that it will proceed practically to an end. Cadmium chloride is completely precipitated as sulphide when there is little hydrochloric acid present, and when a considerable excess of sulphuretted hydrogen has been added.

A balanced action of the same sort, but with the point of balance or equilibrium towards the other end of the reaction, is to be found when a solution of hydrogen sulphide is added to a solution of zinc chloride. A white precipitate of the metallic sulphide is formed, but even though a very large quantity of hydrogen sulphide is present, the precipitation is never complete, and a very moderate quantity of free hydrochloric acid will prevent the precipitation altogether. It is thus possible, by suitably choosing the conditions, to effect a separation of cadmium from zinc by means of sulphuretted hydrogen, although in the two cases we are dealing with balanced actions of precisely the same type. If some dilute hydrochloric acid is added to the solution of the mixed metallic chlorides, hydrogen sulphide will precipitate the cadmium almost completely, and precipitate practically none of the zinc salt, even though it is present in great excess.

If ammonium hydroxide solution is added to a solution of a magnesium salt, say magnesium chloride, part of the metal is precipitated as magnesium hydroxide, in accordance with the equation

$$MgCl_2 + 2NH_4OH = Mg(OH)_2 + 2NH_4Cl,$$

but the precipitation is never complete, for the reverse action

$$Mg(OH)_2 + 2NH_4Cl = MgCl_2 + 2NH_4OH$$

occurs simultaneously, and a state of balance results. In analytical practice we have usually excess of ammonium chloride present from the beginning, so that the addition of ammonium hydroxide produces no precipitate in the solution of magnesium salt. The reverse action can be easily studied by shaking up freshly-precipitated magnesium hydroxide with a solution of ammonium chloride, when the magnesium hydroxide will be found to dissolve (cp. Chapter XXVI.).

We may consider such cases of chemical equilibrium from the same standpoint as we adopted in Chapter X. for physical equilibrium. In the last instance given above, viz. the addition of ammonium hydroxide solution to magnesium chloride solution, if we mix definite amounts of solutions of definite strengths, the precipitation of magnesium hydroxide will come to an end when the reaction has proceeded to a certain ascertainable extent. Equilibrium is then reached, and the system undergoes no further apparent change. We may still conceive the opposed reactions to go on as before, but at such a rate that exactly as much magnesium hydroxide is formed by the direct action as is reconverted into magnesium chloride by the reverse action. Now at the beginning of the action there is no magnesium hydroxide or ammonium chloride present at all; these are only formed as the direct action proceeds. There is therefore at the beginning no reverse action. It is obvious that if a state of balance is to be reached, the rate at which the direct action proceeds must fall off, or the rate at which the reverse action proceeds must increase, or finally both these changes may occur together. As the action progresses, the relative proportions of the reacting substances and the products of the reactions vary, and so we should be disposed to connect the actual rate at which magnesium hydroxide is formed or decomposed with the amounts of the different substances in solution. Further information on this point may be got by adding ammonium chloride to the solution of magnesium chloride from the beginning. If we add a very small quantity of ammonium chloride before we add the ammonium hydroxide, keeping the relative proportions of the other substances the same as before, we shall find that the amount of magnesium hydroxide precipitated is smaller than before, and if we go on increasing the amount of ammonium chloride little by little, we at last reach a point when no magnesium hydroxide is precipitated at all. Evidently, then, the presence of ammonium chloride favours the reverse action, and that in a manner proportionate to the amount added. Increase in the amount of ammonium hydroxide, on the other hand, favours the direct action, so that on the whole we should be inclined to suspect that the rate of a reaction depended on the amount of reacting materials present.

Guldberg and Waage, from a consideration of many experiments, formulated the connection between rate of action and amount of reacting substances in the following simple way. The rate of chemical action is proportional to the **active mass** of each of the reacting substances. This rule must in the first instance be taken to apply to solutions or gases, for it is in their case only that "active mass" can be properly defined. By active mass Guldberg and Waage understood what we usually term the molecular concentration of a dissolved or gaseous substance, *i.e.* the number of molecules in a given volume, or in the ordinary chemical units, the number of gram molecules per litre. It is possible, however, as Arrhenius has suggested, that this molecular concentration in solution is not really a measure of the active mass, and that instead of it we ought to substitute the osmotic pressure of the dissolved substance. For our present purpose, we may take the active mass to be proportional to the molecular concentration without risk of committing any serious error, for, as we have already seen, there is, at least in dilute solution, almost exact proportionality between osmotic pressure and molecular concentration.

Suppose we are dealing with the following chemical action—

$$A + B = C + D,$$

where the letters represent single molecules of the substances as in ordinary chemical formulæ. Let the molecular concentrations of the original substances A and B be a and b respectively. The rate of the reaction will then, according to Guldberg and Waage, be proportional to a and also proportional to b, *i.e.* it will be proportional to the product ab. At the beginning of the action, then, we have the expression

$$\text{Rate} = ab \times \text{constant},$$

if by rate of reaction we mean the number of gram molecules of each of the reacting substances transformed in the unit of time, usually the minute. The constant, therefore, in the above equation, which is generally denoted by k, represents the rate at which the action would proceed if each of the reacting substances were at the beginning of the reaction of the molecular concentration 1, as may easily be seen from the transformed equation

$$k = \frac{\text{Rate}}{ab}.$$

It must be remembered that as the action progresses the concentration of both A and B will fall off, and that the rate at which these substances are transformed into the substances C and D must therefore progressively diminish. If at the time t the concentration of A has diminished by x gram molecules per litre, the concentration of B will have diminished by a similar amount, and the rate at which these substances are then transformed will be

$$\text{Rate}_t = k(a - x)(b - x).$$

The constant k is still the same as in the preceding equation, and has still the same significance, as may be seen from a consideration of the formula. It is indeed characteristic of the reaction, being independent of the concentrations of the reacting substances, although variable with temperature, nature of the solvent, etc. It is customary to call it the **velocity constant** of the action, and the student is recommended to bear in mind that it is the rate at which the reaction would proceed were the reacting substances originally present, and constantly maintained, at unit concentration.

If the reaction $A + B = C + D$ is not reversible, the transformation of A and B into C and D will go on at a gradually decreasing rate until at least one of the reacting substances has entirely disappeared. If the action, on the other hand, is reversible, the transformation of C and D into A and B will begin as soon as any of the former substances are formed by the direct action. If we suppose no C and D to be present when the action commences, we have at the beginning of the direct action $c = 0$ and $d = 0$. At the time t, when x of the original products has been transformed, we have $c = x$ and $d = x$. If k' is the velocity constant of the reverse action, then at the time t

$$\text{Rate}_t = k'x^2.$$

Now after the direct action has proceeded for a certain time, which we may call τ, a state of equilibrium sets in. Let the diminution of the molecular concentration of A and B have at that time the value ξ, then the rate of the direct transformation is

$$k(a-\xi)(b-\xi).$$

The rate of the reverse transformation at the same time is

$$k'\xi^2.$$

But these rates must be equal if the system is to remain in equilibrium, for in a given time as much of A and B must be formed by the reverse action as disappear in the same time by the direct action. The equation

$$k(a-\xi)(b-\xi)=k'\xi^2$$

consequently holds good, and this when transformed gives

$$\frac{(a-\xi)(b-\xi)}{\xi^2}=\frac{k'}{k}=\text{constant}.$$

Since k and k' are independent of the concentration, their ratio is also independent of the concentration, so that for equilibrium we have the product of the active masses of the substances on one side of the chemical equation, when divided by the product of the active masses of the substances on the other side of the chemical equation, giving a constant value no matter what the original concentrations may have been. If we wish to make the formula perfectly general, we may suppose that the concentrations of the products of the direct action were c and d respectively. At the point of equilibrium the concentrations of these substances will then be $c+\xi$ and $d+\xi$, so that the constant magnitude will be

$$\frac{(a-\xi)(b-\xi)}{(c+\xi)(d+\xi)}=\frac{k'}{k}.$$

When, as very frequently happens, the original substances are taken in equivalent proportions, and none of the products of the direct action are present at the beginning, the constant quantity has the simple form

$$\frac{(a-\xi)^2}{\xi^2}=\frac{k'}{k},$$

in which a represents the original molecular concentration of both reacting substances.

No good practical instance of the application of the above formula is known, although approximations to it are in some cases obtainable. The best is perhaps the equilibrium between an ester, water, and the acid and alcohol from which the ester is produced. Thus if we allow acetic acid and ethyl alcohol to remain in contact, they will interact with production of ethyl acetate and water. The action, however, will not be complete, because the reverse action will simultaneously take place, the ethyl acetate being decomposed by the water into acetic acid and ethyl alcohol. The equation for the reversible action is

$$CH_3 . COOH + C_2H_5 . OH \rightleftarrows CH_3 . COOC_2H_5 + H_2O.$$

If the acetic acid and ethyl alcohol are taken in equivalent proportions, the action ceases when two-thirds of the substances have been transformed into ethyl acetate and water. Supposing the active mass of the acid and alcohol to have been originally 1, the active masses at equilibrium will be

Acetic acid $= 1 - \frac{2}{3} = \frac{1}{3}$,
Alcohol $= 1 - \frac{2}{3} = \frac{1}{3}$,
Ethyl acetate $= \frac{2}{3}$,
Water $= \frac{2}{3}$,

and the constant quantity will be

$$\frac{(1-\xi)^2}{\xi^2} = \frac{\frac{1}{3} \times \frac{1}{3}}{\frac{2}{3} \times \frac{2}{3}} = \frac{1}{4}.$$

This constant holds good for any proportions of the reacting substances, being the ratio of the velocity constants of the opposed reactions. We can therefore use it to determine the extent to which a mixture in any proportions of acetic acid and ethyl alcohol will be transformed. Thus, if for 1 equivalent of acid we take 3 equivalents of alcohol, at what point will there be equilibrium? If ξ represents the amount transformed at equilibrium, we have

$$\frac{(1-\xi)(3-\xi)}{\xi^2} = \frac{1}{4},$$

whence $\xi = 0{\cdot}9$, *i.e.* 90 per cent of the acid originally taken will be converted into ester by 3 equivalents of alcohol against 66·6 converted by 1 equivalent of alcohol. Direct experiment has shown that this amount of the acid is actually transformed. In this instance the substances are merely in solution in each other, but the presence of a neutral solvent, such as ether, in no way affects the equilibrium, although it greatly reduces the speed of the opposed reactions.

There is an example of equilibrium in aqueous solution which has been verified with the utmost strictness for a very large number of substances, namely, the equilibrium between the ions of a weak acid or base and the undissociated substance itself. Suppose the substance considered to be acetic acid. If a gram molecule of the acid is dissolved in water so as to give v litres of solution, its active mass is $1/v$ in our units. No sooner is the acid dissolved than it begins to split up into hydrion and acetanion. The rate at which this action progresses is, according to the principle of mass action, proportional to the active mass of undissociated acetic acid present at the time considered. Let the proportion of acetic acid dissociated be m. The proportion undissociated will therefore be $1-m$, with the active mass $\frac{1-m}{v}$. The rate of dissociation will thus be

$$c \cdot \frac{1-m}{v},$$

where c is the velocity constant of the dissociation. But the action is a balanced one, so that undissociated acetic acid will be re-formed from the ions at the same time as the dissociation proceeds by the direct action. When the proportion of the acid transformed into ions is m, each of the ions will have the active mass m/v, and thus we shall have for the rate of reunion

$$c' \cdot \left(\frac{m}{v}\right)^2,$$

if c' is the velocity constant of this reaction. Suppose now, in particular, that m is the proportion decomposed into ions when equilibrium has taken place. The rates of the opposed reactions must then be equal, and we thus obtain the equation

$$c \cdot \frac{1-m}{v} = c'\left(\frac{m}{v}\right)^2,$$

or

$$\frac{m^2}{(1-m)v} = \frac{c}{c'} = k.$$

This is Ostwald's dilution formula referred to on p. 235, and it was first deduced by him from the mass-action principle of Guldberg and Waage. The experimental verification has been given for acetic acid and ammonia (p. 235). What holds good for them is equally true for many hundreds of feeble acids and bases which have been investigated.

It has already been indicated that this dilution law does not hold good for salts or for powerful acids and bases, and we must leave it meantime an open question whether the principle of mass action, the active mass being measured by the molecular concentration, applies to them or not. It would appear not to do so, and we are as yet without data to explain the divergence (cp. p. 242). Dilution laws similar to those of van 't Hoff and Rudolphi can be obtained by assuming that the active mass is measured by a power of the molecular concentration other than the first, fractional powers being admissible. Such assumptions are, of course, purely empirical, and are not applicable to all known cases. Their value is therefore at present rather on the practical than the theoretical side.

The principle of mass action, which has been found above to hold good for substances in solution, also holds good for substances in the gaseous state. Nitrogen peroxide, when dissolved in chloroform, dissociates into simpler molecules (p. 203), according to the equation

$$N_2O_4 \rightleftarrows NO_2 + NO_2.$$

This is quite analogous to the equation for the dissociation of a weak acid or base, the only difference being that the products of dissociation are here of the same kind instead of being of different kinds. If m represents the dissociated proportion, $1 - m$ the undissociated proportion, and v the dilution, we have, as before, the following expression regulating the equilibrium—

$$\frac{m^2}{(1 - m)v} = \text{constant},$$

and this has been proved to be in accordance with the observed facts. Now nitrogen peroxide is also known in the gaseous state, and dissociates under these conditions precisely in the same manner as when it is dissolved in such a solvent as chloroform. The chemical equation for the dissociation is the same as before, and so is the expression for the amount of dissociation. The dilution v, in this case, is the volume occupied by 1 gram molecule of the gaseous substance. In cases of dissociation proper, *i.e.* cases of balanced action into which gaseous substances enter, the amount of dissociation is most readily determined by ascertaining the pressure and density. With a given amount of substance occupying a certain volume at a known temperature it is easy to calculate what pressure it will exert, according to Avogadro's principle, if there is no dissociation of the molecules. If there is dissociation, the pressure will, *cæteris paribus,* be greater, for in the given space there are more molecules than would be if no dissociation had occurred. With nitrogen peroxide, simultaneous determinations of the pressure and density are made at constant temperature, both being varied by changing the volume, and from these the magnitudes entering into the above formula can be calculated. In this case also there is close agreement between the observed numbers and the numbers calculated from the formula.

Considering the matter from the kinetic molecular point of view, it is obvious that the position of equilibrium will in some cases depend on the **volume of the system.** Dilution increases the degree of dissociation of electrolytes in aqueous solution; and dilution increases the dissociation of nitrogen peroxide, whether in the state of solution or in the gaseous state. Each molecule of undissociated material decomposes on its own account, and is independent of the presence of other molecules. The number of undissociated molecules, therefore, which will decompose in a given time is entirely unaffected by the volume which they may be made to occupy. Dilution then does not affect the number of molecules which will dissociate in a given time. But dilution does affect the number of molecules re-formed from the dissociated products in a given time, for here each dissociated molecule must meet with another dissociated molecule if an undissociated molecule is to be reproduced. Now the chance of two molecules meeting depends on the closeness with which the molecules are packed. If the particles are close together, they will encounter each other frequently; if they are far apart, they will meet only rarely. Suppose that we double the volume in which a certain amount of nitrogen peroxide is contained. Each NO_2 molecule has on the average to travel twice as far as before in order to meet another NO_2 molecule. The number of encounters in a given time will therefore be reduced to a half. The rate therefore of the reverse reaction corresponding to the equation

$$N_2O_4 \rightleftarrows 2NO_2$$

is reduced to a half by doubling the dilution; the rate of the direct action is unaffected. If therefore there was equilibrium between the direct and reverse actions before the system was made to occupy a larger volume, this equilibrium will be disturbed and a new equilibrium will be established at a point of greater dissociation. Here there will be proportionately less of the undissociated substance, and proportionately more of the products of dissociation, in order that the rates at which the undissociated nitrogen peroxide is decomposed and re-formed may again be the same.

In general, we may say that when dissociation is accompanied by an increase of volume at constant pressure, as is almost invariably the case, the extent of the dissociation is increased if we increase the volume in which the dissociating substance is contained.

Sometimes the dissociation is not accompanied by change of volume or pressure, and then we find that neither pressure nor volume has any influence on the degree of dissociation. Strictly speaking, perhaps the term "dissociation" ought not to be applied to such cases at all, but in ordinary chemical language we almost always allude, for example, to the decompositfon of hydriodic acid as a dissociation. The decomposition takes place according to the equation

$$2HI \rightleftarrows H_2 + I_2,$$

two volumes of hydriodic acid giving two volumes of decomposition products. Here, before hydrogen and iodine can be produced, two molecules of hydrogen iodide must meet, and before the hydrogen iodide can be re-formed, a molecule of hydrogen must encounter a molecule of iodine. The chances of each kind of encounter will be equally affected by a change in the concentration, so that the equilibrium established for one concentration will hold good at any other concentration. Although, therefore, the velocities of the opposed reactions are altered by alteration in the concentration, they are altered to the same extent, and the position of equilibrium is unaffected. Since with gases we usually effect changes in concentration by changing the pressure, we should expect that change of pressure would have no influence on the dissociation equilibrium of hydrogen iodide. As a matter of fact, it has been found that increase of pressure very slightly increases the amount of dissociation, especially under certain conditions, but this may be due to the action not taking place strictly according to the above equation, or to the volumes of the substances on the two sides of the equation not being exactly equal, owing to a slight divergence from Avogadro's Law.

The above instances of balanced action are all of such a type that the system in which the equilibrium occurs is a homogeneous system—either a homogeneous mixture of gases, or of substances in solution. We have now to consider cases of **heterogeneous equilibrium**, the system consisting of more than one phase. As an example, we may take the dissociation of calcium carbonate by heat, according to the equation

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

Here we are dealing with two solids and one gas. The active mass of the gas may either be measured by its concentration, *i.e.* density, or its pressure, the two being closely proportional. There is evidently a difficulty in expressing the active mass of a solid in a similar way. The pressure of a solid cannot be measured as the pressure of a gas can, and the active mass could scarcely be expected to be proportional to the density of the solid, which is the only direct meaning we can give to concentration in this connection. The most instructive way of looking at such an equilibrium is to imagine it to take place entirely in the gaseous phase, the solids simply affording continuous supplies of their own vapour. Every liquid has, as we have seen, a definite vapour pressure for each temperature. At 360° the vapour pressure of mercury is 760 mm. At the ordinary temperature it is not directly measurable, being too small, but the presence of mercury vapour over liquid mercury may easily be rendered evident at temperatures much below the freezing point. Ice, too, has a vapour pressure of a few millimetres at the freezing point, and there is no very good reason to think that this vapour pressure would disappear entirely at any temperature, however low, although it might become vanishingly small. We may then freely admit the possibility of calcium carbonate or calcium oxide vapour over the respective substances, although the pressure of these vapours is so small that they escape our means of measurement, or even of detection. If we are to assume the existence of these minute quantities of vapour, we must assume that the same laws are followed in their case as in those instances which are accessible to our measurement. In particular, we must assume that at a given temperature calcium carbonate, for example, will have a perfectly definite vapour pressure, which will remain constant as long as the temperature remains constant. We have thus in the gaseous phase a constant concentration or pressure of the vapour of the solid, the presence of the solid maintaining the pressure at its proper value, although the substance may be continually removed from the gaseous phase by the chemical action. This constant concentration is obviously unaffected by the quantity of solid present, as the vapour pressure of a small quantity is as great as that of a large quantity of the same solid. From the above reasoning, then, we conclude that the active mass of a solid is a constant quantity, being in fact proportional to the vapour pressure of the solid, which is constant for any given temperature. Experiment confirms this conclusion, which was, indeed, arrived at by Guldberg and Waage on purely experimental grounds.

For the action

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

if P, P' and p denote the equilibrium pressures (or active masses) of calcium carbonate, calcium oxide, and carbon dioxide respectively, we have at the point of equilibrium the following equation—

$$kP = k'P'p, \text{ or } p = \frac{kP}{k'P'},$$

in which all the quantities are constant except p. At any given temperature, then, the pressure of carbon dioxide over any mixture of calcium carbonate and calcium oxide has a fixed value quite independent of the proportions in which the solids are present. This particular pressure of carbon dioxide, which is called the **dissociation pressure** of the calcium carbonate, is the only pressure of carbon dioxide which can be in equilibrium with calcium carbonate, calcium oxide, and with any mixture of the two. Greater pressures are in equilibrium with calcium carbonate only, smaller pressures are in equilibrium with calcium oxide only. As the temperature increases, the dissociation pressure likewise increases, so that we can get a temperature curve of dissociation pressures resembling that for the vapour pressures of a liquid.

Similar phenomena to the above are met with in the **dehydration** of salts containing water of crystallisation. The hydrated and the anhydrous salts are here the solid substances, and water vapour the gas. For a given temperature each hydrate has a definite dissociation pressure of water vapour over it. There is here, however, the complication that a salt usually forms more than one hydrate, in which case the dehydration often proceeds by stages, the hydrate with most water of crystallisation not passing immediately into water vapour and the anhydrous salt, but into water vapour and a lower hydrate. Take, for example, the common form of copper sulphate, the pentahydrate $CuSO_4, 5H_2O$. At 50° this hydrate gradually loses water (cp. Fig. 20, p. 118), and becomes converted into the trihydrate $CuSO_4, 3H_2O$. As long as any pentahydrate remains, a definite dissociation pressure of 47 mm. of water vapour persists over the solid. If the water vapour is removed, the pentahydrate will give up more water, and the equilibrium pressure will be re-established. If the dehydration still goes on, the pressure will remain constant at 47 mm. until all the pentahydrate has been converted into trihydrate, when the pressure will suddenly fall to 30 mm. This new pressure is the dissociation pressure of the trihydrate, which now begins to lose water and pass into the monohydrate $CuSO_4, H_2O$. As long as there is trihydrate present the pressure of 30 mm. will be maintained, but as soon as all the trihydrate has passed into monohydrate, the pressure again drops suddenly to 4·5 mm., which is the dissociation pressure of the latter substance. The solid dissociation product is now the anhydrous salt, and when all the monohydrate has been converted into this the pressure of water vapour drops to zero.

What here holds good for the dehydration of hydrates also applies to the removal of ammonia from such compounds as $AgCl, 3NH_3$, in which the ammonia may be removed in successive stages, with formation of intermediate compounds, *e.g.* $2AgCl, 3NH_3$.

Sometimes dissociation results in the formation of two gaseous substances derived from one solid, *e.g.* the dissociation of ammonium salts, the solid chloride furnishing both ammonia and hydrochloric acid. In this case also there is a constant dissociation pressure for each temperature. If P is the constant vapour pressure of the undissociated ammonium chloride, and p the gaseous pressure of the ammonia or of the hydrochloric acid, these being equal since the two gases are produced in molecular proportions by the dissociation of the ammonium chloride, we have

$$kP = k'p^2, \text{ or } p^2 = \frac{k'P}{k} = \text{constant},$$

whence the total dissociation pressure $2p$ is also constant. Balanced actions of this kind have been studied with ammonium hydrosulphide and similar compounds which dissociate at comparatively low temperatures. From the above equation it is apparent that the product of the pressures of ammonia and the acid is constant, *i.e.* for the balanced action

$$NH_4HS \rightleftarrows NH_3 + H_2S$$

the constant quantity is the product of the pressures of ammonia and hydrogen sulphide. If these substances are derived entirely from the dissociation of ammonium hydrosulphide, the pressures will be equal, but it is possible to add excess of one or other gas from the beginning, in which case they will no longer be equal. Their product, however, will retain the same value as before, though their sum, *i.e.* the total gas pressure, will have changed. This is evident from the equation

$$kP = k'pp', \text{ or } pp' = \frac{kP}{k'} = \text{constant},$$

in which p and p' represent the pressures of the ammonia and the sulphuretted hydrogen respectively. Since p and p' enter into the equation in the same way, an excess of the one will have precisely the same effect on the equilibrium as an excess of the other. This conclusion also is verified by experiment, as may be seen from the following table, which contains some of the results of Isambert with ammonium hydrosulphide. Under p is the pressure of ammonia in centimetres of mercury, under p' the pressure of hydrogen sulphide, the other columns giving the variable total pressure and the constant product of the individual pressures. For this series the temperature of experiment was 17·3°.

	p	p'	$p+p'$	pp'
	15·0	15·0	30·0	225
Excess of H_2S	10·3	21·4	31·7	220
	5·35	41·9	47·2	224
Excess of NH_3	37·7	6·43	44·1	243
	41·6	5·59	47·2	232

It is true that the numbers in the last column do not exhibit very great constancy, but this is due to experimental error, as comparison with other similar series of numbers serves to show.

In the previous cases of balanced action we have had gaseous substances on one side of the chemical equation only. We now proceed to deal with a case where gaseous substances occur on both sides. If steam is passed over red-hot iron, a ferroso-ferric oxide of the composition Fe_4O_5 is formed, the water being reduced to hydrogen. For the sake of simplicity we may assume that the product of oxidation of the iron is ferrous oxide, FeO, so that we have the equation

$$H_2O + Fe = FeO + H_2.$$

If we continue to pass steam over the solid, all the iron is eventually oxidised, notwithstanding which, however, the action is a balanced one. For if we take the oxide produced, and heat it in a current of hydrogen, the hydrogen is oxidised to water, and the iron oxide reduced to metallic iron, the reduction being complete if the current of hydrogen is continued for a sufficient length of time. The reason why we in each case have the action completed is that the passage of the current of gas disturbs the equilibrium, which is never completely established. The nature of the equilibrium may be seen from the equation

$$H_2O + Fe \rightleftarrows FeO + H_2.$$

On each side we have one solid substance and one gas. Since the gases are now on opposite sides of the equation, the equilibrium is regulated by the quotient of their pressures instead of by their product, as in the preceding case. Let p, P, P', p' be the equilibrium pressures of the reacting substances in the order in which they occur in the chemical equation. We obtain the equilibrium equation

$$kpP = k'p'P', \text{ or } \frac{p}{p'} = \frac{k'P'}{kP} = \text{constant.}$$

The ratio of the pressures of water vapour and hydrogen thus determines the equilibrium. If, as occurs when we pass water vapour over the iron, the ratio of the pressure of water to the pressure of hydrogen is greater than the equilibrium ratio, the action proceeds until all the iron has been converted into oxide. On the other hand, when we pass a current of hydrogen over the heated oxide, the above ratio is always less than the equilibrium ratio, and the oxide is completely reduced. The ratio changes with temperature, and becomes equal to unity at about 1000°. At this temperature, therefore, if we take equal volumes of water vapour and hydrogen, and pass the mixture over either iron or the oxide Fe_4O_5, no chemical action will take place, for the pressures are then in the ratio for equilibrium.

Corresponding to the preceding cases of equilibrium with gases we have similar instances with substances in solution. In aqueous solution, however, the equilibrium is very often complicated by the occurrence of electrolytic dissociation. Several cases of this kind will be considered in a subsequent chapter.

A case of **heterogeneous equilibrium in solution** which is analogous to the dissociation of calcium carbonate is to be found in the action of water on insoluble salts of very weak insoluble bases combined with soluble acids. An organic base such as diphenylamine is so weak that its salts when dissolved in water split up almost entirely into the free acid and free base. Diphenylamine itself is practically insoluble in water, and so is the picrate formed from it by its union with picric acid. When the solid picrate is brought into contact with water, it partially dissociates with formation of insoluble base and soluble picric acid. We have, therefore, the equation

$$\text{Diphenylamine picrate} \rightleftarrows \text{Diphenylamine} + \text{Picric acid}$$

exactly analogous to the equation

$$\text{Calcium carbonate} \rightleftarrows \text{Calcium oxide} + \text{Carbon dioxide,}$$

with the exception that the picric acid is in the dissolved state, whereas the carbon dioxide is in the gaseous state. Now in the gaseous equilibrium we found that for each temperature a certain pressure, or concentration, of gas was produced. We should expect, therefore, that in the solution equilibrium for each temperature there should exist a certain osmotic pressure, or concentration, of the dissolved substance which should be necessary and sufficient to determine the equilibrium, independent of the proportions in which the insoluble solid substances may be present. This has been confirmed by experiment. At 40·6° a solution of picric acid containing 13·8 g. per litre is in equilibrium with diphenylamine and its picrate, either singly or mixed in any proportions, and if diphenylamine picrate is brought into contact with water at this temperature it dissociates until the concentration of the picric acid in the water has reached this point.

If we bring carbon dioxide at less than the dissociation pressure into contact with calcium oxide, no carbonate is formed. Similarly, if we bring at 40·6° a solution of picric acid, having a concentration of less than 13·8 g. per litre, into contact with diphenylamine, no diphenylamine picrate will be formed. On the other hand, if the solution has a greater concentration than 13·8 g. per litre, diphenylamine picrate will be produced until the concentration has sunk to that necessary for the equilibrium. This may be readily shown experimentally, on account of the different colours of diphenylamine and its picrate. The base itself is colourless, picric acid affords a yellow solution, and diphenylamine picrate has a deep chocolate-brown colour. A solution of picric acid at 40·6° containing 14 g. per litre at once stains diphenylamine deep brown, but a solution at the same temperature containing 13 g. per litre leaves the diphenylamine unaffected.

If the weak base were soluble instead of insoluble, we should have an equilibrium for solutions corresponding to the dissociation of ammonium hydrosulphide. Urea is such a base, and the picrate of urea is very sparingly soluble as such in cold water, so that we have the equation

$$\text{Picrate of urea} \rightleftarrows \text{Urea} + \text{Picric acid.}$$

On the left-hand side of the equation we have a solid; on the right-hand side we have two substances in solution. The sparingly soluble urea nitrate and oxalate afford similar instances.

Phenanthrene picrate, when dissolved in absolute alcohol, dissociates into phenanthrene and picric acid, both of which are soluble. This case has been investigated, and found to obey the law of mass action. The calculation is, however, complicated on account of the picric acid being partially dissociated electrolytically, and part of the phenanthrene being associated in solution to larger molecules than that corresponding to the ordinary molecular formula.

There are plenty of instances in solution corresponding to the action of steam on metallic iron. If barium sulphate is boiled with a solution of sodium carbonate, it is partially decomposed, according to the equation

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$

Here both the barium salts are insoluble and the sodium salts soluble, so that there is one solid and one salt in the dissolved state on each side of the equation. The active masses of the barium salts may be accounted constant during the reaction, for although they are generally spoken of as "insoluble," they are in reality measurably soluble in water, cp. p. 318. The aqueous liquid in contact with them will therefore be and remain saturated with respect to them, *i.e.* their concentration and active mass in the solution will be constant. The equilibrium will thus be determined by a certain ratio of the concentrations of the soluble sodium salts, independent of what the actual values of the concentrations may be. Guldberg and Waage found by actual experiment that the concentration of the carbonate should be about five times that of the sulphate if the solution is to be in equilibrium with the insoluble barium salts. Such a solution will neither convert sulphate into carbonate nor carbonate into sulphate.

It should be mentioned that when we are dealing with salts in solution, Guldberg and Waage's Law has only an approximate application if we use concentration in the ordinary sense as the measure of the active mass of the dissolved substances, for by doing so we entirely neglect the effect of electrolytic dissociation. When the reactions are considered more closely, we find that it is usually the ions that are active, so that we should really deal with ionic concentrations in the majority of cases, instead of with the total concentrations of the substances. It happens, however, that in a great many cases the influence of dissociation is such that it affects the two opposed reactions equally, and in such cases the approximate conditions of equilibrium may be arrived at although ionisation is entirely neglected. In the instance given above of the equilibrium between soluble carbonates and sulphates and the corresponding insoluble barium salts, all the substances are highly ionised, and approximately to the same extent on both sides of the equation, so here the application of Guldberg and Waage's Law in its simple form gives results in accordance with experiment.

If we increase the active mass of any substance playing a part in a chemical equilibrium, the balance will be disturbed, and the system will adjust itself to a new position of equilibrium, that action taking place in virtue of which the active mass of the substance added will diminish. Thus if we have carbon dioxide at a pressure such that the gas is in equilibrium with a mixture of calcium oxide and calcium carbonate, and suddenly increase its active mass by increasing the pressure upon it, a new equilibrium will be established by the action

$$CaO + CO_2 = CaCO_3$$

taking place, the tendency of which is to diminish the active mass, or pressure, of the carbon dioxide. Again, if we have an aqueous solution containing sodium sulphate and sodium carbonate in such proportions as to be in equilibrium with the corresponding barium salts, and add an extra quantity of sodium sulphate to the solution so as to increase the active mass of this salt, the equilibrium will be disturbed, and will readjust itself by means of the action

$$Na_2SO_4 + BaCO_3 = Na_2CO_3 + BaSO_4,$$

which will go on until the concentration of the sodium sulphate has fallen to a value which gives the equilibrium ratio with the new concentration of sodium carbonate.

The principle here enunciated is of special importance in its application to cases of dissociation, whether gaseous or electrolytic. For convenience sake it may be stated for this purpose in the following form. If to a dissociated substance we add one or more of the products of dissociation, the degree of dissociation is diminished. Thus phosphorus pentachloride, which when vaporised dissociates according to the equation

$$PCl_5 \rightleftarrows PCl_3 + Cl_2,$$

gives a vapour density little more than half that which corresponds to its usual formula. If, however, the pentachloride is vaporised in a space already containing a considerable quantity of phosphorus trichloride, the vapour density is such as would correspond to the formula PCl_5 for the pentachloride. Here one of the products of dissociation has been added, viz. PCl_3, and the dissociation of the pentachloride has been in consequence diminished to such an extent that the vapour density has practically the normal value.

In the case of the dissociation of ammonium hydrosulphide, the addition of either ammonia or hydrogen sulphide to the normal dissociation products will diminish the degree of dissociation. Here, however, the undissociated substance exists only to a very small extent in the vaporous state, the consequence being that a smaller quantity of the salt is vaporised. This may be seen by reference to the numbers given on p. 257. At 17·3° the dissociation pressure is 30 cm., half of this pressure being due to ammonia and half to hydrogen sulphide. If, now, we allow the hydrosulphide to dissociate into an atmosphere of hydrogen sulphide having a pressure of 36·6 cm., the increase in pressure will only be 10·7 cm., *i.e.* this will be the dissociation pressure under these conditions. If the dissociation is allowed to take place in an atmosphere of ammonia of 36 cm. pressure, we have a similar diminution of the dissociation to about one-third of its normal value.

Suppose two substances are dissociating in the same space, and have a common product of dissociation: it is evident from what has been said that the degree of dissociation of each will be lower than the value it would possess were the substances dissociating into the same space singly. Take, for example, a mixture of ammonium hydrosulphide and ethylammonium hydrosulphide. These substances dissociate according to the equations

$$NH_3(C_2H_5)HS \rightleftarrows NH_2(C_2H_5) + H_2S,$$
$$NH_4HS \rightleftarrows NH_3 + H_2S,$$

and have hydrogen sulphide as a common dissociation product. When they dissociate into the same space, the effect is that as each supplies an atmosphere of hydrogen sulphide for the other to dissociate into, the dissociation pressure of each is diminished below the value it would have were it dissociating alone. Thus at 26·3° ammonium hydrosulphide has a dissociation pressure of 53·6 cm., and ethylammonium hydrosulphide has a dissociation pressure of 13·5 cm. If the two substances did not affect each other when dissociating into the same space, the dissociation pressure of the mixture would be the sum of the dissociation pressures of the components of the mixture, viz. 67·1 cm. The value actually found by experiment is much lower than this, viz. 52·4 cm., which is even lower than the dissociation pressure of ammonium hydrosulphide itself. It should be stated that this result is not in accordance with the law of mass action, if pressures are taken as the measure of the active mass of the gases. The theoretical result is 55·3 cm., somewhat greater than the dissociation pressure of the ammonium hydrosulphide.

When, as in the above instance, two unequally dissociated substances are brought into the same space, the more dissociated substance has a much greater effect on the degree of dissociation of the less dissociated substance than *vice versa.* This we might expect, for the more dissociated substance increases the concentration of the common dissociation product far above the value which would result from the dissociation of the less dissociated substance; while the latter, even if dissociated to its normal extent, would only slightly increase the concentration of the common dissociation product beyond the value obtained from the more dissociated substance alone. There is thus a great relative increase in the first case and a small relative increase in the second, the effects on the dissociation being in a corresponding degree.

It remains now to discuss the **effect of temperature** on balanced action. A rise of temperature is almost invariably accompanied by acceleration of chemical action. In a balanced action, therefore, both the direct and reversed actions are accelerated when the temperature is raised. The effect on the opposed reactions is, however, not in general equally great, with the result that the point of equilibrium is displaced in one or other sense. This displacement is intimately connected with the heat evolved in the reaction. If the direct action gives out a certain number of calories per gram molecule transformed, the reverse reaction will absorb an exactly equal amount of heat. Now rise of temperature always affects the equilibrium in such a manner that the displacement takes place in the direction which will determine absorption of heat. If, therefore, the direct action is accompanied by evolution of heat, the action will not proceed so far at a high as at a low temperature, for if we start with equilibrium at the lower temperature, and then heat the system to a higher temperature, the heat-absorbing reverse action occurs, and the point of equilibrium moves backwards. If, on the other hand, the direct action absorbs heat, the action will proceed farther at high that at a low temperature. In all cases of gaseous dissociation at moderate temperatures the dissociation is accompanied by absorption of heat, so that the degree of dissociation increases as the temperature is raised. Thus the dissociation pressure of calcium carbonate rises with rise of temperature, and so does the dissociation pressure of salts like ammonium hydrosulphide, as the following table shows :—

DISSOCIATION PRESSURE OF AMMONIUM HYDROSULPHIDE

Temperature.	Mm. of Mercury.
7·7°	155
12·2	216
17·6	310
22·4	421
27·6	573

Nitrogen peroxide, again, which at the ordinary temperature is only about 20 per cent dissociated into the simple molecules NO_2, is at 130° practically entirely dissociated.

Since the heat of dissociation into ions is sometimes positive, sometimes negative, a rise of temperature may in some cases be accompanied by increased dissociation, in other cases by diminished dissociation. A considerable diminution of the degree of dissociation with rise of temperature has been proved for hydrofluoric acid and hypophosphorous acid.

The rule which has here been applied to the displacement of chemical equilibrium with change of temperature is equally applicable to physical equilibrium. If we take a quantity of a liquid, and enclose it in a space greater than its own volume, a certain proportion of the liquid will assume the vaporous state, heat being absorbed in the vaporisation. If now we raise the temperature, keeping the volume constant, the equilibrium will be disturbed, and the endothermic action will occur, *i.e.* more liquid will be converted into vapour, and the vapour pressure thus become greater.

A number of cases of balanced action of an interesting type have been recently classified under the name of **dynamic isomerism**. The two substances, ammonium thiocyanate and thiourea, are isomeric, both having the empirical formula CSN_2H_4, and their isomerism at temperatures below 100° does not differ in any special way from the isomerism of other substances. If either substance is fused, however, it is partially transformed into the other isomeride, a balance being attained at a point where the liquid consists of about 80 per cent of ammonium thiocyanate and 20 per cent of thiourea. In this particular instance the substances have no marked tendency at the ordinary temperature to pass into each other when pure, so that the opposed reactions and the balance between them can be studied experimentally. Other instances have been investigated in which a change of one isomeride into the other in solution can be followed in the polarimeter, owing to a difference in the optical activity of the two substances. It is probable that most of the phenomena of "tautomerism" and "desmotropy" met with in organic chemistry are referable to similar causes. Liquids, for example, which are usually written with the group $-CH_2.CO-$, very frequently act as if they contained the enol group, $-CH:C(OH)-$, and the liquids themselves often give values for their physical properties which would accord with their being mixtures of the two isomerides. That the liquids may be such mixtures is probable, seeing that other instances of isomeric balance are now well authenticated.

Cases of balanced action are discussed in the following papers, which may be consulted by the student:—

J. T. Cundall—"Dissociation of Nitrogen Peroxide," *Journal of the Chemical Society*, **59** (1891), p. 1076; **67** (1895), p. 794. Compare also W. Ostwald, *ibid.* **61** (1892), p. 242.

J. Walker and J. R. Appleyard—Picric Acid and Diphenylamine, *ibid.* **69** (1896), p. 1341.

J. Walker and J. S. Lumsden—"Dissociation of Alkylammonium Hydrosulphides" *ibid.* **71** (1897), p. 428.

T. M. Lowry—Dynamic Isomerism, *ibid.* **75** (1899), p. 235.

CHAPTER XXIII

RATE OF CHEMICAL TRANSFORMATION

In the preceding chapter we have had occasion to use the conception of reaction velocity in order to facilitate the discussion of chemical equilibrium, without entering into the question of how such a magnitude can be practically determined. It is only in comparatively few cases that an accurate determination is possible at all, for the vast majority of reactions either take place so rapidly, or are complicated to such an extent by subsidiary reactions, that no specific coefficient of velocity for the reaction can be calculated.

One of the simplest reactions, and one of the earliest to be studied with success, is the **inversion of cane sugar**. When this substance is warmed with a mineral acid in aqueous solution, it is gradually converted into a mixture of dextrose and levulose, and the process of conversion can be accurately followed by means of the polarimeter. The cane-sugar solution has originally a positive rotation, the invert sugar produced by the action of the acid has a negative rotation. If therefore we place the sugar solution in the observing tube of a polarimeter, and read off the angle of rotation from time to time, we can tell how the composition of the solution varies as time progresses without in any way disturbing the reacting system. For example, the original rotation of a cane-sugar solution was found to be 46·75°, whilst the rotation of the same solution after complete inversion was $-18{\cdot}70°$. The total change in rotation, therefore, corresponding to complete conversion of the cane sugar into invert sugar was $46{\cdot}75° + 18{\cdot}70° = 65{\cdot}45°$. After the lapse of an hour from the beginning of the reaction, the rotation was found to be 35·75°. In that time the rotation had thus diminished by 11·00°, so that the fraction of the original sugar transformed was $11{\cdot}00 \div 65{\cdot}45 = 0{\cdot}168$. By a similar calculation the quantity of sugar transformed at any other time could be arrived at.

The following table gives the rotations actually observed at different times:—

Time in Minutes.	Rotation.	Constant.
0	46·75°	...
30	41·00	0·001330
60	35·75	1332
90	30·75	1352
120	26·00	1379
150	22·00	1321
210	15·00	1371
330	2·75	1465
510	− 7·00	1463
630	−10·00	1386
∞	−18·75	...

From this table it is evident that the rate at which the reaction proceeds falls off as less and less cane sugar remains in solution. In the first two hours the change in rotation is 20·75°; in the two hours from 510′ to 630′ the change is only 3·00°. This is in accordance with the principle of Guldberg and Waage that the amount transformed in a given time will fall off as less cane sugar remains to undergo transformation. The chemical equation expressing the reaction is

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{(Dextrose)}}{C_6H_{12}O_6} + \underset{\text{(Lævulose)}}{C_6H_{12}O_6}.$$

As the action progresses, water disappears as well as cane sugar; but if we consider that the action takes place in aqueous solution, it is obvious that any change in the active mass of the water can only be very slight, and so, for practical purposes of calculation, the active mass of the water may be taken as constant. The action is not a balanced one, but proceeds until all the cane sugar has been transformed. If a is the original concentration of the cane sugar, and x the quantity transformed at the time t, the rate of transformation at that time will be, according to the **unimolecular formula**,

$$\frac{dx}{dt} = k(a - x),$$

where dx represents the very small quantity transformed in the very small interval dt starting at the time t, and k is the coefficient of velocity of the action. From this equation the integral calculus enables us at once to find a relation between x and t, the corresponding values for any stage of the reaction in terms of the original concentration and the velocity constant. This relation has the form

$$\log \frac{a}{a - x} = 0{\cdot}4343tk,$$

or

$$\frac{1}{t} \log \frac{a}{a - x} = \text{constant}.$$

The values of the expression $\frac{1}{t} \log \frac{a}{a - x}$ are given in the last column of the preceding table, and it will be seen that they remain tolerably constant throughout the reaction. The agreement between experiment and the theory of Guldberg and Waage is therefore in this case quite satisfactory.[1]

The part played by the acid in the inversion of cane sugar is not well understood. The acid itself remains unaffected, but the rate of the inversion is nearly proportional to the amount of acid present if we always use the same acid. In such an action as this, the acid is said to act as an accelerator, and this behaviour on the part of acids is by no means uncommon, although the different acids vary very much in their accelerative power. As we shall see later, the accelerative power of acids furnishes us with a convenient measure of their relative strengths.

A similar accelerating action of acids is found in the **catalysis of esters**. If an ester such as ethyl acetate is mixed with water, the two substances interact, with formation of acetic acid and ethyl alcohol (cp. Chap. XXII.). This is in reality a balanced action, but if the solution of the ester is very dilute, the transformation is almost complete, and the action becomes of the same simple type as the inversion of cane sugar, the equation being

$$CH_3 . COOC_2H_5 + H_2O = CH_3 . COOH + C_2H_5OH.$$

If no acid is present, the action takes place with extreme slowness, but in presence of the strong mineral acids, such as hydrochloric acid, it progresses with moderate rapidity. Although the progress of the action cannot conveniently be followed by a physical method, as in the sugar inversion, a chemical method may be employed without disturbing the reacting system. At stated intervals a measured portion of the solution is removed and titrated with dilute alkali. As the action progresses, the titre becomes greater, owing to the production of acetic acid, and from this increase we may deduce the amount of transformation. It is found that at each instant the rate of transformation is proportional to the amount of ester present, and a velocity constant may be calculated by means of the same formula as was used for sugar inversion. From a comparison of the velocity constants obtained with different acids, it appears that the relative accelerating influences of the acids is the same for both actions.

Saponification of esters by alkalies affords us an example of a **bimolecular reaction**. The equation for the saponification of ethyl acetate by caustic potash is

$$CH_3 . COOC_2H_5 + KOH = CH_3 . COOK + C_2H_5OH,$$

and the action proceeds until one or other of the reacting substances

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[1] The inversion of cane sugar was studied, both practically and theoretically, by Wilhelmy, with the result arrived at above, before Guldberg and Waage enunciated their principle, and the numbers in the table are taken from Wilhelmy's work.

entirely disappears. If we take both substances in equivalent proportions, and represent the active mass of each by a, the general equation for the rate of transformation will be

$$\frac{dx}{dt} = k(a - x)^2,$$

integration of which leads to the equation

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}.$$

Experimental work confirms this conclusion, the expression on the right-hand side of the last equation being in reality constant. The course of the saponification can be easily followed by removing measured portions of the solution from time to time, and titrating them with acid. As the action proceeds, the amount of acid required to neutralise the potassium hydroxide in solution falls off proportionally. For a given ester, equivalent solutions of the caustic alkalies and the alkaline earths effect the saponification at practically the same rate, the rate of saponification for ammonia being very much smaller. For a given base the rate of saponification is greatly affected by the nature of both the acid radical and the alkyl radical which go to form the ester. Thus at 9·4° the velocity constants of various acetates on saponification by caustic soda are as follows :—

Methyl acetate	3·493
Ethyl acetate	2·307
Propyl acetate	1·920
Isobutyl acetate	1·618
Isoamyl acetate	1·645

While the corresponding numbers for various ethyl esters with the same base at 14·4° are—

Ethyl acetate	3·204
Ethyl propionate	2·186
Ethyl butyrate	1·702
Ethyl isobutyrate	1·731
Ethyl isovalerate	0·614
Ethyl benzoate	0·830

Other instances of bimolecular reactions which have been investigated are the formation of sodium glycollate from sodium chloracetate and caustic soda, according to the equation

$$CH_2Cl \,.\, COONa + NaOH = CH_2(OH) \,.\, COONa + NaCl,$$

and the formation of such salts as tetra-ethyl-ammonium iodide from tri-ethylamine and ethyl iodide, in accordance with the equation

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I.$$

A bimolecular reaction, which is, strictly speaking, a balanced action, but proceeds very nearly to an end in aqueous solution, is the formation of urea from ammonium cyanate. According to the ordinary equation,

$$NH_4CNO = CO(NH_2)_2,$$

we should expect the action to be unimolecular, but experiment has shown that it is a bimolecular reaction in dilute solutions, the reacting substances being the ions of the ammonium cyanate, with the equation

$$NH_4^{\cdot} + CNO' = CO(NH_2)_2.$$

In decinormal solution at ordinary temperatures, about 95 per cent of the ammonium cyanate is converted into urea.

Trimolecular reactions are, comparatively speaking, rare, amongst those which have been most thoroughly investigated being the reduction of ferric chloride by stannous chloride, viz.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

and the reduction of a silver salt in dilute solution by a formate, according to the equation

$$2AgC_2H_3O_2 + HCO_2Na = 2Ag + CO_2 + HC_2H_3O_2 + NaC_2H_3O_2.$$

For such reactions we have the following expression for the rate :—

$$\frac{dx}{dt} = k(a - x)^3,$$

where the reacting substances have each the original active mass a. On integration this becomes

$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2(a - x)^2},$$

and it has been ascertained experimentally that the expression on the right-hand side of the equation is actually a constant.

No action has hitherto been investigated which follows the equation expressing the rate for a higher number of molecules than three. At first sight this is surprising, for in our ordinary chemical equations we are familiar with well-known reactions where the number of reacting molecules is much greater than three. It would appear, however, that these **complicated reactions take place in stages**, so that each is really an action composed of successive simple reactions. To take a simple instance, hydrogen arsenide is decomposed by heat into hydrogen and arsenic vapour. From the vapour density of arsenic it is known that the arsenic molecule contains four atoms under the condition of experiment. We therefore write the equation for the decomposition as follows :—

$$4AsH_3 = As_4 + 6H_2.$$

A study of the rate of the reaction, however, shows that it is not quadrimolecular, as the equation would lead us to suppose, but that it gives numbers agreeing with the unimolecular formula. This is evident from the following table, which gives the values of the expression $k=\frac{1}{t}\log\frac{a}{a-x}$, characteristic of unimolecular reactions, for different times:—

t	k	t	k
3 hours	0·0908	6 hours	0·0905
4 ,,	0·0905	7 ,,	0·0906
5 ,,	0·0908	8 ,,	0·0906

The action whose rate we measure, therefore, is a unimolecular action, most probably

$$AsH_3 = As + 3H,$$

which is then followed by the actions

$$4As = As_4$$
$$2H = H_2.$$

Now, in order that the course of the total action may appear as a unimolecular action, it is a necessary assumption that the rate of the first action given above is much smaller than the rate of the succeeding actions. This is so because, in the first place, it is the slowest of a series of actions which will principally determine the rate from the initial to the final stage, and in the second place, if the total rate is to coincide with the rate of this slowest action, the rate of the others must be incomparably greater than this. An analogy may serve to make the point clear. The time occupied in the transmission of a telegraphic message depends both on the rate of transmission along the conducting wire, and on the rate of the messenger who delivers the telegram; but it is obviously only this last, slower, rate that is of practical importance in determining the total time of transmission.

When we measure the rate of a complicated action, then, we are in general measuring an average rate of a series of reactions which may be progressing successively or simultaneously, and it is the rate of the slowest of these actions which plays the principal part in determining the total rate. Should the other actions proceed at an immeasurably faster rate than the slowest action, the whole action will appear to go at a rate and be of a type regulated by this action alone. Hence it is that we so frequently find complex actions proceeding in such a way as to suggest that they are much simpler in type than the total action really is.

The saponification of an ester of a bibasic acid affords a good instance of the progress of a reaction in stages. For example, the saponification of diethyl succinate by caustic soda has been shown to proceed, not according to the equation

$$C_2H_4(COOC_2H_5)_2 + 2NaOH = C_2H_4(COONa)_2 + 2C_2H_5OH,$$

but according to the equations

$$C_2H_4(COOC_2H_5)_2 + NaOH = C_2H_4(COOC_2H_5)(COONa) + C_2H_5OH,$$
$$C_2H_4(COOC_2H_5)(COONa) + NaOH = C_2H_4(COONa)_2 + C_2H_5OH.$$

On the last assumption, Guldberg and Waage's principle leads to a certain expression for the velocities of the total action involving the two velocity constants of the single actions, and the experimental rate has been found to agree with the theoretical requirements. The fact that the action does in reality proceed in two stages may be easily demonstrated by treating ethyl succinate in alcoholic solution with half the calculated quantity of caustic potash necessary for complete saponification. Instead of half the ester being completely saponified, and half being left untouched, about three-fourths of the original quantity is, under favourable conditions, converted into the potassium ethyl salt $C_2H_4(COOEt)(COOK)$, the product of the first stage, one-eighth remaining unattacked, and one-eighth being converted into the dipotassium salt.

In general, then, it may be accepted as a fact that in actions which are expressed by comparatively complicated chemical equations, involving the interaction of a large number of molecules, we are dealing with a series of simpler actions, not more than three molecules being involved in each of these.

The velocity of a given action is usually greatly affected by **change of temperature**. Almost invariably a rise of temperature is accompanied by a large increase in the rate of the reaction, the speed being very frequently doubled for a rise of five or ten degrees starting at the ordinary temperature. It is somewhat difficult to account for this very high temperature coefficient. On any of the usual hypotheses regarding the rate of molecular motion and its variation with the temperature, it is impossible to assume that the speed of the molecules increases so greatly that they encounter each other twice as often when the temperature rises from 15° to 20°. It has been suggested that only a certain small proportion of the total number of molecules are active at any one temperature, and that this number increases rapidly as the temperature rises. On this supposition ions might be supposed to be almost all in the active state, at least so far as double decompositions amongst acids, salts, and bases are concerned, for these actions progress so rapidly that their speed has never been measured. An action which lends some support to this supposition is that of very dilute acids on zinc, which progresses at a rate which is almost independent of the temperature. This action is, in terms of the dissociation theory,

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2.$$

The solid zinc can scarcely have its active part greatly affected by change of temperature (since at most only the superficial part of it can take part in the action), and the hydrogen ions must be considered nearly all active at the ordinary temperature, as a rise of temperature does not increase the rate of the reaction.

Very slight changes in the **nature of the medium** also greatly affect the speed of a reaction. Thus if we remove 10 per cent of the water in which the conversion of ammonium cyanate into urea is taking place, and bring the solution up to its original volume by adding acetone, which takes no part in the reaction, the rate of the conversion increases by nearly 50 per cent. In ethyl alcohol the rate of transformation of the cyanate into urea is thirty times as great as it is in pure water, other conditions remaining the same, notwithstanding the fact that the number of ions in the alcoholic solution is much smaller than the number in pure water of the same concentration (cp. p. 234).

The following table contains the coefficients of velocity observed for the bimolecular reaction

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$$

in different solvents.

Solvent.	1000 *k*
Hexane	0·180
Heptane	0·235
Xylene	2·87
Benzene	5·84
Ethyl acetate	22·3
Ethyl ether	0·757
Methyl alcohol	51·6
Ethyl alcohol	36·6
Allyl alcohol	43·3
Benzyl alcohol	133
Acetone	60·8

The great range of the speed of one action is very well shown by this table. We cannot imagine that the reacting molecules meet each other in benzyl alcohol 700 times as often in a given time as they do in hexane. Either we must assume that there is a greater proportion of active molecules in the former solvent than in the latter, or that the addition takes place at a larger proportion of the encounters of the reacting molecules, a supposition which is practically identical with the first.

We very frequently find that below a certain temperature chemical action apparently will not occur, while above that temperature the action takes place freely. Thus we speak of the **temperature of ignition** of a mixture of gases, meaning usually thereby the lowest temperature which, when given to one part of the mixture, will produce chemical action in the whole mass. For example, we say that the temperature of ignition of a mixture of air and saturated carbon bisulphide vapour is about 160°, because a glass rod heated to that temperature and applied to any part of the mixture will inflame the whole. If we inquire more closely into such actions, however, we generally find that the action occurs at temperatures below the ignition temperature, but that it will not then propagate itself under ordinary circumstances. The experimental proof of this is given by maintaining the *whole* mixture at a temperature somewhat below the ignition point, and noting after a time if the action has progressed. The reason for the non-propagation at lower temperatures is that the action then progresses only slowly. The heat evolution consequent on the chemical change is therefore spread over such an interval of time that the temperature of the mixture remains below the ignition temperature, the action becoming slower and slower if no external heat is supplied, eventually to cease. At the ignition temperature the action takes place at such a rate that the heat evolution is sufficiently rapid to keep the temperature of the gaseous mixture up to the ignition point, and even to raise it still higher, with the result that the action proceeds with an ever-increasing speed. We therefore see that the so-called temperature of ignition depends on the generally-observed rapid increase in the rate of chemical action with rise of temperature, and may vary with the original temperature of the whole mixture.

The same thing holds good, and may be followed more easily, with certain solids. Solid ammonium cyanate, for instance, may be kept for many months at the ordinary temperature without undergoing any notable transformation into urea, according to the equation

$$NH_4CNO = CO(NH_2)_2.$$

At 60° the action is fairly rapid, if the temperature is kept up externally, but the heat evolution is still too slow to enable the action to go on at an increasing rate. If the external temperature is 80°, however, the action proceeds swiftly, and the rapid heat evolution raises the temperature to such an extent that the whole passes almost instantaneously into fused urea, the melting point of which is 132°.

If the heat evolution is comparatively small, as it is with ammonium cyanate, the increasing rapidity of the reaction may be observed through a considerable range of temperature. If, on the other hand, the heat evolution is great, as it is with most explosives, the action when it takes place perceptibly is usually propagated at once, owing to the rapid rise in temperature of the particles in the immediate neighbourhood of the reacting particles. The rate of propagation of explosion in solid explosives when fired is very great, rising in some instances to about five miles per second. The rate of propagation of the **explosion wave** in gaseous mixtures, such as that of oxygen and hydrogen, is somewhat less than this, averaging about a mile and a half per second, and being therefore of the same dimensions as the average rectilinear velocity of the gaseous molecules at the temperature of the explosion (cp. p. 92).

Substances which react vigorously at the ordinary temperature usually lose their chemical activity entirely when cooled to the temperature of boiling liquid air. This we must attribute to the lowering of the rate of chemical action by fall of temperature, the speed being so greatly diminished that the action does not perceptibly occur at all in any moderate length of time. That there is not an entire cessation of action is probable, since in certain cases we can follow the gradual slackening of the action to extinction as the temperature falls. Thus sodium and alcohol, which react briskly at the ordinary temperature, with evolution of hydrogen, become less and less active as the temperature is lowered, until finally the hydrogen formed by the action is so small in quantity as to escape observation. If we reflect that we often see the reaction velocity halved by a fall of 5° in temperature, we can conceive that a fall of 100° might by successive halving reduce the reaction velocity to a millionth of its original value. We may sometimes find it convenient, in accordance with this, to look upon chemical inactivity as being not absolute inactivity, but rather the progress of a chemical action at a rate too slow for measurement, or even detection.

We have now to consider briefly the points of resemblance between physical transformation and chemical transformation. In the change from solid to liquid, and *vice versa*, there is (for a given pressure) a definite temperature of transformation (p. 64). Above this temperature the solid passes into the liquid; below this temperature the liquid passes into the solid. So it is for the transformation of one crystalline modification into another, as in the example of the two modifications of sulphur. Above the inversion temperature, one modification is stable; below the inversion temperature, the other. If a liquid is cooled to a temperature slightly below its inversion temperature (the freezing point) and brought into contact with the more stable crystalline phase, it will assume the crystalline state, the rate of crystallisation being for small temperature differences proportionate to the degree of overcooling. A maximum rate, however, is attained when the degree of overcooling reaches a certain value, and below the temperature corresponding to this, the rate of crystallisation rapidly falls with further diminution of temperature (cp. p. 66). The same thing has been observed with the reciprocal transformation of crystalline modifications: at first the rate of transformation increases as the temperature falls below the temperature of inversion, afterwards however to diminish rapidly as the fall of temperature proceeds. No doubt monoclinic sulphur, cooled to a temperature considerably below zero, would exhibit little tendency to pass into the more stable rhombic form, for even at ordinary temperatures the process takes a comparatively long time. We have already seen that an overcooled "glass" may remain for a very long time in contact with the more stable crystalline modification if the overcooling is sufficiently great, without crystallisation progressing at a sensible rate. If we heat the "glass," however, to a higher temperature, the transformation proceeds with ever-increasing rapidity until a temperature a few degrees below the inversion point is reached. This is evidently comparable to the chemical transformation of solid ammonium cyanate into urea. Ammonium cyanate is the less stable form, and although it may be kept for a very long time at 0° in contact with urea without undergoing appreciable transformation, the transition goes on at an increasing rate as the temperature is raised. Here the inversion point is not known, but it must at least be considerably over 80°. The reverse transformation of urea into ammonium cyanate has only as yet been investigated in aqueous solution.

When cyanic acid vapour condenses below 150°, it forms cyamelide; when it condenses above 150°, it forms cyanuric acid; the chemical action being in both cases one of polymerisation, as cyanic acid has the formula CNOH, cyanuric acid the formula $(CNOH)_3$, and cyamelide a still more complicated formula, expressed generally by $(CNOH)_n$. This would indicate that cyanuric acid had the inversion point 150°, cyamelide being the stable form below that temperature, and cyanuric acid the stable form above that temperature. The conversion of cyamelide into cyanuric acid above 150° has actually been observed, but the reverse action has not hitherto been noticed, probably on account of its slowness. If we construct a pressure-temperature diagram for the three phases, we shall find it exactly analogous to the diagram for the three physical states of aggregation of water (Fig. 9, p. 68).

From the foregoing instances it is evident that considerable analogy exists between the effect of temperature on chemical and on physical change, especially when the chemical change is reversible: and it may often be found expedient to look upon apparently irreversible chemical changes as being in reality reversible, but with a temperature of inversion so high that the reverse action has never been realised.

It will be noted that in all of the above instances there can be no coexistence in equilibrium of two systems which are mutually insoluble and capable of reciprocal transformation, except at the inversion point. Above the inversion point one of the systems is stable; below the inversion point the other is stable; at the inversion temperature itself, both systems are equally stable. This rule holds good both for chemical and physical changes. If, on the other hand, the chemical systems are mutually soluble, there can be equilibrium at any temperature for which they only form one phase, the proportions of each system present changing in this case with the temperature. The fused mixture of ammonium thiocyanate and thiourea forms an example of this one-phase equilibrium of two reciprocally transformable systems. If we fuse thiourea, a certain proportion of it passes into ammonium thiocyanate with a measurable velocity, and we should expect that a different proportion would be transformed according to the temperature at which the system was maintained. Another example of one-phase equilibrium of reciprocally transformable systems is to be found in the solutions of dynamic isomerides (p. 264), or in the substances themselves if they be liquid. The actual transformation in this case also has been noted, and its velocity measured.

Traces of **water vapour** have been found to play a very important part in determining the occurrence, or at least the rate, of many chemical actions. Thus ammonia and hydrochloric acid, when both in the gaseous state, unite readily under ordinary circumstances to form ammonium chloride. If precautions are taken, however, to have the gases absolutely dry, they may be mixed without any union taking place. On the other hand, ammonium chloride, when vaporised, dissociates to a very great extent into ammonia and hydrochloric acid, as is rendered evident by the vapour density being only about half the normal value calculated from the molecular formula NH_4Cl by the help of Avogadro's principle. If the ammonium chloride is perfectly dry, however, the vapour density is normal, thus showing that no dissociation has taken place. The reversible action

$$NH_3 + HCl \rightleftarrows NH_4Cl$$

is therefore apparently dependent on the presence of traces of water for its occurrence either in the direct or the reverse sense. No satisfactory explanation of the action of the moisture has yet been given. It has not indeed been clearly established whether the action is altogether inhibited by the absence of water vapour or whether it still goes on, but at a greatly diminished rate. In the latter case the action of the water might be comparable to the action of acids in accelerating the inversion of cane sugar, the hydrolysis of esters, and the like.

The following papers dealing with rate of chemical action may be consulted :—

Harcourt and Esson—*Philosophical Transactions*, 1866, p. 193, and 1867, p. 117 : Interaction of Permanganate with Oxalic Acid, and of Hydrogen Peroxide with Hydriodic Acid.

R. Warder—*American Chemical Journal*, 3, No. 5 (1881): Saponification of Ethyl Acetate.

A. A. Noyes and G. J. Cottle—*ibid.* **21**, p. 250 (1899) : Reduction of Silver Acetate by Sodium Formate.

J. Walker and others—*Journal of the Chemical Society*, **67**, p. 489 (1895) ; **69**, p. 195 (1897) ; **71**, p. 489 (1898) : Transformation of Ammonium Cyanate into Urea.

H. B. Dixon—*Chemical News*, **64**, p. 70 (1891) : Explosive Wave.

H. B. Baker—*Journal of the Chemical Society*, **65**, p. 611 (1894) : The Influence of Moisture on Chemical Change.

CHAPTER XXIV

RELATIVE STRENGTHS OF ACIDS AND OF BASES

It is customary and correct to speak of sulphuric acid as a strong acid, and of acetic acid as a weak acid, and the statement is the outcome of our general experience of the chemical behaviour of these substances. In comparing two such acids there is no difficulty ; they are so different in their properties that no one could mistake their relative strengths. But if we compare two acids which are closer together in the scale of strength, say hydrochloric and nitric acids, it is impossible from our general chemical experience alone to say which is the stronger, and we must resort to a more exact definition of strength and to more accurate experiment.

A method which, when properly applied, leads to useful and consistent results, is that of the **displacement of one acid from its salts by another.** If an equivalent of sulphuric acid be added to a given quantity of an acetate in solution, the change in properties of the solution is sufficient to indicate that practically the whole of the sulphuric acid has been neutralised, and the corresponding quantity of acetic acid liberated. There is therefore no doubt that the sulphuric acid is much stronger than the acetic acid, being capable of turning the latter out of its salts. But the method must be applied with caution, or it leads to contradictory and inconsistent results. If, for example, we take sodium silicate in aqueous solution and add hydrochloric acid, sodium chloride will be formed and silicic acid liberated, but yet at a very high temperature, as in the process of glazing earthenware, silicic anhydride in presence of water vapour is capable of decomposing sodium chloride with expulsion of hydrochloric acid. Without any further principle than that of displacement to guide us, the first experiment would show that hydrochloric is stronger than silicic acid, and the second that silicic acid is stronger than hydrochloric acid. Again, if we pour aqueous acetic acid on sodium carbonate, there is immediate effervescence due to the expulsion of carbonic acid. Yet a solution of potassium acetate in nearly absolute alcohol is decomposed by carbonic acid to a great extent with precipitation of carbonate. From these experiments it is impossible to say whether acetic or carbonic acid is the stronger, since the expulsion takes place in different senses according to the conditions of experiment. There is, of course, no doubt among chemists that hydrochloric acid is much stronger than silicic acid, and that acetic acid is much stronger than carbonic acid. We must therefore inquire more closely into the experiments which seem to point to the contrary conclusions. In the first place, it is obvious from the experiments themselves that we are dealing with actions which can, according to circumstances, take place in either sense, *i.e.* with balanced actions. Carbonic acid, or its anhydride and water, can always displace a little acetic acid from its salts, although it is a much weaker acid. If all the substances remain within the sphere of the reaction this displacement will not go far, as the reverse reaction will set in and soon establish equilibrium. The action expressed by the equation

$$CH_3 . COOK + CO_2 + H_2O = KHCO_3 + CH_3 . COOH$$

would therefore speedily come to an end if the products of the action were to remain and accumulate in the system. But if one of the products, say potassium hydrogen carbonate, is insoluble, or nearly so, its active mass cannot increase beyond a certain small amount, however much of it may be formed, for it falls out of solution, *i.e.* the true sphere of action, as soon as it is produced. Whilst, therefore, in aqueous solution, in which all the substances remain dissolved, the carbonic acid succeeds in displacing only a small proportion of the acetic acid, in alcoholic solution it displaces a much larger amount, owing to the insolubility of one of the products of reaction.

In the case of the action of silica on a chloride, we have again one of the substances removed from the sphere of action as it is produced, viz. hydrochloric acid, which at the high temperature of the experiment escapes as vapour. In solution, only an infinitesimally small proportion of hydrochloric acid would be displaced by silicic acid, owing to the reverse reaction which would at once set in, but at the high temperature no reverse action is possible at all, since one of the reacting substances leaves the sphere of action as soon as it is formed.

Similarly, we are not in a position to judge of the relative strengths of hydrochloric and hydrosulphuric acids by experiments with sulphides insoluble in water. Sulphuretted hydrogen will at once expel hydrochloric acid from copper chloride, even if excess of hydrochloric acid is present in solution. Yet sulphuretted hydrogen is a very feeble acid compared to hydrochloric acid. The displacement is due to the insolubility of the copper sulphide, which is removed from the sphere of action as it is produced. That such experiments lead to no definite conclusion may be seen by taking the same acids with another base. Though sulphuretted hydrogen is passed through a solution of ferrous chloride until the solution is saturated with it, a scarcely perceptible precipitate of ferrous sulphide will be formed, and if a little hydrochloric acid is added to the solution from the beginning, no precipitate will be formed at all. Here, then, the same two acids exhibit totally different behaviour relatively to each other, according to the nature of the base for which they are competing.

Now, in the above instances the acids have been selected of as widely different natures as possible, so that the fallacy of the reasoning based on the experiments mentioned is obvious. But similar fallacious reasoning is prevalent, and passes without detection, when experiments are discussed regarding acids where common chemical experience supplies no answer as to their relative strengths. Thus it is almost invariably a settled conviction in the minds of students that sulphuric acid is a stronger acid than hydrochloric acid because it expels the latter from its salts. No doubt this is the fact if we evaporate a solution of the chloride and sulphuric acid to dryness, or nearly so. But, of course, in this case the hydrochloric acid is expelled as vapour, and cannot therefore participate in the reverse reaction. The hydrochloric acid is expelled, not because it is a feebler acid than sulphuric acid, but because it is more volatile.

These examples suffice to show that expulsion of one acid from its salts by another cannot be used as a proof that the latter is the stronger acid, unless the two acids are competing under circumstances equally favourable to both. The proper conditions are secured when the reacting systems form only one phase, namely, that of a solution. As soon as one of the components of the reacting systems is removed as a gas or as an insoluble solid or liquid, the system which does not contain that substance as one of its components is unduly favoured at the expense of the other system.

If we are to compare the strengths of hydrochloric and sulphuric acids, then, we shall do best to take a soluble sulphate and add to it an equivalent of hydrochloric acid, the base being so chosen that the chloride formed is also soluble. Since all salts which have potash or soda as base are soluble, a potassium or sodium salt is generally selected, and the competing acid added to its aqueous solution. Thus equivalent solutions of hydrochloric acid and sodium sulphate may be mixed, and the composition of the resulting solution investigated, in order to ascertain in what proportion the base distributes itself between the two acids, the assumption being that the stronger acid takes the greater share of the base. In general, it is necessary to use a physical method for determining the composition of the solution, since the application of a chemical method would disturb the equilibrium. That an equilibrium is actually being dealt with is ascertainable from the fact that the solution has exactly the same properties in all respects, whether the base was originally combined with the sulphuric acid or with the hydrochloric acid, as will be presently shown in a numerical example. The two methods which have been most extensively applied are the **thermochemical method** of Thomsen and the volume method of Ostwald.

When a gram molecule of sulphuric acid in fairly dilute solution (about one-fourth molecular normal) is neutralised by an equivalent amount of caustic soda of similar dilution, a production of 313·8 centuple calories is observed. The same amount of soda neutralised by hydrochloric acid is attended by a heat evolution of 274·8 K. Now if the addition of hydrochloric acid to a solution of sodium sulphate produced no effect chemically, we should also expect no thermal effect. If, on the other hand, all the sulphuric acid were expelled from combination with the soda, we should expect an absorption of 313·8 – 274·8 K = 39 K. Now an actual heat absorption of 33·6 K per gram molecule was observed by Thomsen. This would indicate that the greater proportion of the base was taken by the hydrochloric acid, an equivalent quanty of sulphuric acid being expelled from its combination with the soda. If we assumed that the heat absorption were directly proportional to the amount of chemical action, the proportion of sulphate converted into chloride would be 33·6 ÷ 39 = 0·86. This proportion, however, is not the correct one, for the sulphuric acid liberated reacts with the normal sodium sulphate remaining, to produce a certain quantity of sodium hydrogen sulphate, the formation of which is attended by absorption of heat, so that the total heat absorption observed is too great. Special experiments show that the correction to be applied in order to eliminate the effect of this action is 7·6 K, the heat absorption due to the displacement of sulphuric by hydrochloric acid thus being 33·6 – 7·6 = 26 K. The proportion of sulphuric acid expelled is therefore 26 ÷ 39, or two-thirds. When, therefore, equivalent quantities of sulphuric and hydrochloric acids compete for a quantity of base sufficient to neutralise only one of them, the hydrochloric acid takes two-thirds of the base and the sulphuric acid one-third. The reverse experiment of adding sulphuric acid to a solution of sodium chloride showed that the final distribution of the base between the acids was the same as above so far as could be judged from the heat effect. Since the hydrochloric acid always takes the larger share of the base, we conclude that it is the stronger acid, at least in aqueous solution.

Thomsen, by working in this way, compiled a table of the **avidities** of different acids, from which it is possible to tell at once how a base will distribute itself between any two of them if all three substances are present in equivalent proportions. The avidities of some of the commoner acids are given below :—

Acid.	Avidity.
Nitric	100
Hydrochloric	100
Sulphuric	49
Oxalic	24

Acid.	Avidity.
Orthophosphoric	13
Monochloracetic	9
Tartaric	5
Acetic	3

In order to find the distribution ratio from this table, we proceed as follows. Let the acids be sulphuric and chloracetic, the avidities being 49 and 9 respectively. If the base and these acids are present in equivalent proportions, the base will share itself between the acids in the ratio of their avidities, *i.e.* the sulphuric acid will take $\frac{49}{58}$ and the chloracetic acid $\frac{9}{58}$.

Ostwald's **volume method** is based on similar principles. Instead of heat changes, the changes of volume accompanying chemical reactions are measured. The substances used by him were contained in aqueous solutions of such a strength that a kilogram of solution contained 1 gram equivalent of acid, salt, or base. The specific volumes of these solutions were carefully determined so that the change of volume produced by chemical action might be ascertained. Thus the volume of a kilogram of potassium hydroxide solution was found to be 950·668 cc., and of a nitric acid solution 966·623 cc. If, on mixing these solutions, no change of volume occurred, the total volume would be 1917·291 cc. But the volume actually found on mixing the solutions was 1937·338 cc. The neutralisation of the acid and base is thus accompanied by an expansion of 20·047 cc. Similarly, changes of volume accompany other chemical reactions, and the extent to which a given action has occurred can be measured by the volume change. A solution of copper nitrate had a volume equal to 3847·4 cc., and an equivalent solution of copper sulphate 3840·3 cc. Solutions of nitric and sulphuric acids had the volumes 1933·2 and 1936·8 respectively. If no action occurred on mixing the copper sulphate solution with the nitric acid solution, the total volume would be 3840·3 + 1933·2 = 5773·5; if complete transformation into copper nitrate and sulphuric acid took place, the total volume would be 3847·4 + 1936·8 = 5784·2. The actual volume found by mixing the copper nitrate and sulphuric acid solutions was 5780·8, and by mixing the copper sulphate and nitric acid solutions 5781·3. These two volumes are practically identical, and we may take as their mean 5781·0. We have therefore the numbers—

	All Copper Sulphate.		Actual.		No Copper Sulphate.
	5773·5		5781·0		5784·2
Difference		7·5		3·2	

The actual equilibrium is evidently nearer the system containing no copper as sulphate than the system containing all the copper as sulphate, and if we assume direct proportionality, the base is shared by the nitric and sulphuric acids in the ratio of 7·5 to 3·2, or nitric acid takes 70 per cent of the base, leaving the sulphuric acid 30 per cent. This result is not quite accurate, as allowance has to be made for the slight volume changes consequent on the action of the respective acids on their neutral salts. When this correction is applied, it appears that the nitric acid takes 60 per cent of the base and the sulphuric acid 40 per cent.

A table of avidities can be constructed for the different acids from similar data, and a comparison with Thomsen's avidities derived from thermochemical experiments shows that the two methods yield results in harmony with each other, at least so far as relative order of the acids is concerned. The actual avidity numbers differ considerably in many instances, but it has to be borne in mind that the thermochemical measurements are on the whole less accurate than the volume measurements, and the numbers derived from them consequently less trustworthy.

In special cases the distribution of a base between two acids may be studied by making use of other physical properties than those already mentioned. For example, measurements of the refractive index of solutions often lead to satisfactory results, and also measurements of the rotatory power when optically active substances are in question. The principle involved is identical with that just described, any differences being merely differences in detail.

A method which differs in principle from the distribution of a base between two competing acids, and may also be applied to the determination of the relative strengths of acids, is to ascertain the **accelerating influence** exerted by different acids on a given chemical action. For example, the inversion of cane sugar has long been known to take place much more rapidly in presence of an admittedly strong acid like sulphuric or hydrochloric acid, than it does in presence of an equivalent quantity of an admittedly weak acid like acetic acid. The strong mineral acids have thus a greater accelerating effect than the weak organic acids, and it is natural to infer that an exact determination of the specific accelerating powers of different acids might lead to a knowledge of their relative strengths. There is no obvious connection between this method and the preceding method of relative displacement, but a connection exists, as will be shown later, and the results obtained are in general quite in harmony with each other.

The **method of sugar inversion** as practised by Ostwald was performed in the following manner. Normal solutions of the various acids were mixed with an equal volume of 25 per cent sugar solution and placed in a thermostat whose temperature remained constant at 25°. The rotation of each solution was taken from time to time, and a velocity constant calculated according to the formula given on p. 266. The order of these velocity constants is the measure of the accelerating powers of the acids, and presumably a measure of their relative strengths.

Another action well adapted to investigating the accelerating power of acids is the **catalysis of methyl acetate** (cp. p. 267). Ostwald mixed 10 cc. of normal acid with 1 cc. of methyl acetate, and diluted the mixture to 15 cc. This solution was then placed in a thermostat at 26°, and its composition ascertained at appropriate intervals in the manner already indicated. A calculation of the velocity constant by the usual formula for unimolecular reaction gave the required measure of the accelerating power.

A comparison of the results obtained by the different methods is given in the following table, the value for hydrochloric acid being made in each case equal to 100, in order to assist the comparison :—

		Velocity Constants.	
	Avidity.	Sugar Inversion.	Catalysis of Acetate.
Hydrochloric	100	100	100
Nitric	100	100	91·5
Sulphuric	49	53	54·7
Oxalic	24	18·6	17·4
Orthophosphoric	13	6·2	...
Monochloracetic	9	4·8	4·3
Tartaric	5	...	2·3
Acetic	3	0·4	0·35

It is at once evident that the order in which the acids follow each other is the same in all cases, and in especial it will be seen that the numbers expressing the accelerating powers of the acids are closely similar, although the accelerating influence was exerted on entirely different chemical actions. The avidity numbers differ considerably from the others, but the general parallelism of the results cannot be denied, and we are therefore justified in adopting the acceleration method as a means of measuring the relative strengths of acids, although its theoretical justification is not immediately obvious.

It was pointed out by Arrhenius that if we arrange the acids in the order of their relative strengths, they are also arranged in the order of the **electrical conductivities** of their equivalent solutions. This may be seen in the following table, the first column of which contains the mean value of the velocity constants of sugar inversion and catalysis of methyl acetate, and the second that of the electric conductivities of equivalent solutions, all values being referred to that for hydrochloric acid as 100 :—

	Velocity Constants.	Electric Conductivity.
Hydrochloric	100	100
Nitric	96	99·6
Sulphuric	54	65·1
Oxalic	18	19·7
Orthophosphoric	6·2	7·3
Monochloracetic	4·5	4·9
Tartaric	2·3	2·3
Acetic	0·4	0·4

The parallelism is here unmistakable, the numerical values in the two columns being often practically identical.

At first sight it appears a matter of difficulty to associate the electric conductivity of an acid with its strength, *i.e.* its chemical activity in so far as it behaves as an acid; but the dissociation hypothesis of Arrhenius furnishes the clue to the nature of the connection. All acids in aqueous solution possess certain properties peculiar to themselves which we class together as acid properties. Thus they neutralise bases, change the colour of certain indicators, are sour to the taste, and so on. We are therefore disposed to attribute to them the possession of some common constituent which shall account for these common properties. On asking what aqueous solutions of the various acids have in common, we find for answer "hydrion" if we adopt the hypothesis of electrolytic dissociation. Let us suppose the peculiar properties of acids to be due to hydrion. How in that case are we to explain the different strengths of the acids? Evidently on the assumption that different acids in equivalent solution yield different amounts of hydrion. The acid which in a normal solution produces more hydrion will be the more powerful acid, so that on this hypothesis the **degree of ionisation** of an acid furnishes a measure of its strength. But if we compare equivalent solutions of different acids under the same conditions, the electrical conductivity is closely proportional to the degree of ionisation of the dissolved substance. This arises from the fact that the speed of hydrion is much greater than the speed of any negative ion with which it may be associated. The conductivity, then, of any acid solution is due principally to the hydrion it contains, so that if we compare the conductivities of solutions of different acids, the values we obtain are nearly proportional to the relative amounts of hydrion in the solutions, and thus to the relative strengths of the acids. Since it is a very easy matter to measure the conductivity of solutions, this method of determining the relative strengths of acids has practically superseded the other methods, especially in the case of the weaker organic acids. For them it is possible to calculate a dissociation constant according to the formula given on p. 235, and this constant is very generally accepted as a measure of their strength, for which reason it is sometimes spoken of as the **affinity constant** of the acids. It will be remembered that the theoretical dissociation formula only applies to half-electrolytes, the strong and highly dissociated mineral acids giving only constants with the empirically modified formulæ of Rudolphi and van 't Hoff. These empirical constants might be used as "affinity constants" for the strong acids, since they, like the true dissociation constants, give a measure of the relative dissociations of different acids independent of the dilution, but as their significance is doubtful, and the degree of constancy attained is not after all very great for the highly-dissociated acids, they have not so far come into general use.

Since the degree of ionisation cannot go beyond 100 per cent, we have here a natural limit set to the strength of acids. The limit is reached at moderate dilutions for some of the monobasic acids, which are therefore the strongest acids which can be met with in aqueous solution. These are hydrochloric, hydrobromic, hydriodic, nitric, and chloric acids amongst the common inorganic acids; amongst the organic acids we have the alkyl sulphuric acids, such as hydrogen ethyl sulphate, and the sulphonic acids, such as benzene sulphonic acid or ethane sulphonic acid. No dibasic acid is as strong as these monobasic acids, sulphuric acid being the strongest of this type. The fatty acids, such as acetic acid, are very much weaker than these.

It should be noted that at great dilutions the differences in strength between acids begin to disappear. At infinite dilution all acids are equally dissociated, so that no one will contribute more hydrion than another, and consequently all acids under these conditions will have the same strength. As has already been indicated, no such state can actually be realised, but it is well to remember that, in general, differences in strength of acids are more marked in comparatively strong solutions than in very dilute solutions. Thus we have the following numbers in the case of acetic acid and its chlorine substitution products, which represent the percentage degree of dissociation or the proportion of available hydrogen existing in the solution as hydrion, *i.e.* in the active state.

	Dilution = 32 Litres	128 Litres	512 Litres
Acetic	2·4	4·7	9·1
Monochloracetic	20	35	57
Dichloracetic	70	88	98
Trichloracetic	90	95	99

At the dilution 32, trichloracetic acid has 37 times as much hydrion as an equivalent solution of acetic acid; at the dilution 512 it has only 11 times as much. It is true that between the dilutions 32 and 512, acetic acid gains only 6·7 per cent, where trichloracetic acid gains 9, but this is on account of the great difference in strength between the acids, and it can be seen that between 128 litres and 512 litres the actual gain of the acetic acid is greater than the gain of the trichloracetic acid, and this would be more and more evident as the dilution proceeded. In the case of the other acids which are more nearly equal in strength, the equalisation of strength as dilution proceeds is much more evident. From 32 litres to 512 litres, trichloracetic acid only gains 9 per cent, where dichloracetic acid gains 28, and monochloracetic acid gains 37. At 32 litres trichloracetic acid is nearly 30 per cent stronger than dichloracetic acid; at 512 litres their strengths are almost equal.

It now remains to show the connection between the degree of ionisation of two acids and the proportion in which they will share a base between them, when both are competing for it in the same solution. Let the acids HA and HA′, and the base NaOH, be dissolved in water so that 1 gram molecule of each is contained in v litres of the mixed solution. For the sake of simplifying the calculation, we shall also suppose that the acids are weak and obey Ostwald's dilution formula (p. 235), that their degree of ionisation at the dilution considered is very small, and that the degrees of ionisation of the sodium salts produced are equal, which will very nearly be the case. Let x be the amount of the acid HA neutralised by the soda, then the quantity of HA′ neutralised will be $1 - x$, since the total quantity of soda is 1. If now h represents the quantity of hydrion in the solution, and d the common ionisation factor of the two sodium salts, we shall have the following quantities of the various substances existing in equilibrium with one another :—

NaA . . .	x, of which $(1-d)x$ un-ionised.
NaA′ . . .	$(1-x)$, of which $(1-d)(1-x)$ un-ionised.
HA . . .	$(1-x)$, of which practically all un-ionised.
HA′ . . .	x, of which practically all un-ionised.
H ion . . .	h, a very small amount, from HA and HA′.
Na ion . .	$d(x+1-x)=d$, from NaA and NaA′.
A ion . . .	dx, from NaA almost entirely.
A′ ion . . .	$d(1-x)$, from NaA′ almost entirely.

Now in order that equilibrium may exist between the un-ionised HA and the ions H and A, the requirements of Ostwald's dilution formula must be fulfilled, and we must have

$$\frac{(\text{H ion}) \times (\text{A ion})}{(\text{un-ionised HA})v} = k.$$

Substituting the values given in the above table, we obtain

$$\frac{hdx}{(1-x)v} = k.$$

Similarly for the acid HA′ we get

$$\frac{hd(1-x)}{xv} = k'.$$

Dividing the first of these equations by the second we have

$$\frac{x^2}{(1-x)^2} = \frac{k}{k'}, \text{ or } \frac{x}{1-x} = \sqrt{\frac{k}{k'}},$$

i.e. the ratio of the avidities of two acids is equal to the square root of the ratio of their dissociation constants, if all the conditions mentioned above are fulfilled.

We can get a direct relation between the avidities and the degree of ionisation at a given dilution by taking account of the dilution formulæ for pure solutions of the acids. For the acids HA and HA′ let the degrees of ionisation at the dilution v be m and m' respectively. We have then

$$\frac{m^2}{(1-m)v} = k, \text{ and } \frac{m'^2}{(1-m')v} = k'.$$

Since the degree of ionisation of the acids is by hypothesis very small, $1-m$ and $1-m'$ become very nearly equal to 1, and consequently by division we have approximately

$$\frac{m^2}{m'^2}=\frac{k}{k'}.$$

But we found above

$$\frac{x^2}{(1-x)^2}=\frac{k}{k'},$$

therefore

$$\frac{x}{1-x}=\frac{m}{m'},$$

i.e. ratio in which a base distributes itself under the conditions named between two acids, is practically equal to the ratio of the degrees of ionisation of the separate acids at the same concentration, or, in other words, is practically equal to the ratio of the electrical conductivities of the acids under similar conditions of dilution. The dissociation theory of Arrhenius, therefore, furnishes us with a satisfactory explanation of the connection betwen the various methods of measuring the strengths of acids; the fundamental assumption being that the activity of acids, as acids, is due entirely to the presence of hydrion, the various acids differing from each other only in the quantity of hydrion produced when equivalent amounts are dissolved in a given quantity of water. The sour taste, the action on indicators, the accelerating effect on sugar inversion, etc., are all attributed to the hydrion, and increase in magnitude as the amount of hydrion increases.

The methods employed for measuring the **relative strengths of bases** are in all respects similar to the methods adopted for acids. The distribution of an acid between two competing bases, the accelerating effect of different bases on a certain chemical action, and the electrical conductivities of equivalent solutions of the bases, have all been investigated, and have been found to lead to consistent results.

If we inquire into what is common to solutions of all bases, we find that the dissociation hypothesis gives us "hydroxidion" for answer. Just as it attributed the essential properties of acids to hydrion, so it attributes the essential properties of alkalies to hydroxidion. This is responsible for the alkaline taste, the action on indicators, and for the power of neutralising acids. Bases differ from one another in strength according as their equivalent solutions produce more or less hydroxidion, that base being the stronger which produces the most.

The **electrical conductivity** of equivalent solutions of the soluble bases gives us a means of judging their relative strengths, but a reference to the table of ionic velocities on p. 222 will show that the value of the conductivity is not such a direct measure of the strength of bases as it is of acids, in view of the fact that the speed of the hydroxidion does not exceed the speeds of the positive ions in the same proportion as the speed of the hydrogen ion exceeds the speeds of the negative ions. The total conductivity of the base is therefore due to a less extent to hydroxidion than the conductivity of an acid is due to hydrion. The degree of ionisation, however, if calculated from the conductivities in the usual way (p. 233), gives the correct measure of the strengths of bases when in equivalent solution, and the dissociation constant of bases has the same significance in this respect as the dissociation constants of acids, the stronger base being that with the greater constant.

A direct **velocity method**, which has been applied to determining the strengths of bases, is the rate at which they saponify methyl acetate (cp. p. 267). The saponification is apparently effected by hydroxidion, and equivalent solutions of different bases will give velocity constants (at the beginning of the saponification at least) which will be proportional to the amount of hydroxidion in the solution, *i.e.* to the strengths of the bases. The following numbers were obtained in fortieth normal solution of the various bases, the value of the constant for lithium hydroxide being made equal to 100 :—

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 strong alkalies, lithia, soda, potash, have practically reached the limit of strength, their ionisation at moderate dilutions being almost complete. The hydroxides of the metals of the alkaline earths are equally strong, as similar experiments have proved. Ammonia, or, as it partially exists in solution, ammonium hydroxide, is a comparatively feeble base, bearing much the same relation to the strong alkalies as the weak organic acids to the strong mineral acids. The alkylammonium hydroxides are all stronger bases than ammonium hydroxide, the tetra-alkyl hydroxides being nearly comparable in point of strength to the caustic alkalies, as indeed is evident from their general chemical behaviour.

The only **acceleration method** hitherto found by means of which the relative strengths of bases may be determined is the transformation of the alkaloid hyoscyamine into the isomeric alkaloid atropine, the course of which can be followed with the polarimeter. The amount of the acceleration here seems to be proportional to the concentration of hydroxidion in the solution, but unfortunately the method cannot be applied with great strictness on account of secondary decompositions of the atropine, which interfere with the calculation of the velocity constant. The bases, potassium hydroxide, sodium hydroxide, and tetramethylammonium hydroxide, were found to have nearly equal accelerating effects, which is in agreement with the results of the saponification methods.

There are certain acids and bases so weak that it is difficult to apply some of the above methods for obtaining their relative strengths in aqueous solution. Their degree of ionisation at practically available dilutions is so slight that a direct measurement either of their accelerating action or their conductivity leads to doubtful results, whilst methods involving formation of their salts may also prove useless owing to the **decomposing influence of water**. Hitherto we have spoken of water as a perfectly neutral substance, but this is far from being the case. So long, indeed, as we deal with strong acids and bases, and the salts formed from them, the solvent water in which they are contained may be regarded as neutral, but if either very weak acids or very weak bases are in question, the chemical nature of the water must be taken into consideration.

Ordinary tap-water has a very considerable electrical conductivity, *i.e.* it must contain ions in moderate quantity. The conductivity of distilled water is very much less, so we conclude that the conductivity of the tap-water is chiefly due to impurity. The more care that is devoted to the distillation of the water the less does its conductivity become, but it is difficult to procure and keep water with a conductivity at 18° of less than 1×10^{-10} times that of mercury. Kohlrausch, however, on purifying water in platinum vessels by distillation in vacuo, and condensing the pure vapour directly in the resistance vessel, found that the purest water he could obtain had a conductivity of $0{\cdot}036 \times 10^{-10}$. This conductivity must be accepted as the specific conductivity of pure water, for it is in close accordance with numbers calculated from the chemical and electrical behaviour of the substance. If the conductivity is not due to dissolved impurity, the ions with which the electricity travels must come from the water itself. Since water contains only hydrogen and oxygen, the ions we should expect are hydrion and hydroxidion. This assumption accounts very well for the chemical and electrochemical behaviour of water, and affords the desired basis of a numerical comparison between the results of the different investigations. Corresponding to the very small conductivity, the ionisation is very small. At 25° the amount of hydrogen contained in water in the form of hydrion is about 0·1 milligrams per ton, the amount of hydroxidion being 17 times as great as this. These amounts, although excessively minute, are sufficient to confer on the water the properties of a weak acid on account of the hydrion, and of a weak base on account of the hydroxidion. Chemically speaking, these properties are most evident in the phenomena of salt hydrolysis or

hydrolytic dissociation. If a salt, when dissolved in water, is only affected by the solvent in so far as electrolytic dissociation is concerned, its solution is neutral, since there are in it neither free hydrion nor free hydroxidion in appreciable quantity. This we find to be the case with salts derived from strong acids and strong bases, *e.g.* sodium chloride, potassium sulphate, and the like. If, on the other hand, we dissolve in water a salt formed by the neutralisation of a strong acid by a weak base, the solution has a distinctly acid reaction, *i.e.* must contain free hydrion in quantity. Examples of such salts are the chlorides or nitrates of aluminium, copper, and zinc among inorganic compounds, and the same salts of aniline, pyridine, and urea amongst organic compounds. If the base is as weak as diphenylamine, treatment with water is sufficient to decompose it almost entirely into free acid and free base (cp. p. 258).

If the salt is formed from a strong base and a weak acid, it is equally decomposed by water, but the reaction of the solution is then alkaline, as in it there is an excess of hydroxidion. Examples of such salts are to be found in sodium or potassium borate, carbonate, or cyanide, and in the soaps.

In order to understand how salts of the above types come to possess an acid or an alkaline reaction, we have to consider the relative degrees of ionisation of the acid and base liberated from the salts by the action of the water. Suppose the salt to be formed by the neutralisation of a strong base, say caustic soda, by a weak acid, say carbonic acid. We may assume provisionally that the salt is decomposed by the water according to the following equation :—

$$Na_2CO_3 + 2H_2O = 2NaOH + H_2CO_3.$$

The base and acid are produced by the decomposition in equivalent quantities, but the base, being a strong one, is highly ionised, whilst the acid, being a weak one, is scarcely ionised at all. From the base, then, is produced hydroxidion in comparatively large amount, while the acid supplies very little hydrion. There is thus a great excess of hydroxidion over hydrion, and the solution has in consequence an alkaline reaction. This is all the more marked inasmuch as the hydrolysis takes place, in all probability, according to the equation

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH,$$

the acid salt being formed instead of the free acid. Now the acid salt supplies no hydrion at all, as far as we can judge, so that practically the whole of the hydroxidion produced by the hydrolysis remains in the solution as such, and thus imparts to it a strong alkaline reaction.

With such a salt as aniline hydrochloride the reverse is the case. The free base, phenylammonium hydroxide, produced according to the equation

$$NH_3(C_6H_5)Cl + H_2O = NH_3(C_6H_5)OH + HCl,$$

is very feeble, and consequently yields little hydroxidion. The acid produced, on the other hand, is almost fully ionised, so that the solution will have a very large excess of hydrion, and a correspondingly strong acid reaction.

If we take a series of weak bases combined with the same acid, say hydrochloric acid, to form salts, and measure the degree of hydrolytic dissociation in equivalent solutions of these salts, we can form an estimate of the relative strengths of the bases. The weaker the base is, the more of it will be expelled from combination with the acid by the competing base water. The greater, then, the degree of hydrolytic dissociation in a series of salts under the same conditions, the weaker is the base which is in combination with the acid.

The determination of the **degree of hydrolytic dissociation** is often somewhat difficult. It might be thought that the free acid could be titrated with an alkali and an indicator, but a little consideration shows that this is impossible. Suppose that the salt were hydrolysed to the extent of 5 per cent. As soon as we have neutralised that 5 per cent of acid by a strong base, the originally undecomposed proportion of the salt is hydrolysed by the action of the water, and more acid is produced. Although this in turn is neutralised by the addition of a strong base, the process of hydrolytic dissociation still goes on, and the solution will not become neutral until all the acid which was originally combined with the weak base has passed into combination with the strong base with which we titrate the solution. A solution of aniline hydrochloride behaves towards caustic alkali and phenol-phthaleïne exactly like an equivalent solution of hydrochloric acid, owing to the progressive hydrolysis of the salt.

In determining the degree of hydrolysis, then, a method must be employed which will not disturb the hydrolytic equilibrium. Measurements of optical or other physical properties have been employed with some degree of success, and also reaction velocity methods. For example, we can tell approximately how much free hydrochloric acid there is in a solution of aniline hydrochloride or urea hydrochloride, by ascertaining at what rate they catalyse methyl acetate or invert cane sugar (cp. p. 282). The velocity constant for the catalysis of methyl acetate is approximately proportional to the amount of free hydrochloric acid in the solution, so that a determination of the one leads to a knowledge of the other. Similarly, we can ascertain how much free caustic soda there is in a solution of sodium carbonate by finding at what rate the solution saponifies ethyl acetate, the initial rate of saponification being nearly proportional to the amount of free alkali in the solution.

The following tables will serve to indicate the extent of hydrolysis of some common salts of weak bases and weak acids :—

PERCENTAGE HYDROLYSIS OF HYDROCHLORIDES OF WEAK BASES

$t=25°$; $v=32$.

Aniline	2·6
Paratoluidine	1·5
Orthotoluidine	3·1
Urea	95

The urea hydrochloride undecomposed by the water apparently only amounts to one-twentieth of the whole. The hydrolysis of the salts of the aromatic bases, on the other hand, is comparatively slight, and experiments on the rate of sugar inversion at 80° indicate that the hydrolysis suffered by the hydrochloride of a weak inorganic base like alumina is of the same order of magnitude.

That an insoluble base like aluminium hydroxide, $Al(OH)_3$, should apparently exist in solution is at first sight inexplicable. When we consider, however, that the base or insoluble basic salt may exist in the state of pseudo-solution (p. 205) the difficulty disappears. As a matter of fact, it is found that salts of insoluble bases give aqueous solutions which are not "optically void," but which scatter light, thus proving that they are not in reality homogeneous but contain an insoluble substance, the base or basic salt, in pseudo-solution. Salts of soluble bases give "optically void" solutions, provided that the acid also is soluble.

PERCENTAGE HYDROLYSIS OF SALTS OF WEAK ACIDS

$t=25°$; $v=10$.

Potassium phenolate	3·1
Potassium cyanide	1·1
Borax	0·5
Sodium acetate	0·01

Acetic acid is usually spoken of as a weak acid, but the above table shows that it is much more powerful than any of the other acids mentioned, the hydrolysed part only amounting to a ten-thousandth of the whole under the specified conditions.

The extent of hydrolysis of a salt produced by the interaction of a strong acid and a weak base, or *vice versa*, increases with increasing dilution. According to the law of mass action, which is in this case applicable (cp. p. 301),

$$k \times \text{act. mass of salt} \times \text{act. mass of water} = k' \times \text{act. mass of acid} \times \text{act. mass of base}.$$

Now for dilute solutions the active mass of the water is a constant, so that

$$\frac{\text{act. mass of acid} \times \text{act. mass of base}}{\text{act. mass of salt}} = \text{constant}.$$

Let the total amount of material considered be 1 gram molecule dissolved in v litres of water, and let the hydrolysed portion be x. Then

$$\left(\frac{x}{v}\right)^2 \div \frac{1-x}{v} = \frac{x^2}{(1-x)v} = \text{constant}.$$

As v increases, x must, according to the formula, increase likewise, and if the extent of hydrolysis x is small, it will increase very nearly proportionally to the square root of the dilution, as may be shown in the manner adopted for the closely similar dissociation equilibrium (p. 235).

When both the acid and base which go to form the salt are weak, the simple law of mass-action does not apply, and the extent of the hydrolysis is nearly independent of the dilution. This has been shown to be the case for the acetate of urea, which is an example of a salt of this kind.

The theory of the hydrolysis of salts was originally given in a paper by ARRHENIUS, *Zeitschrift für physikalische Chemie*, **5**, p. 16 (1890).

OSTWALD's papers on the Affinity Constants of Organic Acids are in the same journal, **3**, pp. 170, 241, 369 (1889).

CHAPTER XXV

EQUILIBRIUM BETWEEN ELECTROLYTES

In the chapter on balanced action we have seen that when the active mass of one or more of the products of a dissociation is increased, the degree of dissociation is diminished (p. 261). This rule is especially important when we deal with solutions of salts, acids, and bases, all of which are electrolytically dissociated, and that to very different degrees. In cases of gaseous dissociation we can usually add one of the products of dissociation without adding anything else at the same time. This cannot be done with dissolved electrolytes, for the nature of the dissociation is such that the solution must always remain electrically neutral, although the products of dissociation are electrically charged. When, therefore, we add one of the products of dissociation to an electrolytically dissociated substance, we are compelled to add at the same time an electrically equivalent quantity of an ion oppositely charged. Thus if we consider a solution of hydrogen acetate, we find that we can only add hydrion by adding an acid, say hydrochloric acid, which not only contributes hydrion but chloridion as well. Similarly, if we wish to increase the amount of acetanion in the given volume, we can only do so by adding to the solution an acetate, which yields metallion at the same time as it yields acetanion. Notwithstanding this complication, however, the equilibrium equation for hydrogen acetate still remains the same, namely—

$$\text{act. mass } H^{\cdot} \times \text{act. mass } C_2H_3O_2{}' = \text{const.} \times \text{act. mass undiss. } C_2H_4O_2,$$

whether a small quantity of another ion is added or not, so that if we increase the active mass of either the hydrion or the acetanion, the active mass of the un-ionised hydrogen acetate is also increased, *i.e.* the degree of ionisation is diminished.

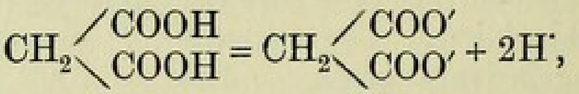
As has already been indicated, the effect on the degree of ionisation is greater when the substance considered is only slightly ionised. Now acetic acid, even in moderately dilute solution, is only feebly ionised, so that the addition of an equivalent quantity of a strongly ionised acid like hydrochloric acid practically reduces the ionisation of the acetic acid to zero. Suppose, for example, that at the given dilution hydrochloric acid is fifty times more ionised than acetic acid, the addition of an equivalent of the former will practically reduce the quantity of acetanion to a fiftieth part of the original value, for it has increased the amount of hydrion about fifty-fold, and the product of the active masses of the ions must remain practically constant, the active mass of the un-ionised hydrogen acetate suffering but little change from the diminution of the ionisation. The degree of ionisation is thus reduced to about a fiftieth part of its former magnitude. A similar reduction takes place if we add an equivalent quantity of an alkaline acetate to a solution of acetic acid. Although the acid itself is feebly ionised, its salts are as highly ionised as those of strong acids, with the result that the amount of the acetanion is greatly increased, and the amount of hydrion correspondingly diminished. This reduction of the ionisation of weak acids by the addition of their neutral salts to the solution is of great practical importance, as the amount of hydrion which they produce, and consequently their activity as acids, is thereby greatly reduced (Chap. XXIV.).

The addition to a strong acid of an equivalent or greater quantity of one of its neutral salts has very little effect on its activity as an acid, as measured by the proportion of hydrion to which it gives rise. This is due to the acid as well as the salt being almost completely ionised. If, for example, we add an equivalent of sodium chloride to a solution of hydrogen chloride, we at most double the amount of chloridion. The increase of the un-ionised amount is, however, also relatively great, so that to fulfil the requirements of the equilibrium formula a very small diminution of the amount of hydrion is necessary, and consequently the activity of the acid is little affected.

What holds good for acids likewise holds good for bases, the strength of which is measured by the proportion of hydroxidion derived from them. If to a feebly ionised solution of ammonium hydroxide we add ammonium chloride, which is highly ionised, we greatly increase the amount of ammonion, and diminish to a corresponding extent the amount of hydroxidion necessary for equilibrium. The base ammonium hydroxide, then, loses much of its activity when accompanied in solution by ammonium salts. Strong bases like potassium hydroxide are only slightly affected by the addition of a neutral salt yielding the same metallion, for although the relative change on the undissociated proportion may be great, the same actual change has a very slight effect on the ionised proportion, and thus leads to only a slight diminution in the concentration of hydroxidion.

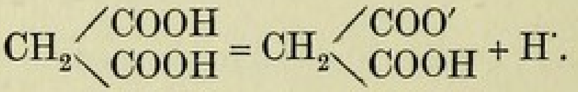
The addition of neutral salts to a dibasic acid like sulphuric acid is a much more complicated phenomenon than the addition of neutral salts to monobasic acids. This is chiefly due to the formation of acid salts, which dissociate rather as salts than as acids. Thus when we add an equivalent of sodium sulphate to a solution of hydrogen sulphate, a certain proportion of the two original salts remains in the solution, accompanied however by the intermediate acid salt, sodium hydrogen sulphate, $NaHSO_4$. The sodium sulphate dissociates largely into the ions $Na^{\cdot}$ and SO_4''; the sulphuric acid dissociates into $H^{\cdot}$ and SO_4'', but also produces ions HSO_4'; the sodium hydrogen sulphate, finally, dissociates chiefly into $Na^{\cdot}$ and HSO_4'. There are therefore three un-ionised substances in solution, viz. H_2SO_4, Na_2SO_4, and $NaHSO_4$; and at least four kinds of ions, viz. $Na^{\cdot}$, $H^{\cdot}$, HSO_4', and SO_4'', so that the equilibrium is somewhat complex.

In this connection it may be stated that dibasic acids very generally dissociate in solution into one hydrogen ion and the residue of the molecule, the second replaceable hydrogen atom not splitting off as an ion until the greater quantity of the first has been removed. Thus sulphuric acid in fairly strong solution in all probability contains comparatively little of the ion SO_4'', the dissociation being principally into $H^{\cdot}$ and HSO_4'. At greater dilutions, however, the ion SO_4'' appears in quantity, probably owing to the splitting up of the hydrosulphanion HSO_4' into $H^{\cdot}$ and SO_4''. One result of this is that weak dibasic acids give a dissociation constant of exactly the same character as that of a monobasic acid, the formula used in deriving which assumes that the ionisation takes place into two ions only. Thus malonic acid does not primarily dissociate according to the equation



$$CH_2\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} = CH_2\begin{matrix}\diagup COO'\\ \diagdown COO'\end{matrix} + 2H^{\cdot},$$

but according to the equation



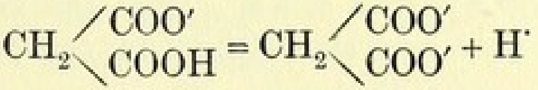
$$CH_2\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} = CH_2\begin{matrix}\diagup COO'\\ \diagdown COOH\end{matrix} + H^{\cdot}.$$

The equilibrium is therefore of exactly the same type as the dissociation equilibrium of acetic acid, and follows the same law.

This is seen in the following table, which gives the dissociation constant for malonic acid (cp. p. 235):—

v	μ	$100m$	$100k$
16	53·07	14·85	0·159
32	72·32	20·20	0·159
64	97·15	27·15	0·158
128	128·5	35·9	0·157
256	165·9	46·4	0·157
512	208·8	58·6	0·162
1024	253·2	70·8	0·168

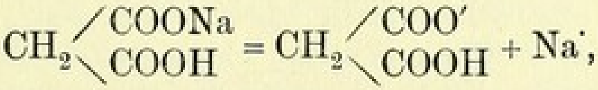
The constancy of the expression $100k = \frac{100m^2}{(1-m)v}$ in the last column shows that the primary dissociation is into two ions and not into three, in which case the expression $\frac{m^3}{(1-m)v^2}$ would be constant. It will be noticed that after 50 per cent of the first hydrogen has split off as ion, the constant begins slightly to rise. The rise probably indicates that the second hydrogen atom is now being affected, *i.e.* that the action



$$\mathrm{CH_2}\begin{array}{l}\diagup \mathrm{COO'}\\ \diagdown \mathrm{COOH}\end{array} = \mathrm{CH_2}\begin{array}{l}\diagup \mathrm{COO'}\\ \diagdown \mathrm{COO'}\end{array} + \mathrm{H}^{\cdot}$$

has commenced to be appreciable. The exact point at which this second action begins varies very much with different acids. Many acids show the secondary dissociation when the primary has proceeded to the extent of about 50 per cent; but some acids—maleïc acid for example—give a good constant up to 90 per cent primary dissociation.

For acid salts of comparatively feeble polybasic acids one may say that almost invariably the primary dissociation is into metallion and the rest of the molecule, no hydrion appearing until this primary dissociation is far advanced, although, as indicated above, hydrion may arise from the acid itself produced by the action of the water. Thus sodium hydrogen malonate dissociates primarily according to the equation



$$\mathrm{CH_2}\begin{array}{l}\diagup \mathrm{COONa}\\ \diagdown \mathrm{COOH}\end{array} = \mathrm{CH_2}\begin{array}{l}\diagup \mathrm{COO'}\\ \diagdown \mathrm{COOH}\end{array} + \mathrm{Na}^{\cdot},$$

and the acid character of the solution, judged by the methods of the preceding chapter, is very feebly marked.

In general, when we mix two electrolytic solutions, we cannot calculate the conductivity of the mixed solution from those of the components by the simple alligation formula,[1] because each dissolved substance affects the dissociation of the other, and thus alters the number of carrier ions. From the law of mass action, however, as applied to electrolytic equilibrium, we ascertain that there must be certain solutions which can be mixed together without alteration in the amount or nature of the ions, and therefore without change in the average conducting power. Such solutions are called **isohydric**, and we shall first investigate the conditions for isohydry in the case of two electrolytes giving rise to a common ion, say HA and HA′, each of which obeys Ostwald's dilution law. Let the dilutions of the two isohydric solutions be v and v' respectively, and their degrees of ionisation m and m'. For the acid HA we have the equilibrium equation

$$\frac{m^2}{(1-m)v} = k,$$

---

[1] If two substances when mixed retain their specific values of a property unchanged by the process of mixture, the specific value of the same property for the mixture can be calculated by the alligation formula $\frac{aA+bB}{a+b}$, in which a and b represent the proportions of the components, and A and B the specific values of the property for the components.

and for the acid HA′ the corresponding equation

$$\frac{m'^2}{(1-m')v'}=k'.$$

If now we mix these isohydric solutions, the volume becomes $v+v'$, and the amount of hydrion $m+m'$. For the acid HA under the new conditions we have now the equilibrium equation

$$\frac{(m+m')m}{(1-m)(v+v')}=k.$$

Dividing this equation by the first, we obtain

$$\frac{(m+m')v}{(v+v')m}=1, \text{ or } \frac{m+m'}{m}=\frac{v+v'}{v};$$

whence

$$\frac{m'}{m}=\frac{v'}{v},$$

or

$$\frac{m}{v}=\frac{m'}{v'}.$$

Now $\frac{m}{v}$ is the concentration of hydrion in the acid HA, and $\frac{m'}{v'}$ is the concentration of hydrion in the isohydric solution of the acid HA′, and these two concentrations prove to be equal. We may say, therefore, that solutions of electrolytes containing a common ion are isohydric when the concentration of the common ion in the different solutions is the same.

It is often convenient for purposes of calculation to imagine an actual mixed solution to be split up into its component isohydric solutions, which may then be ideally mixed at any time without any change in the ionisation of the electrolytes occurring. For example, a solution containing equivalent quantities of hydrogen acetate and sodium acetate may be imagined to exist in a rectangular vessel with a movable vertical partition through which water can freely pass, but not the dissolved substances. Let the hydrogen acetate be on one side of the partition and the sodium acetate on the other. The partition is now to be moved until the concentration of the common ion, acetanion, is the same on both sides. Since the sodium acetate is highly ionised, it must receive most of the water in order that the concentration of the acetanion may be as small as that derived from the slightly ionised hydrogen acetate. The position of the partition for isohydry must therefore be as shown in Fig. 43, which represents a horizontal section of the vessel, the liquid rising to the same level on both sides of the diaphragm. It must be borne in mind that concentrating the solution of hydrogen acetate does not involve an equal concentration of the hydrion or acetanion, for as the dilution diminishes, the degree of dissociation, and therefore the proportion of ions, diminishes also, although at a smaller rate. Beginners are apt to reason that if the solution of one electrolyte is ten times more ionised than an equivalent solution of another, it is only necessary to concentrate the second solution to a tenth of its volume in order that the ionic concentrations of the two solutions may become equal. In view of the diminution of the degree of ionisation as the dilution diminishes, a much greater degree of concentration is necessary.

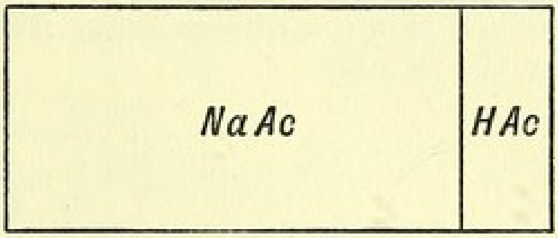


Fig. 43.

If we consider the mixing of two salts which have no common ion, say NaCl and KBr, the problem becomes much more complicated. When the two salts are mixed, we have not only the substances originally in solution, *i.e.* the un-ionised salts NaCl and KBr, and their ions, $Na^{\cdot}$, $K^{\cdot}$, Cl', and Br', but also the new un-ionised substances NaBr and KCl. Let there be prepared isohydric solutions of the different salts, NaCl being made isohydric with NaBr, by getting the natrion of the same concentration in both solutions; KCl may then be made isohydric with NaCl by making the chloridion of the same concentrations in the two solutions. KBr may finally be made isohydric with KCl by equalising the concentrations of the kalion. Any two of these solutions then which possess a common ion may be mixed in any proportions without change in the dissociation. If we wish to mix all four, we must take volumes of the solutions such that the products of the volumes of reciprocal pairs are equal. If a, b, c, d be the volumes of the isohydric solutions of NaCl, NaBr, KCl, and KBr respectively, such that

$$ad = bc,$$

then the solutions may be mixed in these proportions without change in the ionisation. Using a diagrammatic representation similar to that adopted for mixtures of pairs of electrolytes with a common ion, we get the diagram Fig. 44, which fulfils the desired condition.

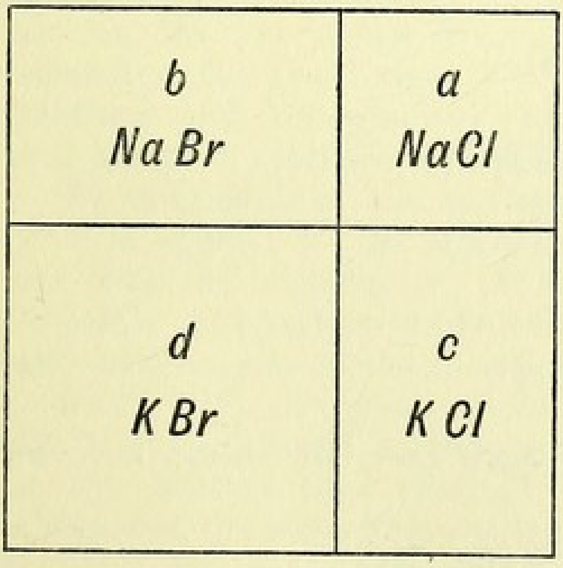


Fig. 44.

The proof of the condition may be given on the supposition that the substances obey Ostwald's dilution law. Let a, b, c, d be the volumes of the isohydric solutions which when mixed will produce no change in the ionisation. Before mixing, the equilibrium of the sodium chloride will, assuming its quantity to be unity, be represented by the formula

$$\frac{\frac{m}{a}\cdot\frac{m}{a}}{\frac{1-m}{a}}=\frac{m^2}{(1-m)a}=k,$$

where m is the degree of dissociation. Let the solutions be now mixed. The amount of natrion has now increased in the ratio of $a+b$ to a, since b volumes of NaBr have been added to the original a volumes of NaCl, and the concentration of the natrion is the same in both solutions. But the volume in which this quantity is contained is now $a+b+c+d$, so that the active mass of the natrion is now $m\times\frac{a+b}{a}\times\frac{1}{a+b+c+d}=\frac{m(a+b)}{a(a+b+c+d)}$. Similarly the amount of chloridion increases in the ratio of $a+c$ to a, and its active mass becomes $\frac{m(a+c)}{a(a+b+c+d)}$. The un-ionised proportion of sodium chloride remains the same as before, viz. $1-m$. We have therefore for the new equilibrium the equation

$$\frac{\frac{m(a+b)}{a(a+b+c+d)}\cdot\frac{m(a+c)}{a(a+b+c+d)}}{\frac{1-m}{a+b+c+d}}=k,$$

whence, since k is also equal to $\frac{m^2}{(1-m)a}$,

$$\frac{m^2(a+b)(a+c)}{(1-m)a^2(a+b+c+d)}=\frac{m^2}{(1-m)a},$$

$$\frac{(a+b)(a+c)}{a(a+b+c+d)}=1,$$

$$a^2+ab+ac+bc=a^2+ab+ac+ad,$$

$$bc=ad,$$

which was to be proved.

According to Guldberg and Waage's Law, we should have for equilibrium in the balanced action

$$\mathrm{NaCl}+\mathrm{KBr}\rightleftarrows\mathrm{NaBr}+\mathrm{KCl}$$

the expression

$$\frac{[\mathrm{NaCl}]\times[\mathrm{KBr}]}{[\mathrm{NaBr}]\times[\mathrm{KCl}]}=\text{constant},$$

where the formulæ in square brackets represent the active masses of the respective substances. This equilibrium formula takes no account of electrolytic dissociation of the various salts, and is only valid under certain conditions of dissociation. The correct formula is

$$\frac{[\text{diss. NaCl}] \times [\text{diss. KBr}]}{[\text{diss. NaBr}] \times [\text{diss. KCl}]} = 1,$$

as may be deduced from the above relation $ad = bc$. Since all the solutions to which these letters refer are isohydric in pairs, *i.e.* have the same concentration of ions, the volumes a, b, c, d are proportional to the quantities of the ions in the various solutions, *i.e.* to the dissociated quantities of the salts, and not to their total quantities. When all the substances are highly ionised, Guldberg and Waage's Law leads to very nearly the same result as when the ionisation is considered, and the same holds true when two of the four substances are highly ionised. When, however, one or three of the substances are highly ionised, there is usually a great discrepancy between the two modes of calculating the equilibrium, Guldberg and Waage's Law being no longer even approximately true, except in special circumstances.

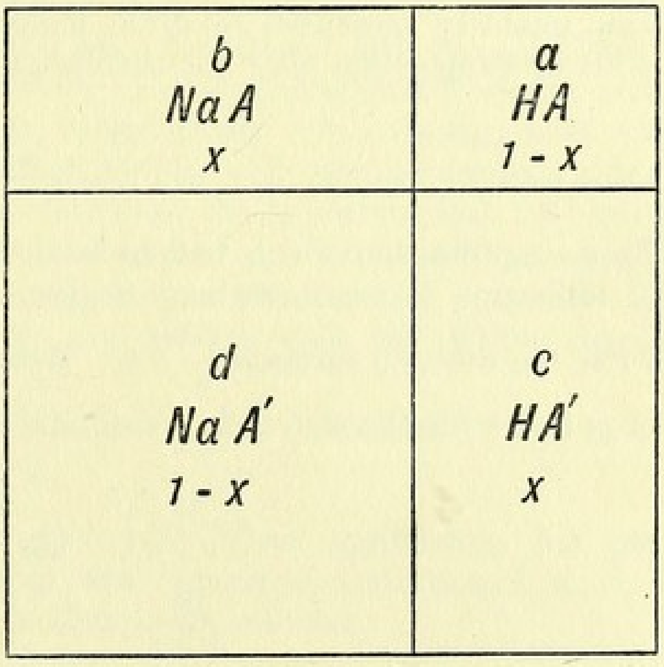


Fig. 45.

As an example of the application of the theory of isohydric solutions as applied to the equilibrium of four ionised substances, we may take the distribution of a base between two acids obeying Ostwald's dilution law and find the relation of the distribution ratio to the ratio of the dissociation constants of the acids. Let, as before (p. 285), one gram molecular weight of each of the substances HA, HA′, and NaOH be dissolved in a certain volume of water, and let the solution thus obtained be ideally split up into isohydric solutions of the same ionic concentration i. We thus get the diagram Fig. 45.

The volumes are again represented by a, b, c, d, and the following table gives the data necessary for the calculation, if x is the amount of HA neutralised by the soda :—

	HA.	NaA.	HA′.	NaA′.
Total quantity	$1-x$	x	x	$1-x$
Ionised quantity	ia	ib	ic	id
Degree of ionisation (m)	$\frac{ia}{1-x}$	$\frac{ib}{x}$	$\frac{ic}{x}$	$\frac{id}{1-x}$
Dilution (v)	$\frac{a}{1-x}$	$\frac{b}{x}$	$\frac{c}{x}$	$\frac{d}{1-x}$

As the concentration of the ions is the same in all the solutions, the ionised quantities are equal to the volumes of the solutions multiplied by the common ionic concentration i. The degree of ionisation, m, is the ratio of the ionised to the total quantity, and the volume divided by the quantity contained in it gives the volume which contains unit quantity measured in gram molecules, *i.e.* the dilution v. The acids by supposition obey the theoretical dilution law

$$\frac{m^2}{(1-m)v}=k.$$

By a simplification which has been already adopted when the degree of ionisation is small, we may neglect m in comparison with 1, and write the dilution formula $\frac{m^2}{v}=k$. Now, substituting the above values of m and v for the acid HA, we obtain

$$\frac{\left(\frac{ia}{1-x}\right)^2}{\frac{a}{1-x}}=\frac{i^2a}{1-x}=k,$$

and similarly for the acid HA′, we obtain

$$\frac{i^2c}{x}=k'.$$

Division then gives

$$\frac{ax}{c(1-x)}=\frac{k}{k'}.$$

Now for equilibrium we have

$$ad=bc, \text{ or } a/c=b/d,$$

whence
$$\frac{bx}{d(1-x)}=\frac{k}{k'}.$$

As before, we may assume that the two sodium salts are ionised to the same extent, so that in their case the ratio of the ionised quantities is the ratio of the total quantities, *i.e.*

$$\frac{ib}{id} = \frac{x}{1-x}.$$

We thus obtain finally the relation

$$\frac{x^2}{(1-x)^2} = \frac{k}{k'}, \text{ or } \frac{x}{1-x} = \sqrt{\frac{k}{k'}},$$

that is, the ratio of distribution of the base between the two acids is equal to the ratio of the square roots of the dissociation constants of the acids, a result already obtained on p. 286 under the same assumptions.

The student who desires to familiarise himself with the equilibrium of electrolytes in solution is advised to study the subject from the point of view of isohydric solutions, in particular when dealing with two electrolytes containing a common ion, or with double decompositions between electrolytes. In this last case the important fact to bear in mind is that the product of the ionised quantities on one side of the equation is equal to the product of the ionised quantities on the other. If, for example, we are dealing with the double decomposition

$$\underset{m_1}{CH_3 . COONa} + \underset{m_2}{HCl} \rightleftarrows \underset{m_3}{CH_3 . COOH} + \underset{m_4}{NaCl},$$

and the quantities of these substances, when equilibrium has been attained, are m_1, m_2, m_3, m_4, with the degrees of ionisation d_1, d_2, d_3, d_4 in the mixed solution, we have always the relation

$$m_1 d_1 \times m_2 d_2 = m_3 d_3 \times m_4 d_4.$$

This relation we can combine with our knowledge of the general nature of the ionisation of the various substances, and its variation with dilution, to ascertain the actual character of the equilibrium. Thus Arrhenius, to whom the theory is due, has shown that the avidities of two monobasic acids at a given dilution are approximately proportional to the degrees of ionisation which they would have if each were dissolved separately in the given volume of solvent. This we showed above to be the case for two weak acids, but it is equally true if both acids are strong, or if one is strong and the other weak. In the case of dibasic acids, like sulphuric acid, the theory cannot easily be applied owing to the excessively complicated nature of the equilibrium caused by the presence of acid salts (cp. p. 295).

It is easy, too, to prove from the theory that the degree of ionisation of a weak acid in presence of one of its salts is nearly inversely proportional to the quantity of salt present. If the weak acid should be in presence of several strongly ionised electrolytes, it can also be shown that its degree of ionisation will be the same as if the ionised parts of these electrolytes were the ionised parts of a salt of the given acid.

We have now to examine the nature of the **equilibrium between the aqueous solution of a salt and the solid salt** itself. To each temperature there corresponds a certain solubility of the salt, *i.e.* a certain osmotic pressure of the dissolved substance in the solution which is in equilibrium with the solid. Now this osmotic pressure is made up of more than one component: it is the sum of the partial pressures of the undissociated salt and of the ions derived from the salt. The question thus arises: Is it the total osmotic pressure in the solution which directly regulates the equilibrium with the solid salt, or the osmotic pressure of the un-ionised dissolved salt, or finally the osmotic pressure of the ions? The most probable reply to this question is that it is the osmotic pressure of the un-ionised substance which directly determines the equilibrium, and there are many facts which support this conclusion. The un-ionised salt here plays the part of intermediary between the ions and the solid: it is in equilibrium with the ions on the one hand and with the un-ionised solid on the other. Considered in this aspect, the constant total solubility of a solid salt at a given temperature in water is due to the constant concentration of un-ionised substance in the solution, which in its turn is in equilibrium with a constant concentration of the ions. It is possible, however, to supply additional quantities of one or other of these ions to the solution, and we have to inquire into the effect this will have on the solubility equilibrium.

In order to secure conditions favourable for calculation and for experimental verification of the results deduced from the theory, it is advisable to consider the equilibrium in the case of a sparingly soluble salt, so that the solutions considered are dilute. As an example we may take silver bromate, $AgBrO_3$, the concentration of the saturated solution of which at 24·5° is 0·0081 normal. The primary equilibrium which determines the solubility is here supposed to be that between the solid silver bromate and the un-ionised silver bromate in the solution. The concentration of this last will remain constant if the temperature remains at 24·5° and the solvent remains water. The addition of a small quantity of a perfectly neutral substance, such as alcohol, sugar, and the like, does not appreciably affect the solubility of any substance in water, since the nature of the solvent practically remains the same. Besides the un-ionised silver bromate in the solution, we have argention and bromanion. We can increase the concentration of argention by adding a soluble silver salt, and we can increase the concentration of bromanion by adding a soluble bromate. Suppose that we add such a quantity of silver nitrate as to double the amount of argention after equilibrium has been attained.

The concentration of the un-ionised silver bromate will, by hypothesis, remain the same as before. But the dissociation equilibrium of silver bromate requires that the product of the concentration of the ions should be equal to a constant into the concentration of the un-ionised salt, *i.e.* should remain constant. If, therefore, the concentration of the argention is doubled, the concentration of the bromanion must be halved, in order that the product of the two may have the same value as before. Bromanion can only fall out of solution along with an equivalent quantity of some positive ion, and since the only kind of positive ion in the solution is argention, bromate of silver must be precipitated in order to re-establish equilibrium. The effect, then, of adding silver nitrate to the silver bromate solution is to diminish the solubility of the silver bromate, and that in a degree depending on the amount of silver nitrate added. The addition of a soluble bromate acts in precisely the same way. The amount of bromanion at equilibrium is increased, and the amount of argention must be proportionately diminished in order to secure the constancy of the product of the two ions.

The following numerical example will afford an insight into the mode of calculation. As has already been stated, the concentration of a saturated silver bromate solution at 24·5° is 0·0081 normal. If we assume the salt to be entirely ionised, the product of the ions is

$$0{\cdot}0081 \times 0{\cdot}0081 = 0{\cdot}0000656.$$

Now a quantity of silver nitrate is added, which, when dissolved in the same water as contains the silver bromate would make the solution 0·0085 normal with respect to silver nitrate. Again we assume that the silver nitrate is entirely ionised. Suppose that the concentration of the silver bromate now remaining in the solution is x, a smaller quantity than before. The concentration of argention will then be $0{\cdot}0085 + x$, and the concentration of bromanion will be x. We have therefore the product of these concentrations equal to the former product, *i.e.*

$$(0{\cdot}0085 + x)x = 0{\cdot}0000656,$$

whence

$$x = 0{\cdot}0049.$$

We should consequently expect the addition of silver nitrate to reduce the strength of the saturated solution of silver bromate from 0·0081 to 0·0049. An actual determination showed that the solubility was reduced to 0·0051, which is in fair agreement with the theoretical result. It must be noted, however, that the theoretical result was deduced on the erroneous assumption that the degree of ionisation of the various substances remained the same throughout the experiments. This is, of course, not the case, as the degree of ionisation at the dilutions considered is not equal to unity, and is diminished on the addition of the silver nitrate. It is easy, however, to take account of the change in the degree of ionisation of the silver salts by making use of conductivity determinations, although the formula for equilibrium then becomes somewhat complicated. Making the necessary corrections in the above case, the theoretical number comes out equal to 0·00506, which is very nearly the value observed for the solubility. Since silver nitrate and sodium bromate have practically the same effect so far as ionisation is concerned, we should expect equivalent quantities of these two salts to diminish the solubility of silver bromate equally. Experiment shows that an amount of sodium bromate equivalent to the silver nitrate added in the above experiment diminishes the solubility to 0·0052, a value very nearly identical with the former value.

When two sparingly soluble salts yielding a common ion are shaken up with the same quantity of water, each diminishes the solubility of the other in a degree which can be calculated as in the previous instance. Thus the saturated solutions of thallium chloride, TlCl, and thallium thiocyanate, TlSCN, have a concentration of 0·0161 and 0·0149 respectively in gram molecules per litre. For the constant product of ionic concentrations we have, therefore, $0·0161^2$ and $0·0149^2$, if each is fully ionised. If the solubility of the chloride in presence of the thiocyanate is x, and the solubility of the thiocyanate in presence of the chloride is y, these two numbers give the concentrations of the chloridion and thiocyanion respectively, while their sum, $x+y$, gives the concentration of the thallion. We thus obtain the simultaneous equations

$$x(x+y) = 0·0161^2,$$
$$y(x+y) = 0·0149^2,$$

whence $x = 0·0118$, and $y = 0·0101$, the numbers found by experiment being in good agreement, viz. 0·0119 and 0·0107. By taking account of the degree of ionisation as deduced from the conductivity the harmony between the experimental and calculated values is even more marked. The lowering of the solubility of an electrolyte by the introduction into the solution of another electrolyte possessing a common ion with the first is a phenomenon of very general occurrence, the only exceptions being when the two substances form a double salt or act on each other chemically in the solution. Instances of the application of the theoretical results will be given in the next chapter.

ARRHENIUS, "Theory of Isohydric Solutions," *Zeitschrift für physikalische Chemie*, 2, p. 284 (1888); "Equilibrium between Electrolytes," *ibid.* **5**, p. 1 (1890).

CHAPTER XXVI

APPLICATIONS OF THE DISSOCIATION THEORY

When many of the ordinary chemical reactions are looked upon from the standpoint of the theory of electrolytic dissociation, they present an aspect very different from that to which we are accustomed. The **neutralisation** of strong acids by strong bases in dilute solution is a typical example. If the acid is hydrochloric acid, and the base sodium hydroxide, we have the equation

$$\mathrm{HCl + NaOH = NaCl + HOH.}$$

Now on the dissociation theory all the substances concerned in this action are highly ionised in aqueous solution, the water itself being the only exception. Writing, then, the equation for the ions, we obtain

$$\mathrm{H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + HOH,}$$

or, eliminating what is common to both members of the equation,

$$\mathrm{H^{\cdot} + OH' = HOH.}$$

The neutralisation of a strong acid by a strong base consists then essentially in the union of hydrion and hydroxidion to form water. So long as the base, acid, and salt are fully ionised, their nature makes no difference whatever on the character of the chemical act of neutralisation. This we find to be in conformity with many experimental facts. For example, the **heat of neutralisation** of one equivalent of a strong acid in dilute solution by a corresponding quantity of a strong base is very nearly 137 K, as the following table shows, the base used being caustic soda :—

Acid.	Heat of Neutralisation.
Hydrochloric	137 K
Hydrobromic	137 ,,
Hydriodic	137 ,,
Chloric	138 ,,
Bromic	138 ,,
Iodic	138 ,,
Nitric	137 ,,

A similar table for the heats of neutralisation of bases by an equivalent of hydrochloric acid shows that the heat of neutralisation is independent of the base, as long as it is fully ionised.

Base.	Heat of Neutralisation.
Lithium hydroxide	138 K
Sodium hydroxide	137 ,,
Potassium hydroxide	137 ,,
Thallium hydroxide	138 ,,
Barium hydroxide	139 ,,
Strontium hydroxide	138 ,,
Calcium hydroxide	139 ,,
Tetramethylammonium hydroxide	137 ,,

When we deal with weak acids or weak bases the heats of neutralisation often diverge greatly from the mean value for the highly ionised substances. Thus the heats of neutralisation of some comparatively feebly ionised acids by sodium hydroxide are given in the following table, the acids not being so feeble, however, as to have their sodium salts sensibly hydrolysed in aqueous solution (cp. p. 289):—

Acid.	Heat of Neutralisation.
Metaphosphoric acid	143 K
Hypophosphorous acid	151 ,,
Hydrofluoric acid	163 ,,
Acetic acid	134 ,,
Monochloracetic acid	143 ,,
Dichloracetic acid	148 ,,

Corresponding numbers for weak bases neutralised by hydrochloric acid are:—

Base.	Heat of Neutralisation.
Ammonium hydroxide	122 K
Methylammonium hydroxide	131 ,,
Dimethylammonium hydroxide	118 ,,
Trimethylammonium hydroxide	87 ,,

The explanation of these divergences from the value for highly dissociated substances is simple. Ammonium hydroxide is only feebly ionised at the dilution considered; the chemical action is not chiefly

$$H^{\cdot} + OH' = H_2O,$$

but

$$H^{\cdot} + NH_4OH = H_2O + NH_4^{\cdot},$$

i.e. from the "normal" heat of neutralisation must be subtracted the heat necessary to decompose NH_4OH into the ions $NH_4^{\cdot}$ and OH'. The heat of ionic dissociation for acids and bases is not as a rule great, so that in the majority of cases the heat of neutralisation even of weak acids and bases does not greatly diverge from the value 137 K. The divergence may be in the one direction or the other, according as heat is absorbed or developed by the ionic dissociation (cp. p. 263).

When acids or bases are so weak that their salts undergo extensive hydrolytic dissociation in aqueous solution, *i.e.* are partially split up into free acid and base, the heat of neutralisation is very small. This is owing to the fact that the neutralisation is incomplete, free hydrion or free hydroxidion remaining in the solution.

If we consider the **displacement of a weak acid from its salts** by a strong acid in the light of the dissociation hypothesis, we find that the resistance of the weak acid to ionisation is the determining circumstance in the reaction. Thus if the salt is sodium acetate and the strong acid is hydrochloric acid, the customary equation becomes

$$Na^{\cdot} + C_2H_3O_2{}' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + HC_2H_3O_2,$$

or

$$C_2H_3O_2{}' + H^{\cdot} = HC_2H_3O_2.$$

The action is essentially a union of hydrion with acetanion, and the nature of the acetate or of the strong acid is a matter of indifference, provided that they are both almost dissociated at the dilution under consideration. Similarly, the displacement of a weak base from its salts by a highly ionised base consists essentially in the union of a positive ion with hydroxidion, thus

$$NH_4{}^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + NH_4OH$$
$$NH_4{}^{\cdot} + OH' = NH_4OH.$$

The **solution of a metal** in an aqueous and strongly dissociated acid is principally transference of a positive electric charge from hydrogen to the metal: thus if zinc is the metal and hydrochloric acid the highly dissociated acid, we have

$$Zn + 2H^{\cdot} + 2Cl' = Zn^{\cdot\cdot} + 2Cl' + H_2,$$

or

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2.$$

Similarly, the displacement of bromine from a soluble bromide by chlorine is chiefly a transference of an electric charge from bromine to chlorine :—

$$Cl_2 + 2K^{\cdot} + 2Br' = Br_2 + 2K^{\cdot} + 2Cl',$$

or

$$Cl_2 + 2Br' = Br_2 + 2Cl'.$$

When two highly dissociated salts are brought together in solution, we have an ionic equation such as the following, if double decomposition is supposed to occur :—

$$\underbrace{Na^{\cdot} + Cl'} + \underbrace{K^{\cdot} + Br'} = \underbrace{Na^{\cdot} + Br'} + \underbrace{K^{\cdot} + Cl'}.$$

Both sides of this equation are the same, *i.e.* no chemical change has taken place at all. This of course only holds good as long as all the substances remain in the solution. If the solution is evaporated, that salt which is the least soluble will in general fall out first.

We obtain a similar equation for the action of a strong acid on the salt of an equally strong acid, for example—

$$\underbrace{\mathrm{H}^{\cdot} + \mathrm{Cl}'} + \underbrace{\mathrm{K}^{\cdot} + \mathrm{Br}'} = \underbrace{\mathrm{H}^{\cdot} + \mathrm{Br}'} + \underbrace{\mathrm{K}^{\cdot} + \mathrm{Cl}'}.$$

Here again both sides of the equation are the same, and thus no action has taken place. It is usual to say that in this case the base is equally divided between the two acids, but it may be seen from the above equation that the ions are free to combine in any way according to circumstances. If one of the acids is weaker than the other, then more of it will exist in the un-ionised state, so that the other acid is said to have taken the greater share of the base.

From the examples already given it is evident that the equations involving ions are usually of a much more general character than the ordinary chemical equations, and more frequently bring out the essential phenomenon common to a number of actions of the same type, as, for instance, neutralisation, and the displacement of a weak acid or base by a stronger.

The special actions employed in testing for metallic and acid radicals are practically always reactions of the ions, so that our ordinary tests are **tests for ions**. Copper, for example, gives a black precipitate with hydrogen sulphide, but not under all conditions. As long as the copper to be tested for is in the form of dicuprion $\mathrm{Cu}^{\cdot\cdot}$, the black precipitate is formed when sulphuretted hydrogen is introduced into the solution. But if the copper ceases to be dicuprion, and becomes part of a more complex ion, the precipitation will not take place. This is the case if we add potassium cyanide to the solution of a cupric salt until the original cyanide precipitate is dissolved. The copper in the solution is then in the state of the complex salt, usually written $2\mathrm{KCN}$, $\mathrm{Cu(CN)_2}$. The formula of this salt should be written $\mathrm{K_2Cu(CN)_4}$, for on solution in water it is ionised into kalion $\mathrm{K}^{\cdot}$ and the complex negative ion cupricyanidion $\mathrm{Cu(CN)_4}''$. The copper is no longer in the form of dicuprion, but exists merely as a part of the complex ion, and has in this state no reactions of its own. Sulphuretted hydrogen added to such a solution produces no precipitate, and use is made of this fact to separate copper from cadmium. Cadmium, it is true, when its salts are treated with excess of potassium cyanide, ceases for the most part, like copper, to be a positive ion, and enters into the composition of the complex negative ion $\mathrm{Cd(CN)_4}''$, but this ion is not by any means so stable as the corresponding ion containing copper. All such compound ions have the tendency to split up into simple ions, according to equations like the following:—

$$\mathrm{Cd(CN)_4}'' = \mathrm{Cd(CN)_2} + 2\mathrm{CN}',$$
$$\mathrm{Cd(CN)_2} = \mathrm{Cd}^{\cdot\cdot} + 2\mathrm{CN}',$$

and this tendency exists to different extents with different ions. With the complex ion containing cadmium it is very pronounced; with the complex ion containing copper it is much less evident. In the solution of $K_2Cu(CN)_4$ there is thus a scarcely appreciable quantity of dicuprion $Cu^{\cdot\cdot}$, while in the solution of $K_2Cd(CN)_4$ the ion cadmion $Cd^{\cdot\cdot}$ exists in moderate proportions. The former solution then is scarcely affected by hydrogen sulphide, while the latter is freely precipitated. A solution of potassium ferrocyanide, $K_4Fe(CN)_6$, is almost entirely free from diferrion, $Fe^{\cdot\cdot}$, and exhibits none of the ordinary reactions of ferrous salts.

The commonest reaction for silver is the production of a precipitate of silver chloride by the addition to the silver solution of a soluble chloride. This reaction is for argention, $Ag^{\cdot}$, and not for silver in general. If we add potassium cyanide to a silver solution until the original precipitate of silver cyanide redissolves, the addition of a soluble chloride fails to produce a further precipitate. Here again the silver has become part of a fairly stable complex negative ion argenticyanidion, $Ag(CN)_2'$, which gives off very little argention by dissociation, so that the ordinary reagents for argention may fail to detect its presence. The same holds good for the solution of a silver salt in presence of sodium thiosulphate. When we add this salt to a solution of silver nitrate, we obtain first a white precipitate of silver thiosulphate, $Ag_2S_2O_3$, which on further addition of sodium thiosulphate dissolves with formation of the double salt $NaAgS_2O_3$. This salt dissociates chiefly into the ion $Na^{\cdot}$ and the complex negative ion argenti-thiosulphanion, AgS_2O_3', so that very little argention is at any one time in the solution, and the ordinary reagents produce none of the characteristic silver reactions.

A change in the quantity of electricity associated with a positive or negative radical is accompanied by an entire change in the properties of the radical. Thus the reactions of diferrion, $Fe^{\cdot\cdot}$, are entirely different from the reactions of triferrion, $Fe^{\cdot\cdot\cdot}$; and the reactions of permanganion, the ion of the permanganates, MnO_4', differ greatly from the reactions of manganion, the ion of the manganates, MnO_4''. In connection with such changes in the electric charges of ions, the student will find it useful to remember that addition of a positive charge or removal of a negative charge corresponds to what is generally known as **oxidation** in solution; and that removal of a positive charge or addition of a negative charge corresponds to **reduction**. Thus we are said to oxidise a ferrous salt to a ferric salt when we convert the ion $Fe^{\cdot\cdot}$ into $Fe^{\cdot\cdot\cdot}$, or reduce a permanganate to a manganate when we convert the ion MnO_4' into the ion MnO_4''. In the first instance a positive charge is removed; in the second a negative charge.

If we write the equation

$$2FeSO_4 + H_2SO_4 + Cl_2 = Fe_2(SO_4)_3 + 2HCl,$$

on the supposition that all the electrolytes are fully ionised, we obtain

$$2Fe^{\cdot\cdot} + 2H^{\cdot} + 3SO_4'' + Cl_2 = 2Fe^{\cdot\cdot\cdot} + 2H^{\cdot} + 3SO_4'' + 2Cl',$$

or

$$2Fe^{\cdot\cdot} + Cl_2 = 2Fe^{\cdot\cdot\cdot} + 2Cl'.$$

The whole action, from this point of view, reduces itself to the simultaneous appearance of positive and negative charges. The diferrion assumes a positive charge and is "oxidised" to triferrion. The uncharged chlorine assumes a negative charge and is "reduced" to the chloridion. In this instance no oxygen has been transferred, so that it is only by analogy that we can call such a process one of oxidation. It is precisely in these cases, however, that the above mode of viewing the action is sometimes of service. When actual transference of oxygen takes place, the composition alters as well as the charge of the ions, and the ionic conception of the process can only be applied to groups of substances which do not change in composition. Thus if we consider the action

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

to take place at such an extreme degree of dilution that all the electrolytes are fully dissociated, the equation becomes

$$10Fe^{\cdot\cdot} + 16H^{\cdot} + 2K^{\cdot} + 18SO_4'' + 2MnO_4' = 10Fe^{\cdot\cdot\cdot} + 2K^{\cdot} + 2Mn^{\cdot\cdot} + 18SO_4'' + 8H_2O,$$

or

$$5Fe^{\cdot\cdot} + 8H^{\cdot} + MnO_4' = 5Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot} + 4H_2O.$$

Here again we have the "oxidation" of diferrion to triferrion. The group $8H^{\cdot} + MnO_4'$ has lost six positive and one negative charge in becoming the group $Mn^{\cdot\cdot} + 4H_2O$, *i.e.* has lost on the whole five positive charges, and has therefore been "reduced" by this amount.

When a metal passes into solution as an ion, it gains one or more positive charges, and thus acts as a reducing agent. Thus in the action

$$Zn + H_2SO_4 = ZnSO_4 + H_2,$$

or

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2,$$

the zinc has been "oxidised" to the state of zincion, while the hydrogen has been "reduced" from the ionic condition to the state of free hydrogen. It is scarcely customary to apply the terms oxidation and reduction to the passage of hydrogen or a metal from the free state to the state of combination in an acid or salt, but the application is obviously justifiable. Free zinc and free hydrogen are undoubtedly reducing agents under proper conditions, while the ionic zinc or hydrogen, in zinc sulphate or sulphuric acid, can in no sense be looked on as reducing substances in dilute solution.

Many applications are made in the laboratory and in the operations of technical chemistry of the **diminution in solubility** suffered by a salt, acid, or base when there is added to the solution another electrolyte having one ion in common with the original electrolyte (p. 304). If we wish to prepare a pure specimen of sodium chloride, we make a strong solution of the impure salt, and pass hydrochloric acid gas into it, or add to it strong hydrochloric acid solution. The bulk of the sodium chloride is precipitated, and in a higher state of purity than the salt originally dissolved. Suppose the sodium chloride solution to be saturated, or nearly saturted. The addition of the highly ionised and extremely soluble hydrogen chloride greatly increases the amount of chloridion, and the quantity of natrion must consequently be diminished by separation of sodium chloride, in order that the product of the ionic concentrations shall be maintained nearly constant. Even if the solution is not nearly saturated to begin with, the addition of chloridion in sufficient quantity from the hydrogen chloride may bring the ionic product up to the constant value, and thus determine the precipitation of a portion of the sodium chloride.

If the above process of purification is to be effective, it is essential that the added substance should be considerably more soluble than the original substance, especially if the two are about equally ionised, as is the case with most salts, strong acids, and strong bases. If we attempted to precipitate a saturated solution of the soluble sodium chloride by the addition of the comparatively sparingly soluble barium chloride, we should find very little sodium chloride to be thrown down. This is because the ionic solubility product of barium chloride is much smaller than the corresponding product for sodium chloride, owing to the smaller solubility and also to some extent to the smaller degree of ionisation. The addition of barium chloride contributes therefore very little chloridion to the salt solution, and consequently the natrion is not greatly reduced in quantity by precipitation. The effect is all the smaller, because the great concentration of chloridion from the sodium chloride necessitates a very small amount of barion from the barium chloride, in order that the ionic solubility product may not be exceeded, *i.e.* the solubility of barium chloride in saturated salt solution is much lower than in water, so that very little of the salt passes into solution to displace the sodium chloride.

The sodium salts of aromatic sulphonic acids are often obtained pure from solution by the addition of sodium chloride or caustic soda. These salts are, as a rule, much less soluble than either sodium chloride or sodium hydroxide, and are therefore thrown out of solution in great part when natrion from strong brine or solid caustic soda is added.

Organic acids may often be readily precipitated from aqueous solution by the addition of hydrogen chloride, the hydrion being here the active substance. Even a comparatively soluble acid like sulphocamphylic acid may be thrown out of its aqueous solution almost entirely by saturating with gaseous hydrogen chloride.

The **salting out** of soap is one of the oldest applications of the principle under discussion. When a fat is saponified with a moderately dilute solution of caustic soda, the whole gradually passes into solution, and to produce a good soap it is necessary to separate the sodium salts of the fatty acids which constitute it from the glycerine formed during the saponification and the excess of caustic alkali that was employed. The separation can be easily effected by the addition of common salt or a strong brine. The sodium salts of the higher fatty acids are comparatively slightly soluble in water, and thus the addition of a soluble salt like sodium chloride throws them almost completely out of solution as a curdy mass. If the fat is saponified by a strong solution of caustic soda, there may be enough sodium in the form of natrion in this solution to throw the soap out as it is produced.

If a fat is saponified with potash instead of with soda, a solution of the potassium salts of the fatty acids is obtained. This solution, if strong enough, assumes on cooling a consistency expressed by the name of "soft" soap. Soft soaps are not in general salted out as such, but are used while still mixed with glycerine and excess of alkali. If we wish to obtain the potassium salts free from these admixtures, we may do so by adding to the solution a strong solution of potassium chloride. The potassium salts of the fatty acids then separate out as a somewhat gelatinous mass, containing a considerable quantity of water and still retaining the characteristics of a soft soap.

In the old process of manufacturing hard or soda soaps, the fat was saponified with potash, as that alkali was most readily obtainable from wood ashes. To the solution obtained on saponification sodium chloride was then added. The effect of this was to throw out, not a soft potash soap, but a hard soda soap, in virtue of double decomposition taking place between the sodium chloride and the potassium salts, whereby potassium chloride and the sodium salts were produced. These sodium salts were then thrown out by the excess of sodium chloride. The addition of sodium chloride to a solution of the potassium salts could not to any considerable extent throw them out as such from solution, for these substances have no common ion. If we consider that kalion, natrion, chloridion, and the anions of the fatty acids exist simultaneously in the solution, it is evident that these free ions may combine in pairs in two ways, the natrion which was originally associated with the chlorine having now the choice of combining with the anions of the fatty acids. This actually occurs, because the ionic solubility product of the sodium salts of these acids is much less than the corresponding magnitude for the potassium salts, the sodium salts being much less soluble. Under the given conditions the actual ionic product of the natrion and the anions exceeds the solubility value, and thus a portion of the sodium salts falls out of the solution, the potassium remaining behind mostly as potassium chloride.

If we consider the saturated aqueous solution of any salt, the addition of a non-electrolyte will in general affect the solubility to a much smaller extent than the addition of an electrolyte containing one ion in common with the substance originally dissolved. There will, of course, always be some effect, for the solvent is changed by the addition of the foreign substance, and any change in the nature of the solvent has its effect on the solubility of the substance considered. If the substance added is not itself a solvent for the original substance the general effect will be slight precipitation from the saturated aqueous solution. If we add a small quantity of an electrolyte which contains no ion in common with the original electrolyte dissolved, the effect is generally to diminish the actual value of the ionic product of the latter, and thus increase its solubility. This comes about because the addition of the second electrolyte produces double decomposition, so that some of the original ions go to form part of un-ionised molecules. If double salts or acid salts may be formed, of course the equilibrium is thereby greatly complicated, and it is impossible to tell without further information how the addition of the new substance may affect solubilities.

The addition of a salt of a weak acid to the acid itself is frequently carried out in the operations of analytical chemistry in order to reduce the strength of the acid, *i.e.* in order to reduce the concentration of hydrion (p. 294). If we take a solution of ferrous sulphate and add to it a large excess of sodium acetate, it is comparatively easy to precipitate the iron as ferrous sulphide by means of sulphuretted hydrogen. If no sodium acetate is added, the precipitation does not take place, a dark coloration at most being effected. The old explanation of this difference was that by the addition of sodium acetate to the ferrous sulphate solution the acid liberated by the hydrogen sulphide according to the equation

$$\mathrm{FeSO_4 + H_2S = FeS + H_2SO_4}$$

would at once act on the sodium acetate, producing sodium sulphate and acetic acid :—

$$\mathrm{H_2SO_4 + 2NaC_2H_3O_2 = 2HC_2H_3O_2 + Na_2SO_4}.$$

The ferrous sulphide was supposed to be easily soluble in sulphuric acid, but insoluble in the acetic acid. This explanation is insufficient, however, for if we take ferrous sulphate and add to it no more sodium acetate than is necessary for double decomposition, the precipitation takes place to a slight extent only; and if we now add acetic acid, the precipitate originally formed dissolves up. Acetic acid, therefore, in these circumstances dissolves ferrous sulphide. If, however, we now add more sodium acetate to the same solution, the ferrous sulphide is reprecipitated, The reprecipitation is consequently due to the reduction of the degree of ionisation of the acetic acid by the addition of sodium acetate, and not to double decomposition alone, as was formerly supposed.

Ammonium chloride acts in a similar way on a solution of ammonium hydroxide, greatly reducing the ionisation and therefore the strength of the base. This fact is taken advantage of in the analytical separation of iron, chromium, and aluminium from zinc, manganese, magnesium, etc. The trihydroxides $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ are extremely weak bases, whilst the dihydroxides $Zn(OH)_2$, $Mn(OH)_2$, $Mg(OH)_2$, etc., are comparatively strong. If ammonia solution is added to any salt of these metals, the hydroxides are in each case precipitated, although the precipitation may sometimes only be partial. If, however, excess of ammonium chloride (or other ammonium salt) is present at the same time, the strength of the ammonium hydroxide as a base is so greatly reduced that although it is still capable of completely precipitating the very feeble trihydroxides, the salts of the stronger dihydroxides remain undecomposed. It must be borne in mind, however, that this is not the only mode of action of ammonium chloride, for it has also the property of favouring the formation of complex ammoniacal ions, and thus preventing precipitations which would otherwise occur on the addition of ammonium hydroxide.

It was stated on page 304 that the addition of any highly ionised electrolyte, say sodium chloride, would have practically the same effect on the ionisation of acetic acid as the addition of a highly ionised acetate. Whilst this is true, it must not be supposed that the addition of sodium chloride to a solution of a ferrous salt, which has enough acetic acid in it just to prevent precipitation by sulphuretted hydrogen, will have the same ultimate effect as an equivalent quantity of sodium acetate. The degree of ionisation of the acetic acid is indeed diminished in the same ratio as before, but hydrochloric acid is simultaneously formed by double decomposition, and as this is highly ionised, the amount of hydrion in the solution, after the addition of the sodium chloride, is rather greater than before, so that there is an actual increase in the total active acidity of the solution. Precipitation of the sulphide therefore does not occur.

In analytical chemistry it is a common practice to wash a precipitate with the fluid precipitant, especially in quantitative operations. The theoretical basis of this is, of course, that the sparingly soluble precipitate has an ion in common with the precipitant, so that it is less soluble in the solution of the latter than in pure water. If other circumstances permit, therefore, it is advisable to wash with a diluted solution of the precipitant rather than with water alone.

When solutions of two electrolytes are brought together, and it is theoretically possible by **double decomposition** to obtain a substance which is insoluble, then, in general, the double decomposition actually takes place. Thus when any sulphate is added to any barium salt, double decomposition invariably takes place, barium sulphate being deposited. From the point of view of the dissociation theory the explanation is at once apparent. The solubility product of the ions of barium sulphate is very small, and as soon, therefore, as barion and sulphanion are brought together in quantity to exceed this solubility limit, barium sulphate falls out. Now all barium salts yield ions freely in solution, and all soluble sulphates behave in like manner. Precipitation of barium sulphate therefore invariably occurs, unless, indeed, the solutions are so extremely dilute that the solubility product is not reached.

Exceptions to this rule are only encountered when there is the possibility of the existence or formation of complex ions, or when an acid or a base is one of the pair of substances. If we add a solution of silver sodium thiosulphate to a solution of sodium chloride, there is the theoretical possibility of the action

$$NaAgS_2O_3 + NaCl = Na_2S_2O_3 + AgCl,$$

but this action does not occur because there is so little argention given off by the sodium silver thiosulphate that the solubility product of silver chloride is not exceeded, practically all the silver in solution being in the form of the complex ion AgS_2O_3'. For the same reason, where cyanides or ammonia are present, there is frequently no precipitation where such might be expected by double decomposition.

If sulphuric acid itself is added to a barium salt, barium sulphate is precipitated as readily as if any other sulphate had been employed. It is different in the case of tartrates. If calcium chloride is added to sodium tartrate solution, a precipitate of calcium tartrate is formed. Should tartaric acid, however, be used instead of sodium tartrate, no precipitate is produced. The reason for this difference in behaviour is not far to seek. When sodium tartrate is employed, tartranion is abundantly present in the solution, the sodium salt being highly ionised, and the solubility product of calcium tartrate is far surpassed. When hydrogen tartrate is employed, we have comparatively little tartranion, for tartaric acid is not highly ionised. The ionic product of calcion and tartranion therefore falls short of the solubility product for calcium tartrate, and there is no precipitation. For the same reason, some metallic solutions are easily precipitated by an alkaline sulphide and not at all by sulphuretted hydrogen. In general, it may be said that when all the substances concerned are highly ionised in solution, and complex ions are excluded, the precipitation occurs when there is the theoretical possibility of it; while if one of the reacting substances is feebly ionised, the precipitation may only take place to a limited extent or not at all. The precipitation may be almost perfect, even when a feebly ionised substance is concerned, if the solubility product is vanishingly small, *i.e.* if the substance is scarcely at all soluble. This is the case, for example, with silver sulphide, so that sulphuretted hydrogen, although very sparingly dissociated, easily precipitates this substance from a solution of silver nitrate.

In intimate connection with the formation of precipitates on mixing electrolytic solutions, there is the **solubility of precipitates** in solutions of electrolytes. It must be borne in mind that the so-called **insoluble substances** are merely sparingly soluble substances, and that the presence of electrolytes in the solvent water only alters the solubility by affecting the concentration of the ions which by their union might form the precipitate. Kohlrausch, from measurements of the electric conductivity of the saturated solutions, determined the solubility of some of the commoner "insoluble" substances, and his results are given in the following table, the solubility being expressed in parts per million, *i.e.* milligrams per litre, at 18°:—

	Solubility.
Silver chloride	1·7
Silver bromide	0·107
Silver iodide	0·0035
Mercurous chloride	3·1[1]
Mercuric iodide	0·5
Calcium fluoride	14
Barium sulphate	2·6
Strontium sulphate	107
Calcium sulphate	2070
Lead sulphate	46
Barium oxalate	74
Strontium oxalate	45
Calcium oxalate	5·9
Barium carbonate	24
Strontium carbonate	11
Calcium carbonate	13
Lead carbonate	3
Silver chromate	28
Barium chromate	3·8
Lead chromate	0·2
Magnesium hydroxide	9

The solubility product of silver chloride in water is very small, corresponding to the very slight solubility of the salt. If we have the solid salt in presence of water, and add nitric acid to the solution, we disturb the equilibrium very little. The dissolved silver chloride is almost entirely ionised, and the silver nitrate and hydrogen chloride, which might be formed from it by the action of the nitric acid, would

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[1] This value is probably too high owing to hydrolytic dissociation. Another method gives 1·2 mg. per litre.

be likewise almost entirely ionised. The addition of nitric acid, therefore, does not appreciably affect the argention and chloridion in the solution, and therefore is without influence on the solubility of the silver chloride. Consider, on the other hand, the effect of the addition of hydrochloric acid on the solubility of calcium tartrate. The calcium tartrate in the aqueous solution is highly ionised, but the addition of hydrochloric acid at once liberates tartaric acid, which is only slightly ionised in the presence of the highly ionised calcium chloride, etc. The concentration of the tartranion is therefore much reduced, and the ionic product falls below the solubility product, *i.e.* the solution becomes unsaturated with respect to calcium tartrate. More of this salt, therefore, dissolves up, and the process of solution goes on until the ionic product once more reaches the solubility product. It is evident from these considerations that a given quantity of hydrochloric acid will not dissolve an unlimited amount of calcium tartrate. If, however, we take a sufficient excess of acid, a given amount of calcium tartrate can always be entirely dissolved.

In general we may say that strong acids in aqueous solution will not appreciably dissolve salts of equally strong acids, or even of acids nearly as strong, for any double decomposition that takes place in solution does not then appreciably affect the concentration of the ions which regulate the solubility. On the other hand, strong acids will in general easily dissolve insoluble salts of weak acids, for then the weak acid is liberated, which being slightly ionised, reduces the ionic product, with the result that the solid dissolves to restore the solution equilibrium. Sometimes, when the solubility product of the salt of the weak acid is excessively small, as it is in the case of silver sulphide, even an equivalent of a strong acid like nitric acid will not dissolve up an appreciable quantity, for the solubility product is soon reached when silver nitrate and hydrogen sulphide begin to accumulate in the solution. Weak acids, as we might expect, do not dissolve the "insoluble" salts of stronger acids. Whilst calcium oxalate is freely soluble in hydrochloric acid, it is almost insoluble in acetic acid. In the first case the concentration of oxalanion in the aqueous solution is diminished by the addition of the hydrochloric acid, whereas in the second it is not sensibly affected. Calcium oxalate, therefore, must dissolve in hydrochloric acid solution to restore the solubility product. When acetic acid solution is added, the ionic product scarcely departs from the solubility value, so that no calcium oxalate need pass into solution.

As has already been indicated, the number of ions of a given kind in a solution may be greatly altered by the formation of **complex ions.** If to a saturated solution of silver chloride in contact with the solid there is added a quantity of potassium cyanide, the free cyanidion unites with a portion of the argention to form the complex ion AgC_2N_2'. The ionic product of silver and chloride ions, therefore, falls below the equilibrium value, *i.e.* below the solubility product, with the result that silver chloride must dissolve in order to restore equilibrium. If the quantity of cyanide added is small, the silver chloride need not dissolve wholly, but if a sufficient excess of cyanide is employed, the solution of the silver chloride will be complete. Should the solubility product be extremely small, as is the case with silver sulphide, potassium cyanide has only a slight solvent action, and the silver sulphide dissolved is easily reprecipitated on addition of potassium sulphide. The solvent action of sodium thiosulphate or ammonia on "insoluble" silver compounds is similar in origin, the increased solubility being due to the formation of complex ions with corresponding disappearance of argention. It will be noticed that the solubility of silver chloride, bromide, and iodide in water (given in the table on p. 318), is the same as the order of their solubility in ammonia, as an application of the above theory would lead us to expect.

The theory of electrolytic dissociation affords some assistance in understanding the action of the **indicators** used in acidimetry and alkalimetry. The indicators are themselves acid or alkaline in nature, but are necessarily very feeble compared with the acids or alkalies whose presence they indicate. Their action depends on a change of colour which they undergo on neutralisation. Phenol-phthalein, for example, is a substance of very weak acid character, being in aqueous solution almost entirely un-ionised and colourless. If, however, we add a strong alkali such as sodium hydroxide to it, the sodium salt is formed and imparts an intense pink colour to the solution. All the soluble salts of phenol-phthalein are thus coloured,[1] and the colour is of the same intensity in equivalent solutions if these solutions are very dilute, so that we are justified in concluding in terms of the dissociation hypothesis, that the colour is due to the anion from phenol-phthalein, as this is the substance common to all dilute solutions of salts of phenol-phthalein. The undissociated substance has no colour. Let us consider what happens as we titrate a solution of an acid, using phenol-phthalein as an indicator. In presence of the acid, the indicator, being a very feeble acid, is even less ionised than it would be in pure water, and consequently no colour is perceptible. As soon, however, as the acid originally present in the solution is neutralised and a drop of alkali in excess is added, the corresponding alkaline salt of phenol-phthalein is formed, *i.e.* the anion from the phenol-phthalein is produced, and the solution at once assumes the pink tint characteristic of it.

In order to have a sharp indication of the neutral point, it is necessary first that the acid to be titrated should be considerably

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[1] Phenol-phthalein is an example of a "pseudo-acid," *i.e.* an acid the salts formed from which have not the same chemical constitution as the acid itself. Thus when soda is added to a solution of phenol-phthalein the pink salt obtained is not, strictly speaking, a salt of the colourless phenol-phthalein at all, but a salt of an isomeric acid. This circumstance, however, in no way affects the explanation given in the text.

stronger than phenol-phthalein itself, and that the alkali should be a strong alkali. If the acid to be titrated is so feeble that its salts even with strong bases suffer hydrolytic dissociation in aqueous solution, it is obvious that phenol-phthalein is incapable of sharply indicating the neutral point, for long before sufficient alkali for complete neutralisation has been added, the salt formed will begin to split up into free acid and free base, part of which will neutralise the phenol-phthalein, and thus produce a faint pink colour which will gradually deepen in intensity as the addition of alkali progresses. Carbolic acid, and other phenols, therefore, cannot be titrated with alkali and phenol-phthalein, on account of the hydrolysis which their salts suffer (cp. p. 292). Polybasic acids, too, very frequently form normal salts which are partially hydrolysed in aqueous solution, and with them also no definite indication of the neutral point can be obtained. Thus the ordinary sodium phosphate, *i.e.* di-sodium hydrogen phosphate, although formally an acid salt, has an alkaline reaction to phenol-phthalein on account of its slight hydrolysis. Phenol-phthalein roughly indicates neutrality in the case of carbonic acid when sodium hydrogen carbonate exists in the solution, and gives a strong pink colour with the normal sodium carbonate. Since carbonic acid thus behaves as an acid to phenol-phthalein, *i.e.* since carbonic acid is a stronger acid than phenol-phthalein, it must be excluded from the alkali with which acids are titrated. This is best done by using baryta as the alkali, and keeping it protected from the carbonic acid of the atmosphere. Any carbonic acid which may have been originally present settles down as barium carbonate, and the clear liquid is therefore free from this source of disturbance.

If the base employed is not a strong base, the indication in this case also is uncertain owing to hydrolysis. Thus ammonia should never be used in titrations with phenol-phthalein as indicator, for the ammonium salt of phenol-phthalein, being the product of the union of a weak base with a very weak acid, is hydrolysed in aqueous solution, and thus the neutrality point is not sharply indicated, even though the salt of ammonia with the acid originally in the solution undergoes no hydrolysis. Looked at from another point of view, the ammonium salt formed by the neutralisation of the acid so diminishes the strength of a small amount of ammonia added in excess that the ammonia is unable to ionise the phenol-phthalein sufficiently to give the deep pink colour requisite for a sharp indication, and thus more ammonia must be added, the colour gradually deepening in intensity.

Phenol-phthalein then forms a good indicator when weak acids are titrated with strong bases.

The application of the dissociation theory to explain the action of other indicators is not so simple as in the case of phenol-phthalein, because these indicators are usually amphoteric, *i.e.* acidic or basic according to circumstances, and thus form two series of salts, one series with strong acids, and another with strong bases. There may, therefore, be more than one kind of coloured ion in solution, besides, perhaps, coloured un-ionised indicator, so that the interpretation of the actual colours of the different solutions on the dissociation theory is sometimes difficult.

Many applications of the electrolytic dissociation theory to ordinary laboratory work will be found in

W. Ostwald, *The Scientific Foundations of Analytical Chemistry.*

CHAPTER XXVII

ELECTROMOTIVE FORCE

In the chapter on the kinetic theory (p. 102) it was indicated that the equilibrium of a solid and its saturated solution might be conceived as the balancing of two opposed forces—the solution tension or tendency of the solid to pass into the dissolved state on the one hand, and the osmotic pressure exerted by the dissolved substance on the other. A similar conception may be applied to the equilibrium existing between a metal such as zinc, and a solution containing the same metal as a positively charged ion, *e.g.* a solution of zinc sulphate. To the metallic zinc may be attributed a certain electrolytic solution-tension, or tendency to pass into solution in the ionic state. This tendency is balanced by the osmotic pressure of the positively-charged zinc, or zincion, in the solution, and a certain osmotic pressure of zincion will exist at which metallic zinc will neither enter the solution nor be deposited from it. This definite osmotic pressure which just balances the solution tension of the zinc is spoken of as the **electrolytic solution pressure** of zinc.

It is obvious, however, that there must be a profound difference between this equilibrium of a metal and its electrolytic solution, and the equilibrium between a solid salt and its solution. In the latter case, if the solubility value of the osmotic pressure is not reached, salt is seen to dissolve, and if the solubility value is exceeded, salt is seen to be deposited. Now in the case of zinc and zinc sulphate, the metal may be brought into contact with an aqueous solution of the salt of any concentration whatever, *i.e.* of any osmotic pressure of zincion, and yet there is neither perceptible passage of zinc into solution, nor deposition of zinc from solution. The reason is not far to seek. When the salt passes into solution, positively charged ions are produced, but at the same time an equivalent quantity of negatively charged ions are also formed, and pass into solution with them. When metallic zinc, on the other hand, passes into solution as positively charged zincion, no negative ion is formed at the same time, so that the solution becomes electrostatically charged with positive electricity, and the metallic zinc in consequence negatively charged. The electrical charges prevent the uniform diffusion throughout the solution of the zincion produced from the metallic zinc, and there is formed at the surface of contact of the metal and the solution an electrical double layer (negative on the metal, positive in the solution) resembling a charged condenser. The electrical stress resulting from this double layer serves to compensate the difference between the actual osmotic pressure of the zincion and the electrolytic solution-pressure of the zinc.

Should the osmotic pressure of the metallion exceed the electrolytic solution pressure of the metal, as is the case, for example, with copper in a solution of copper sulphate, metallic copper will be deposited on the surface of the electrode. The electrode therefore becomes positively charged, and the solution negatively charged, the negative charge being carried by the sulphanion which forms one side of the electrical double layer at the surface of separation of metal and solution. Here again we have an electrical stress compensating the difference between the actual osmotic pressure and the electrolytic solution pressure.

When a metal then is brought into contact with one of its salts, an electromotive force is set up at the surface of contact, which, when the ionic osmotic pressure is less than the solution pressure, would cause a current (positive electricity) to flow from metal to solution, and when the ionic osmotic pressure exceeds the solution pressure, would cause a positive current to flow from solution to metal, provided the conditions are such as to permit the establishment of a current in the system. Since the electrical double layer is only of molecular thickness, the solution or deposition of an extremely small quantity of metal is sufficient to establish equilibrium, so that no noticeable chemical change occurs when a metal is immersed in an aqueous solution of one of its salts, unless indeed the metal, like sodium, decomposes water.

The magnitudes representing the electrolytic solution pressures of metals are generally inconveniently large or inconveniently small. Thus, for the calculated solution pressure of zinc we have a magnitude of the order of 10^{18} atmospheres, and for the solution pressure of silver 10^{-15} atmospheres. Instead of using them, therefore, we shall deal with the differences of potential between metals and solutions containing the corresponding metallions, *i.e.* with the electromotive force (due to the difference between the solution pressure of the metal and the actual osmotic pressure of the metallion) which resides at the surface of contact between metal and solution. These **electrode potentials** are susceptible of direct measurement and are of great practical importance, as the electromotive force of all galvanic combinations is principally due to them. In **galvanic cells** two metallic conductors are immersed in one or more electrolytic conductors, and it is at the surface of separation of the metallic and electrolytic conductors that the chief electromotive force resides. The other sources of electromotive force are at the junction of the two metallic conductors, and that at the junction of the electrolytic conductors. The electromotive force at the metallic junction does not, however, exceed a few millivolts for most metals, and that at the junction of the electrolytes is also small, if salt solutions alone are used, for these give rise to ions which do not differ greatly in velocity, and it is in general to difference in the speeds of the ions that the electromotive force at the contact of two electrolytic liquids is due (p. 327). These sources of electromotive force then may be frequently neglected for practical purposes, and the metal-solution contact regarded as the sole seat of the electromotive force of the galvanic combination.

With regard to the practical determination of electrode-potentials, it is evident that we cannot construct a system connected with a measuring instrument, whether galvanometer or electrometer, with less than two metallic electrodes in contact with the solution or solutions. In actual experiment we therefore of necessity deal with two electrode-potentials, and measure their algebraic difference.

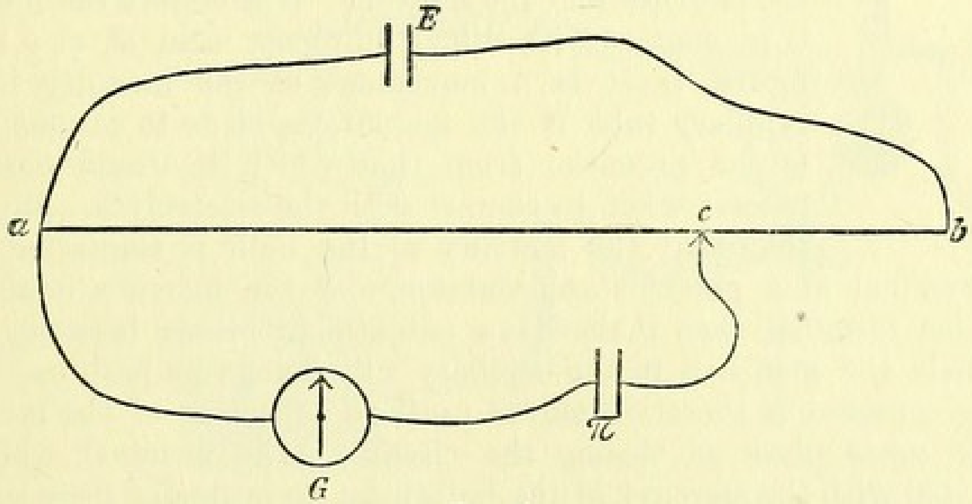

Fig. 46.

The **method of measurement** of electromotive force generally adopted in physico-chemical laboratories is as follows:—The wire *ab* (Fig. 46) is stretched along a divided scale and provided with a sliding contact *c*. The two ends of the wire are connected with the opposite poles of a battery of constant electromotive force (say one or two accumulators) greater than the electromotive force to be measured. The combination π whose electromotive force is to be determined is connected with the sliding contact *c* on the one hand, and on the other with one end of the measuring wire through the galvanometer (or electrometer) *G*. The contact is moved along the wire until the measuring instrument indicates zero. Then a cell of known electromotive force, π_0, is substituted for the unknown combination, and the sliding contact again moved until zero is indicated. The lengths of the wire read off are now proportional to the electromotive forces of the unknown and known cells, *i.e.* $ac : ac_0 = \pi : \pi_0$. The substitution of the two cells is of course carried out by means of an appropriate key, which breaks contact with π while making it with π_0.

As cell of known electromotive force the Clark element (E. M. F. = 1·433 volt at 15°), was formerly almost exclusively employed, but this has been practically superseded by the Weston cell (E. M. F. = 1·0189 volt at all ordinary temperatures), and the cadmium cell (E. M. F. = 1·0186 + 0·00004 (20° − t°) volt between 15° and 20°), which are superior to it by having a much smaller temperature coefficient.

The electrometer most frequently employed in physico-chemical laboratories is the form of Lippmann's capillary electrometer shown in Fig. 47. The surface tension of a liquid metal such as mercury in contact with an electrolytic solution depends on the difference of potential between the mercury and the solution. If therefore the mercury is in contact with dilute sulphuric acid as at *a* in the figure, there is a movement of the mercury in the capillary tube if the mercury is made to assume a different potential from that which it would normally possess when in contact with the electrolyte. Suppose then that the mercury in the bulb is connected with one terminal of a galvanic combination, and the mercury in *ab* with the other terminal, then if there is a potential difference between these terminals the meniscus in the capillary will change its position. The sliding contact *c* is therefore moved until no deflection of the mercury surface takes place on closing the circuit. The terminal which is connected with the mercury of the bulb must be protected from contact with the sulphuric acid by being sealed within a glass tube throughout the whole length immersed in the acid.

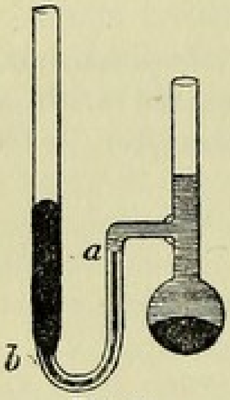

FIG. 47.

By suitably combining the various electrodes and electrolytic solutions, and measuring the electromotive force of the combinations, it is possible to obtain the relative values of electrode potentials such as those given in the table on p. 329. The absolute values of the electrode potentials are somewhat uncertain owing to the difficulty of obtaining an electrode which has the same potential as the solution in which it is immersed. It is generally assumed that this condition is fulfilled with the mercury dropping electrode. Here the mercury issues from a jet in a fine stream, which breaks up into drops just after it comes into contact with a solution of sulphuric acid. The charge assumed by the mercury is carried off by the rapid succession of drops, so that the still unbroken stream of mercury may be assumed to have the same potential as the solution with which it is in contact. If then we combine this dropping electrode (of zero electrode potential) with another metallic electrode immersed in the same solution, the electromotive force of the combination is equal to the difference of potential of the second metal and the acid. Knowing now this difference of potential, we may proceed to combine this second electrode with other electrodes and obtain the electrode potentials of these.

The calomel electrode is largely made use of as a standard **normal electrode** of known potential difference with which other electrodes may be combined for measurement. It is constructed as shown in Fig. 48. The bottom of the bottle is covered by a layer of mercury above which is placed a layer of calomel and then a normal solution of potassium chloride up to the stopper. Metallic connection with the mercury is made by a platinum wire sealed through the end of a glass tube, which contains a drop of mercury and a conducting wire after the manner of the Arrhenius electrolytic cell (p. 226). The second tube which passes through the stopper is bent at right angles and connected by a rubber tube and clip with another piece of glass tubing bent so as to be conveniently immersed in liquids. All these tubes are completely filled with the potassium chloride solution. The potential of this calomel electrode is generally accepted as – 0·560 volt.

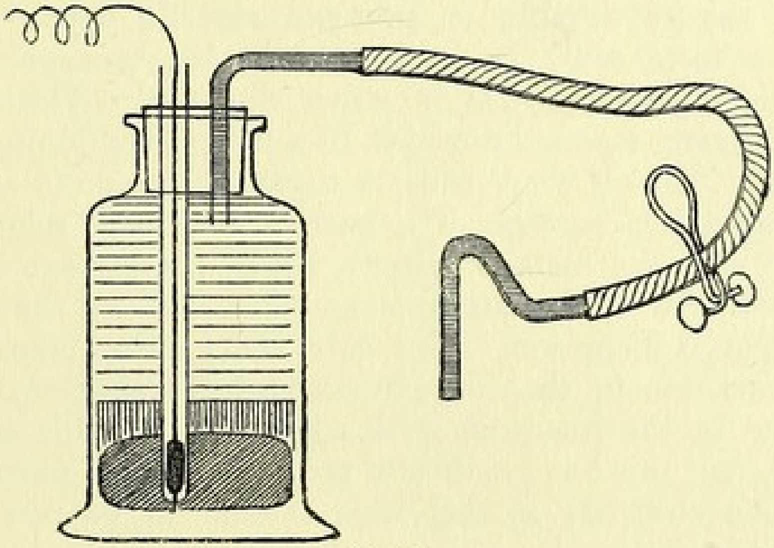

FIG. 48.

Its chief advantage lies in the fact that it can be combined with very many other metallic electrodes in neutral solutions of their salts. The speeds of the ions of neutral salts do not differ very much from each other, and in consequence the electromotive force developed at the junction of solutions of different salts is comparatively small. On the other hand, if the liquids are acid or alkaline they contain hydrion or hydroxidion, both of which move at much greater rates than the "neutral" ions (cp. p. 222), and thus develop considerable electromotive forces when brought into contact with other solutions.

The reason why there is an electromotive force at the junction of solutions with ions of different velocities, or even of different solutions of the same substance whose anion and kation move at different rates, was pointed out by Nernst, to whom the application of the osmotic and ionisation theories to electromotive force is due. Consider two solutions of hydrochloric acid of different concentrations in contact with each other. The relative speeds of migration of the ions may be taken as their relative rates of diffusion in solution (cp. p. 223). The hydrion of the stronger solution will therefore tend to diffuse into the weaker solution at a greater rate than the chloridion. But if the diffusion actually takes place, the dilute solution will become positively charged from the arrival of hydrion, and the concentrated solution will become negatively charged from the excess of chloridion remaining. There will therefore be set up a difference of potential between the two solutions, which would not exist if anion and kation had the same rate of migration, for then the ionised substance would diffuse as a whole without disturbance of electric neutrality.

In order that an electrode may be used as a normal electrode, it must be of the **reversible** or **non-polarisable** type; that is, its electromotive force must be unaffected by the passage of a slight current through the electrode in either direction. This condition is fulfilled with many metals immersed in solutions containing the corresponding ion. Thus if we consider a copper electrode in a solution of copper sulphate, the passage of a current from the solution to the metal merely deposits metallic copper, whilst the passage of a current from the metal to the solution is accompanied by the solution of metallic copper as dicuprion. The only change that takes place then is a slight variation in the concentration of the electrolytic solution (in particular of the dicuprion with which the metallic copper is in equilibrium), and this has practically no effect on the potential of the electrode. An electrode of this kind is said to be reversible with regard to the kation.

The calomel electrode, on the other hand, is reversible with regard to the anion, *i.e.* the only effect caused by the passage of a current one way or other is to make a slight variation in the concentration due in the first instance to the chloridion. Thus if a current passes from solution to metal, metallic mercury is deposited from the mercurous chloride, the chloride radical originally united with the metal passing into solution as chloridion to neutralise the kation brought by the positive current. Similarly if the current passes from metal to solution, metallic mercury is converted into mercurous chloride, the necessary chloride radical being derived from the chloridion of the solution. The following schemes may serve to elucidate the process :—

FIRST CASE

1. Hg Hg | HgCl HgCl | K· Cl′ K· Cl′ K· Cl′ . . . ← K·
2. Hg Hg Hg | Cl Hg | Cl′ K· Cl′ K· Cl′ K· Cl′ K· . . .

SECOND CASE

1. Hg Hg | ClHg ClHg | Cl′ K· Cl′ K· Cl′ K· → . . .
2. Hg | HgCl HgCl HgCl | K· Cl′ K· Cl′ . . . K·

From measurements of the electromotive force of suitable galvanic combinations the following table of electrode potentials has been constructed. The numerical values are the potential differences in volts between the metals and normal solutions of the corresponding metallion. In the case of metals which decompose water at the ordinary temperature the direct measurement is of course impossible, but for the sake of completeness numbers for these derived indirectly by calculation from thermochemical data have been given within brackets. The calculation is somewhat uncertain, but the numbers probably give at least the correct relative positions of these metals in the table. The values for magnesium and aluminium are also very doubtful.

Electrode Potential in Volts for Normal Solutions of Kations

Potassium	$K^{\cdot}$	(+2·9)
Sodium	$Na^{\cdot}$	(+2·5)
Barium	$Ba^{\cdot\cdot}$	(+2·4)
Strontium	$Sr^{\cdot\cdot}$	(+2·3)
Calcium	$Ca^{\cdot\cdot}$	(+1·9)
Magnesium	$Mg^{\cdot\cdot}$	+1·5 ?
Aluminium	$Al^{\cdot\cdot\cdot}$	+1·0 ?
Manganese	$Mn^{\cdot\cdot}$	+0·80
Zinc	$Zn^{\cdot\cdot}$	+0·50
Cadmium	$Cd^{\cdot\cdot}$	+0·15
Iron	$Fe^{\cdot\cdot}$	+0·07
Thallium	$Tl^{\cdot}$	+0·045
Cobalt	$Co^{\cdot\cdot}$	−0·045
Nickel	$Ni^{\cdot\cdot}$	−0·05
Tin	$Sn^{\cdot\cdot}$	−0·1 ?
Lead	$Pb^{\cdot\cdot}$	−0·12
Hydrogen	$H^{\cdot}$	−0·27
Copper	$Cu^{\cdot\cdot}$	−0·60
Arsenic	$As^{\cdot\cdot\cdot}$	−0·6 ?
Bismuth	$Bi^{\cdot\cdot\cdot}$	−0·7 ?
Antimony	$Sb^{\cdot\cdot\cdot}$	−0·8 ?
Mercury[1]	$Hg^{\cdot}$	−1·02
Silver	$Ag^{\cdot}$	−1·04
Palladium	$Pd^{\cdot\cdot}$	−1·1 ?
Platinum	$Pt^{\cdot\cdot\cdot\cdot}$	−1·2 ?
Gold	$Au^{\cdot\cdot\cdot}$	−1·4 ?

The application of the preceding table may be seen from the following instance. If a rod of zinc is immersed in a normal solution of zincion, an electromotive force of 0·50 volts is produced at the surface of contact which tends to drive a current from metal to solution. Similarly if a rod of copper is immersed in a normal solution of dicuprion, the potential difference produced tends to drive a current from metal to solution with a force of −0·60 volts, or, in other words, tends to drive a current from solution to metal with a force of +0·60 volts. If now we combine the two systems into a closed circuit by connecting the metal rods by a wire and bringing the solutions into electrical contact through the walls of a porous pot,

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[1] The kation of the mercurous salts is probably the dyad $Hg_2^{\cdot\cdot}$ and not the monad $Hg^{\cdot}$.

which gives free passage to the ions but prevents mechanical mixing of the two solutions, a current will pass from metal to solution in the zinc compartment, from solution to metal in the copper compartment, and back from copper to zinc by the metallic connecting wire. The electromotive force in this circuit due to the contact of metals and electrolytic solutions is $+0{\cdot}50+0{\cdot}60=1{\cdot}10$ volts. But the passage of the current does not alter the general nature of the system, the only changes that take place being deposition of copper, solution of zinc, and corresponding changes in the concentration of the electrolytes. The system will therefore continue to afford a current at a practically constant electromotive force, and may be used as a galvanic cell. It is in fact the ordinary Daniell cell, the electromotive force of which by direct measurement is 1·09 volt, in agreement with the foregoing value.

If a cell is constructed with both metallic poles of the same metal, and each immersed in a solution of the same salt of the same concentration, say zinc poles in zinc sulphate solution, the electromotive force at the two surfaces of contact will be of the same magnitude but oppositely directed, so that no current will pass through the circuit. Since, however, the electromotive force at the contact of metal and solution depends on the ionic concentration of the solution, if the system consists of two zinc rods immersed in zinc sulphate solutions of different concentrations, the oppositely directed electromotive forces will not exactly neutralise each other, and there will be a small differential electromotive force in the circuit due to the difference of concentration of the two zinc sulphate solutions. Such a cell is termed a **concentration cell**, and the electromotive force in the case of an electrolyte with univalent ions of equal velocities of migration is found to be 0·057 to 0·058 volts when one solution has ten times the ionic concentration of the other, the direction of the current being from the dilute to the concentrated solution, and the transference of the dissolved substance being such that the concentrations tend to become equal. The electrode potential between a monad metal and the normal solution of the corresponding metallion is thus 0·058 volt smaller than the electrode potential between the same metal and a decinormal solution of the metallion. The table of electrode potentials can therefore be easily converted from normal solutions to solutions of any other concentration. For kations of greater valency the increase of electrode-potential for a tenfold increase of dilution is $\frac{0{\cdot}058}{n}$, where n is the electrovalency. Thus the electrode-potential of zinc in a decinormal solution of zincion is

$$0{\cdot}50+\frac{0{\cdot}058}{2}=0{\cdot}53 \text{ volt.}$$

Since the electrode potentials of two metals of the same electrovalency, say zinc and copper, are affected to the same extent by change in concentration of the solutions with which they are in contact, it follows that the electromotive force of a Daniell cell, so far as it is derived from the contact of metal with solution, remains unchanged if the solutions of copper and zinc sulphates are of the same ionic concentration, no matter how that concentration may vary.

The arrangement of the metals in the table of electrode potentials is usually called the **electro-chemical list** of the metals, and gives, with some exceptions, the order in which they replace one another from solutions of their salts. Thus magnesium turns out zinc from a solution of a zinc salt, zinc expels copper from a solution of a copper salt, copper displaces silver, and silver displaces gold.

The position of hydrogen in the table should be noted. All the metals which precede it are capable of displacing hydrogen from a hydrogen salt, say hydrochloric acid, whilst those which follow it in the list can only displace the hydrogen from an acid under exceptional circumstances. Occasionally anomalies present themselves. Thus aluminium readily dissolves in dilute hydrochloric acid, but is practically unaffected by dilute oxygen acids such as sulphuric and nitric acids, even at the boiling point. A similar anomaly is met with in the action of aluminium on solutions of copper salts. Copper nitrate and copper sulphate may be brought into contact with aluminium without deposition of copper occurring, but if copper chloride is used, or if sodium chloride is added to the sulphate or nitrate solutions, precipitation of copper immediately follows. This anomalous behaviour is probably connected with the circumstance that metallic aluminium under many conditions becomes readily coated with a protective film of oxide.

When a metal which precedes hydrogen in the electro-chemical list is brought into contact with the aqueous solution of a salt of another metal which also precedes hydrogen, two things may evidently occur. Take, for example, magnesium in a solution of zinc sulphate. Magnesium, even at the ordinary temperature, decomposes water with evolution of hydrogen. When brought into a solution of zinc sulphate therefore it may displace hydrogen from the water; but it can also displace zinc from the zinc sulphate. As a matter of fact both of these actions proceed simultaneously. Hydrogen is slowly evolved from the beginning, and zinc is seen to be deposited on the magnesium. As the action progresses the evolution of hydrogen becomes much brisker. This is apparently due to the zinc and magnesium forming a couple (like the zinc-copper couple) which is much more active in decomposing water than either metal separately (cp. p. 244).

Since the electrode potentials in the table are applicable to metals in normal solutions of the corresponding metallion, and become greater as the concentration of the metallion diminishes, it is evident that for a given difference in the table of electrode potentials the most favourable conditions for a metal A displacing a metal B from solutions of its salts are that the concentration of the metallion A should be as small as possible and that the concentration of the metallion B should be as great as possible. Magnesium, for example, decomposes water very slowly, the concentration of the hydrion in water being extremely small. If now the water is acidified, the action becomes much more vigorous owing to the increased concentration of the hydrion. The magnesium hydroxide formed by the action of magnesium on water is very sparingly soluble, yet owing to its comparatively great ionisation it not only furnishes magnesion in the solution but also greatly diminishes the concentration of hydrion by increasing the concentration of hydroxidion, for the product of the concentration of hydrion and hydroxidion must remain constant on account of the constant active mass of the un-ionised water. By the addition of ammonium chloride to the water it is possible to counteract both of these retarding influences. In the first place the highly ionised magnesium hydroxide is replaced by ammonium hydroxide, which in presence of the large excess of ammonium chloride is scarcely ionised at all. Thus the concentration of hydroxidion is kept down, and the concentration of hydrion in a proportionate degree increased. In the second place a complex ammoniacal ion containing magnesium is produced, and the concentration of magnesion thus lowered. Magnesium accordingly gives a brisk evolution of hydrogen with a moderately concentrated solution of ammonium chloride.

Both zinc and aluminium evolve hydrogen from solutions of the caustic alkalies. Here the concentration of hydrion must be extremely small, but this is more than compensated for by the practical absence of zincion and aluminion from the solution, the dissolved metals passing into the anions of the zincate and aluminate which are produced. Aluminium will not expel zinc from an aqueous solution of zinc chloride, but if caustic soda is added to the solution of zinc chloride till the precipitate of hydroxide at first produced dissolves as sodium zincate, aluminium will then freely precipitate metallic zinc from the solution. This we must attribute to the circumstance that the concentration of aluminion in a solution of sodium aluminate is much smaller than the concentration of the zincion in a solution of sodium zincate, though both are vanishingly small.

By removing a metallion from solution as a complex ion, it is possible to invert the position of two elements widely apart in the electro-chemical list. Thus metallic copper (in contact with platinum) will readily displace hydrogen from a solution of potassium cyanide, on account of the copper which passes into solution becoming a constituent of a complex cuprocyanidion (cp. p. 310), so that practically no cuprion exists in the solution at all. Similarly, and for the same reason, it is possible to throw out zinc from a zinc solution containing excess of potassium cyanide, by means of metallic copper.

It is thus apparent that the displacement of one metal by another is often determined by the *ratios* of ionic concentrations, which may be themselves so small in absolute magnitude as to defy our ordinary means of detection.

Polarisation and Electrolysis

As long as we are dealing with reversible combinations, the passage of an electric current through the system in no way alters the nature of the electrode or of the liquid surrounding the electrode, except in so far as it may effect a change in the concentration of the electrolyte, which has little effect on electromotive force. The electromotive force therefore of the combination is practically constant, and if we apply to the system an opposed electromotive force of a magnitude greater than the direct electromotive force of the cell, a current will pass through the system in the reverse direction to that which the cell itself would generate. Since a metal immersed in the solution of one of its own salts is in general a reversible electrode, we can, as we have already seen, get a reversible combination of zero electromotive force by immersing two strips of the same metal, say copper in a solution of copper sulphate. The slightest electromotive force applied to this system will effect the passage of a current one way or other, copper being deposited on one electrode and dissolved from the other, and the current will continue to pass indefinitely if the concentration of the copper sulphate round the electrodes is maintained at the same value, say the saturation value at the experimental temperature. Suppose now we immerse platinum electrodes instead of copper electrodes in the copper sulphate solution. The electromotive force of the combination is still zero, but we find that we can get no current of any magnitude to pass until the electromotive force applied to the system exceeds a certain value. The reason for this is obvious. As soon as a current passes through the system, copper is deposited on one electrode and sulphanion is discharged at the other with production of sulphuric acid and oxygen. The electrodes and solutions round the electrodes are no longer the same as they were originally, for in place of two platinum plates immersed in copper sulphate solution we have now one platinum plate (the kathode) covered with a thin coating of copper, and the other platinum plate (the anode) partially charged with oxygen and surrounded by a mixture of copper sulphate and sulphuric acid. A combination of this sort possesses an electromotive force of its own, which acts against the direct electromotive force and neutralises it if the direct force is of insufficient magnitude. The reverse electromotive force is called the **electromotive force of polarisation**, and is always encountered where the electrodes are non-reversible. When the direct electromotive force is of sufficient strength to overcome the electromotive force of polarisation a steady current may be made to pass through the system. Oxygen will then be evolved at the anode, and sulphuric acid will accumulate around it. If now the direct current is interrupted, the electromotive force of polarisation will produce a polarisation current in the opposite direction to the original current, and this current will flow, at a rapidly diminishing rate, until equilibrium is attained. In the case just considered, one of the products of the continued action of the direct current, oxygen namely, escapes from the system, all but a small residue absorbed by the platinum, so that the polarisation current almost instantaneously falls off owing to the consumption of this small quantity of oxygen.

Secondary cells, or **accumulators**, depend for their action on a polarisation current. In the ordinary type, the electrodes of the uncharged cell may be said to consist of lead and lead sulphate immersed in diluted sulphuric acid, the metallic lead acting as a conductor and a support for the lead sulphate. Such a combination of one liquid and similar electrodes possesses no electromotive force. When a current is passed through the system, however, the following action takes place :—

$$2PbSO_4 + 2H_2O = \overset{\text{Kathode}}{Pb} + \overset{\text{Anode}}{PbO_2} + 2H_2SO_4.$$

The lead sulphate on the kathode is converted into lead sponge and on the anode into lead dioxide, the concentration of the sulphuric acid increasing. Here all the products of the direct current, the charging current, are retained within the cell, and a very large amount of lead sulphate can in this way be converted into metal and peroxide. When the charging is complete, and the two electrodes connected through an external conductor, the polarisation electromotive force of about two volts immediately starts a current, the discharge current, in the direction opposite to that of the charging current, and this goes on with very slowly diminishing electromotive force until a large proportion of the lead and lead peroxide have again become converted into lead sulphate, according to an equation which is the reverse of that given above, namely,

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O.$$

Here the polarisation current is maintained because the nature of the electrodes undergoes no important change while a very large quantity of material is being transformed.

The polarisation electromotive force of a combination may be investigated by closing the polarisation circuit through a measuring instrument simultaneously with the breaking of the primary circuit. The operation may be repeated as frequently as we please by the vibration of a tuning fork, which alternately makes and breaks the primary circuit at the same time as it breaks and makes the polarisation circuit. If the rate of vibration is sufficiently great this is tantamount to observing the electromotive force of a steady current of polarisation generated by a known steady primary current.

It is occasionally of importance to investigate the anodic and kathodic polarisation separately. This may be done by introducing a third electrode, a non-polarisable calomel electrode being very generally employed, which is combined in a polarisation circuit with the electrode under investigation. The electromotive force of the non-polarisable electrode being known, the polarisation of the other electrode can be easily calculated from the total electromotive force of the circuit.

The electrode potentials given in the table on p. 329 may be looked upon from the point of view of **electrolysis** as well as of current generation. In order to deposit zinc in quantity on a kathode from a normal solution of zincion it is obviously necessary that the difference of potential of 0·5 volts between zinc and normal zincion should be compensated by the electrolysing current, for as soon as more than a very minute quantity of zinc separates out on the electrode, which is assumed not to act on the zinc, that electrode behaves as a zinc electrode. The electrode potentials then may be considered as the **discharging potentials** for kations. Since in order to study the electrolysis of a solution between unattacked electrodes it is necessary to know the discharging potential of the anion of the electrolyte as well as that of the kation, a similar table for the commoner negative radicals may be constructed. The ionic concentration is once more normal, except in the case of oxidion and hydroxidion, which are the values for solutions in which the concentration of hydrion is normal.

DISCHARGING POTENTIALS OF ANIONS

Iodidion	I'	– 0·80
Bromidion	Br'	– 1·22
[Oxidion	O''	– 1·36]
Chloridion	Cl'	– 1·59
[Hydroxidion	OH'	– 1·96]
Sulphanion	SO_4''	– 2·2
Hydrosulphanion	HSO_4'	– 2·9

It is of course impossible to obtain some of these discharged ions in the free state, so that the methods adopted for the measurement of the electrode potentials of the metals are not here available. The numbers given have been mostly derived from observations of the magnitude of direct currents and the corresponding polarisation currents which they produce. The values given in the table are all negative, and for the elements express approximately their electroaffinity or tendency to combine with negative electricity. Thus chlorine will displace bromine from a bromide in virtue of its greater electroaffinity for negative electricity, just as zinc will displace copper from a copper salt in virtue of its greater electroaffinity for positive electricity. As before (p. 330), a diminution of the concentration to one-tenth of its value will augment the discharging potential of a univalent anion by 0·058 volt. From the known concentration of hydroxidion in water it may be calculated that a potential difference of about $1{\cdot}96 - 0{\cdot}8 = 1{\cdot}16$ volts is required to discharge it from normal hydroxidion solution, as against 1·96 volts in normal hydrion solution.

The decomposing current, *i.e.* the minimum current which will effect continued electrolysis, may be calculated from the discharging potentials as follows:—Since the kathodic and anodic electrode potentials act against each other, the electromotive force of the current through the system is equal to the algebraic difference of the electrode potentials of kathode and anode. The kathodic potential is therefore taken with the sign given in the table on p. 329, and the electrode potential of the anions on p. 335 with the negative sign reversed, *i.e.* with the positive sign. Thus in a solution of hydrochloric acid of normal ionic concentration the decomposing current will be

$$\overset{\text{Kathode}}{-0{\cdot}27} - (\overset{\text{Anode}}{-1{\cdot}59}) = 1{\cdot}32 \text{ volt.}$$

In a decinormal ionic solution it will be

$$-0{\cdot}27 + 0{\cdot}06 - (-1{\cdot}59 - 0{\cdot}06) = 1{\cdot}44 \text{ volt.}$$

To effect the **decomposition of water** with discharge of hydroxidion, a practically constant electromotive force is required, which may be calculated from the values given for normal hydrion solution, viz.

$$-0{\cdot}27 - (-1{\cdot}96) = 1{\cdot}69.$$

Since the product of the hydrion and hydroxidion concentrations is constant in aqueous solutions and equal to the product for pure water, and since the increase or diminution of electrode potentials depends on the ratios of concentrations, it follows that whatever addition may be made to the kathodic potential for hydrogen will be compensated by a corresponding diminution in the anodic potential for hydroxyl, so that the decomposing value for water will remain constant at 1·69 volts whether the solution is neutral, strongly acid, or strongly alkaline.

A well-investigated and instructive instance of discharging potentials is afforded by the electrolysis of sulphuric acid in approximately normal solution, and may here be given in rough outline. The only positive ion to be considered in this case is hydrion, but in the solution the following anions must be supposed to exist—hydrosulphanion, sulphanion, hydroxidion, and oxidion, the last two in vanishingly small amounts in comparison with the first two. The electromotive force of the corresponding decomposing currents will be

Kathode.		Anode.		
Hydrion . . .	−0·27	Oxidion . . .	+1·36	=1·09 volts
,,	−0·27	Hydroxidion . . .	+1·96	=1·69 ,,
,,	−0·27	Sulphanion . . .	+2·2	=1·93 ,,
,,	−0·27	Hydrosulphanion . . .	+2·9	=2·63 ,,

If the electrolysing current has an electromotive force of 1·09 volts, continuous electrolysis might be expected to take place, as oxidion would then be discharged at the anode, but the amount of electrolysis could scarcely be great owing to the minute quantity of oxidion in the vicinity of the anode at any one time. This decomposition has actually been observed by taking a large platinised platinum plate as anode and the point of a thin platinum wire as kathode. With an electromotive force of 1·1 volts, hydrogen may be seen to come off at the platinum point, though no visible change occurs at the anode, the small amount of oxygen liberated being absorbed by the large platinum surface. Reversing now the electrodes and saturating the platinised kathode with hydrogen, oxygen may be seen to come off at the point which serves as anode when the electromotive force of the direct current reaches about 1·69 volts, *i.e.* attains the decomposing value for hydroxidion. Even here, however, the extent of electrolysis is slight owing to the small amount of hydroxidion in the solution. It is only when the electromotive force of the current is raised to such an extent as to discharge freely the sulphanion and hydrosulphanion, which exist in plenty in the solution, that the electrolysis becomes really brisk. For the preparation of detonating mixture by the electrolysis of water acidulated with sulphuric acid an electromotive force of 2 – 3 volts is always used, corresponding to the discharging values for sulphanion and hydrosulphanion.

A considerable amount of discussion has taken place as to whether the oxygen and hydrogen which appear at the electrodes when a solution of a salt like potassium sulphate is electrolysed, are primary or secondary products of the electrolysis. There is no doubt that hydrogen and oxygen do appear as primary products of the electrolysis of such a salt solution when the electromotive force employed is just beyond the decomposing value for water, but when large electromotive forces are used and the electrolysis proceeds briskly, the oxygen and hydrogen are in all probability secondary products formed by the action of the discharged ions on water (cp. p. 216).

S. Arrhenius, *Electro-chemistry.*

M. Le Blanc, *Electro-chemistry.*

N. T. M. Wilsmore, "Electrode Potentials." *Zeitschrift für physikalische Chemie*, **35** (1900), p. 291.

W. Ostwald, *ibid.* p. 333.

CHAPTER XXVIII

THERMODYNAMICAL PROOFS

THE experience of practical and scientific men alike goes to show that it is impossible to construct a perpetual motion machine. In the general acceptance of the term, a perpetual motion machine is one from which more energy can be obtained than is put into it from the outside. This may be termed a perpetual motion of the first class. But another kind of perpetual motion machine might exist—one, namely, which could by a recurring series of processes continuously afford mechanical energy at the expense of the heat of surrounding bodies at the same temperature as itself. This kind of perpetual motion is also impossible, and has been termed perpetual motion of the second class. It must be clearly understood that not only have such machines never been constructed, but that no increase in our experimental skill at present conceivable could lead to their construction. If therefore in argument we find that an imaginary series of processes would lead to a perpetual motion of either of the kinds mentioned above, we conclude that such a series of processes can have no real existence.

The denial of the possibility of the existence of the two sorts of perpetual motion is contained in the two following positive and general statements, which are known as the **First and Second Laws of Thermodynamics**, respectively.

I. The energy of an isolated system remains constant.

II. The entropy of an isolated system tends to increase.

With the second law in its general and formal aspect we shall have here little to do, and shall use in its stead the negative proposition given above. Entropy is a function which, while theoretically of great value as indicating the direction in which chemical or other processes take place, and in fixing generally the conditions of equilibrium, is not susceptible of direct measurement, and is consequently of less obvious and immediate practical importance.

The first law states the principle of the Conservation of Energy—by an isolated system being meant a system which can neither give up energy to its environment nor absorb energy from it. The sum of the different kinds of energy in such a system is always the same, no matter what forms the energy may assume. In order to ascertain practically that the sum of the energies is constant, we must obviously have one kind of unit in which all energies may be expressed. If we work with only one kind of energy, we express its amount in the appropriate unit. Thus we express amount of heat in calories; electrical energy in volt-coulombs, or the like; and mechanical energy in foot-pounds or gram-centimetres. In dealing with different kinds of energy, we may take any of these units as the standard in which we express all the different varieties, for we know the factors necessary for converting one unit into any of the others. One calorie, for example, is under all circumstances equivalent to 42,650 gram-centimetres, so that if we wish to add heat energy and mechanical energy together, we must either multiply each calorie of heat energy by 42,650 to convert it into gram-centimetres, or divide the number of gram-centimetres by the same number in order to find their equivalent in calories. A few simple deductions from the First Law, involving only the consideration of thermal and mechanical energy, will now be given.

When a small quantity of heat dQ is supplied to a gram-molecular weight of a perfect gas at constant volume, the heat goes entirely to raise the temperature of the gas, and we may therefore write $dQ = C_v dT$; where C_v is the heat capacity of the gram molecule at constant volume (cp. p. 35), and dT the small rise of temperature which this amount of gas experiences. If the heat is supplied to the gas under constant pressure, it not only goes to raise the temperature, but is also partially converted into work done by the gas during expansion. If p is the constant pressure, and dv the change of volume, this work is represented by the product pdv. Now according to the First Law

$$dQ = C_v dT + pdv, \tag{1}$$

since no other kind of energy is involved, the internal energy of a perfect gas being independent of its volume (cp. p. 38).

In the gas equation for the gram molecule ($pv = RT$), p, v, and T are variable, so that on differentiation we obtain

$$pdv + vdp = RdT. \tag{2}$$

By eliminating dT from equations (1) and (2) we obtain

$$dQ = \frac{C_v + R}{R} pdv + \frac{C_v}{R} vdp\,;$$

or since $C_p = C_v + R$, as was shown on p. 35,

$$dQ = \frac{C_p}{R} pdv + \frac{C_v}{R} vdp.$$

Now, if the pressure, volume, and temperature of the gas be allowed to change adiabatically, *i.e.* in such a way that heat neither enters nor leaves the system, we have $dQ=0$, and consequently

$$C_p p dv + C_v v dp = 0.$$

Introducing into this equation the ratio of specific heats $k = C_p/C_v$, we have

$$kpdv + vdp = 0\ ;$$

or

$$k\frac{dv}{v} + \frac{dp}{p} = 0.$$

This equation, when integrated between the values pv and p_1v_1, gives

$$k(\log_e v_1 - \log_e v) + \log_e p_1 - \log_e p = 0\ ;$$

whence

$$k = \frac{\log_e p - \log_e p_1}{\log_e v_1 - \log_e v};$$

or

$$\frac{p}{p_1} = \left(\frac{v_1}{v}\right)^k.$$

These results are of importance as they enable us to ascertain the ratio of the specific heats of gases by observations of pressures and volumes under circumstances in which heat can neither leave nor enter the gas considered. For example, during the rapid compressions and dilatations which constitute the passage of sound through a gas, there is no time for the heat change at any portion of the gas to communicate itself by conduction to neighbouring portions, so that the process instead of being isothermal, is, so far as any given portion of the gas is concerned, an adiabatic process, the gas being cooled at each dilatation and warmed at each compression. The gas then does not in these circumstances obey Boyle's Law, which holds good only for *isothermal* change of pressure and volume, but the law given above, where the pressure is not inversely proportional to the volume, but to the k-th power of the volume. It is owing to this circumstance that we can deduce the ratio of specific heats of a gas from the speed at which sound travels in it.

We have now to find the law connecting the volume of a gas with its absolute temperature when it is heated adiabatically, *i.e.* by compression, since no heat as such must enter the system. This can easily be done by eliminating pdv from equations (1) and (2), the result being

$$\begin{aligned} dQ &= (C_v + R)dT - vdp \\ &= C_p dT - vdp \\ &= C_p dT - \frac{dp}{p}\,.\,RT, \end{aligned}$$

since $pv = RT$.

For an adiabatic compression $dQ=0$, so that

$$C_p dT - \frac{dp}{p} \cdot RT = 0,$$

$$\frac{C_p}{C_p - C_v} \cdot \frac{dT}{T} - \frac{dp}{p} = 0\,;$$

$$\frac{k}{k-1} \cdot \frac{dT}{T} - \frac{dp}{p} = 0.$$

Integrating between T, p, and T_1, p_1, we obtain

$$\frac{k}{k-1}(\log_e T_1 - \log_e T) - (\log_e p_1 - \log_e p) = 0,$$

$$k \log_e \frac{T_1}{T} = (k-1)\log_e \frac{p_1}{p},$$

$$\left(\frac{T_1}{T}\right)^k = \left(\frac{p_1}{p}\right)^{k-1}$$

But since in an adiabatic process $\frac{p_1}{p} = \left(\frac{v}{v_1}\right)^k$, we obtain finally

$$\left(\frac{T_1}{T}\right)^k = \left\{\left(\frac{v}{v_1}\right)^k\right\}^{k-1}$$

or

$$\frac{T_1}{T} = \left(\frac{v}{v_1}\right)^{k-1}$$

This result we shall find useful in calculating the maximum amount of work which can be obtained from a given quantity of heat under given conditions, a problem which we shall now proceed to solve.

According to our statement of the second law, no work can be obtained from the heat contained in a number of bodies all having the common temperature of their surroundings. In order to convert heat into work, we must have *temperature differences.* A body in cooling through a certain range of temperature parts with a certain amount of heat, and a definite fraction of that heat may be transformed into work. In actual practice, different engines will effect the conversion of different amounts of the heat, but there is a theoretical limit which no engine, however perfect, can exceed, and it is our task to find what that limit is.

The process of reasoning is essentially the same as that of Carnot, who introduced the conceptions necessary for the solution of the problem, and arrived at the desired result, although to him heat was a material substance, and not, as we now believe, a form of energy. The fundamental conception is that of a **reversible cycle** of operations. By a cycle of operations is understood a series of processes which leaves the system considered in exactly the same state as it was initially, and the term reversible applies not merely to the direction of the mechanical operation, but to the complete physical reversibility of all the processes involved.

A reversible heat-engine after converting a certain amount of heat into work will return to its original state in every respect if made to act backwards step by step, so that the work obtained is entirely converted into heat by its agency. Such an engine is of the maximum possible efficiency, for if any engine were more perfect, a perpetual motion could be obtained. This may be shown as follows. Let A be a reversible engine, and let B be an engine which under the same conditions can convert a larger proportion of heat into work than A. Let the two engines work between the same temperatures, and suppose that when a quantity of heat Q is given to A, the proportion q is converted into mechanical work. If the work corresponding to q is now done upon this engine so that the processes are reversed, the system will arrive exactly at its initial state, the quantity of heat $Q-q$ being raised from the lower to the higher temperature. Now instead of letting the engine A act directly, take in its stead the more perfect engine B, and supply it at the higher temperature with the quantity of heat Q. A greater proportion of this than before is converted into work, say q', the quantity of heat $Q-q'$ falling to the lower temperature. By using the reversible engine to perform the reverse transformation of work into heat, we can regain the original quantity of heat Q at the original temperature, by expending mechanical energy equivalent to q, the quantity of heat $Q-q$ being at the same time raised to the higher temperature. In the whole series of operations, then, the heat $q'-q$ has been taken in at the lower temperature and an equivalent amount of work has been gained. This cycle of operations can be repeated as often as we choose, so that here we should have a system capable of giving an indefinitely large amount of work at the expense of heat at the lower temperature, which might be the uniform temperature of the surroundings, *i.e.* we should have realised a perpetual motion of the second class. We conclude, then, that an engine more perfect than the reversible engine A cannot exist. It will be noticed that nothing is said as to the nature of the working substances in the reversible or the other engine, so that the conclusion is perfectly general. We are at liberty therefore to use any kind of reversible engine in our calculations in order to ascertain the maximum quantity of heat which can be converted into work, and we shall find it convenient to take for our working substance a perfect gas, on account of the simplicity of the laws which it obeys.

We must first of all investigate if the processes through which we put the working substance are really reversible. The **condition of reversibility** is that the state of the system at any time does not differ sensibly from equilibrium, for then the slightest variation in the conditions will determine the occurrence of the process in the one direction or the other. If, therefore, we communicate heat to the gas, we must so arrange that the gas and the heat source have temperatures differing from each other by an infinitely small amount. Similarly, if the gas is to part with heat, it must do so to a heat-sink with a temperature lower than its own only by an infinitesimal quantity. If the gas is to be compressed, the external pressure at any instant must be only greater by an infinitely small amount than the pressure of the gas itself; and if the gas is to be expanded, the external pressure must be less than the pressure of the gas by an infinitesimal difference. The machine of course must be absolutely frictionless, for otherwise some work would have to be expended in moving the machine, and thus converted into heat, independent of the gaseous working substance which is alone considered. From all this it is obvious that a reversible engine is an engine which can never be realised in practice. For an engine to be strictly reversible, there should be no departure from the conditions of equilibrium at any stage, in which case no process could occur at all, for the occurrence of any process naturally involves a departure from equilibrium. If the departure from the equilibrium conditions were infinitely small, the process would occupy an infinitely long time in its performance. We see then that a reversible process is an ideal, just as a perfect gas in an ideal. Neither can ever be met with in practice, but this in no way impairs the value of the theoretical conclusions deduced by their aid.

The series of operations which we shall perform on the gas will be best seen in the pressure-volume diagram, Fig. 49. We begin with the gas in the state represented in the diagram by the point 1. At the constant temperature T we let the gas slowly expand until its pressure and volume are indicated by the point 2. The form of the curve obtained during the expansion is the rectangular hyperbola of gases (cp. p. 81). We next isolate the gas from the heat source of constant temperature T, and let the expansion continue adiabatically until the point 3 is reached Since the pressure varies more rapidly with the volume in an adiabatic than in an isothermal process (p. 340), the line 2, 3 will be more inclined to the volume axis, than 1, 2, as is shown in the diagram. As no heat can enter the system during the adiabatic expansion, the temperature will fall, say to T'. We now bring the gas into contact with a heat reservoir at the temperature T', and compress it isothermally until a point 4 is reached, such that when the compression is continued adiabatically, the adiabatic curve will pass through the initial point 1, where the process is stopped and the cycle thus completed.

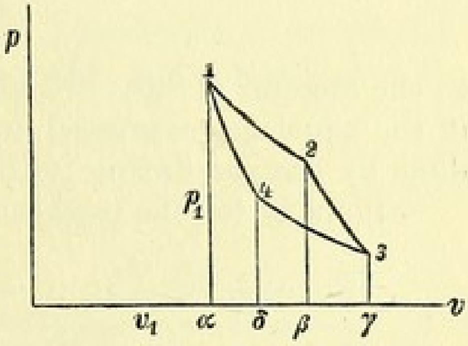

Fig. 49.

In this cycle a certain quantity Q of heat has been absorbed by the gas at the higher temperature T, and the quantity Q' has been given out by the gas at the lower temperature T'. At the same time a certain amount of work has on the whole been performed. The gas on expanding does work, and this work is measured by the product of each pressure into the corresponding change of volume. In the diagram, therefore, the work performed by the gas on expansion is measured by the area α, 1, 2, 3, γ. When the gas was compressed, work was done upon it, and this work in the diagram appears as the area γ, 3, 4, 1, α. The total work obtained then from the gas during the cycle is the difference of these areas, viz. the quadrilateral, 1, 2, 3, 4.

To obtain actual numerical relations we may consider a gram molecule of the gas, for which the previous equations of this chapter are valid. During the isothermal expansion 1, 2, the gas absorbed Q units of heat at the temperature T, while it expanded from the volume v_1 to the volume v_2. In equation (1), p. 339,

$$dQ = C_v dT + p dv$$

we may put dT equal to zero, since we are considering an isothermal process, and for p we may substitute $\frac{RT}{v}$. We thus obtain

$$dQ = RT\frac{dv}{v}, \tag{1a}$$

which, when integrated between the limits v_1 and v_2, gives

$$Q = RT \log_e \frac{v_2}{v_1}$$

as the amount of heat absorbed by the gas. The right hand member of the equation, expressed in mechanical units, is of course the work done by the gas during isothermal expansion from v_1 to v_2.

Similarly for the isothermal compression 3, 4 we obtain

$$-Q' = RT' \log_e \frac{v_4}{v_3},$$

or

$$Q' = RT' \log_e \frac{v_3}{v_4}.$$

The sign of Q' is in the first equation of this pair different from that of Q above, since in one case the system gains heat, and in the other loses it. Division now gives

$$\frac{Q}{Q'} = \frac{T \log_e \frac{v_2}{v_1}}{T' \log_e \frac{v_3}{v_4}}. \tag{3}$$

For the adiabatic expansion 2, 3, we have (p. 341)

$$\frac{T}{T'} = \left(\frac{v_3}{v_2}\right)^{k-1}$$

and for the adiabatic compression 4, 1

$$\frac{T'}{T}=\left(\frac{v_1}{v_4}\right)^{k-1}$$

whence $$\frac{v_3}{v_2}=\frac{v_4}{v_1} \text{ or } \frac{v_2}{v_1}=\frac{v_3}{v_4}.$$

Equation (3) therefore reduces to

$$\frac{Q}{Q'}=\frac{T}{T'},$$

i.e. the heat absorbed is to the heat given out as the absolute temperature of the absorption is to the absolute temperature at which the heat is lost by the system. A slight alteration gives the equation in the form

$$\frac{Q-Q'}{Q}=\frac{T-T'}{T},$$

i.e. the proportion of the absorbed heat which is converted into work is equal to the temperature difference between the two isothermal operations divided by the temperature of absorption. A form which we shall find useful in subsequent calculations is

$$Q-Q'=\frac{T-T'}{T}\cdot Q. \qquad (4)$$

These results, although derived from a consideration of the behaviour of gases, are valid for all reversible cycles, and can therefore be applied in every case for which we can show all the operations involved to be reversible.

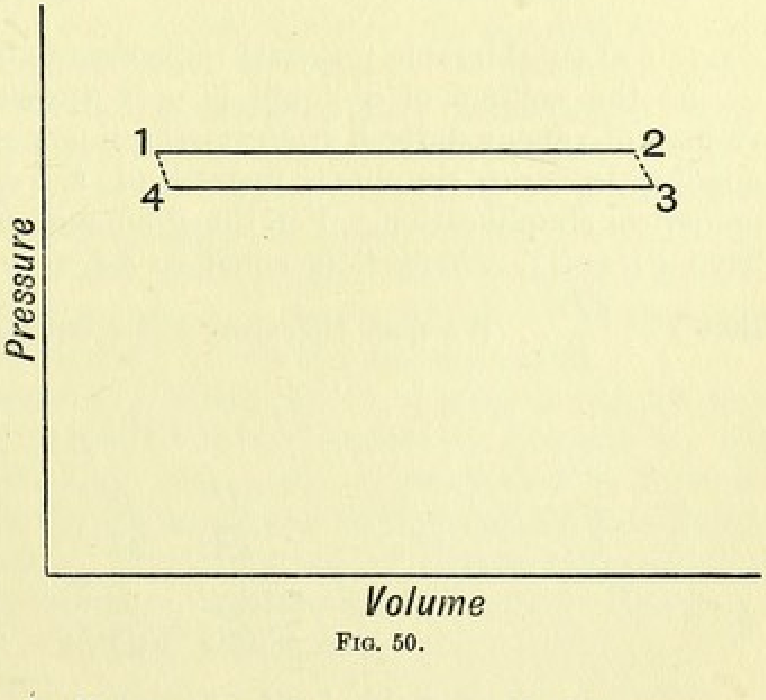

FIG. 50.

The first application of equation (4) will be to the process of **vaporisation**. Let us consider a quantity of liquid under a pressure P which is equal to the vapour pressure of the liquid at the constant temperature chosen. An infinitesimal diminution of the pressure on the liquid will cause it gradually to pass into vapour if this pressure and the constant temperature are maintained. Suppose one gram-molecular weight of vapour to be produced in this way, and let the isothermal process be represented in the indicator diagram (Fig. 50), by the line 1, 2, which is parallel to the axis of volumes, the pressure being constant. Now expand the vapour adiabatically from the original pressure P to a pressure which is dP lower, the temperature at the same time falling. The pressure and volume may then be represented by the point 3. At a temperature $T-dT$ for which the vapour pressure of the substance is $P-dP$, compress the vapour isothermally to liquid and finish the compression adiabatically until the original pressure, temperature, and volume are regained. The work done upon the system is equal to the area of the figure 1, 2, 3, 4, which is practically the product of the line 1, 2 into the vertical distance between 1, 2 and 3, 4. Now the line 1, 2 in the diagram represents the difference in volume between the liquid and the vapour, and the distance between the two horizontal lines represents the difference of vapour pressure dP due to a difference of temperature dT. For the work done then we have the product $dP\,(V-v)$, where V is the molecular volume of the vapour, and v the molecular volume of the liquid. The quantity of heat absorbed at the higher temperature T is Q, the molecular heat of vaporisation of the liquid at this temperature. The quantity which has been transformed into work is consequently $Q\,\frac{dT}{T}$ according to equation (4). If we express the heat in mechanical units, as we can do by multiplying the heat units by $J=42{,}650$ (see p. 6) we obtain the equation

$$dP(V-v)=JQ\,\frac{dT}{T}, \tag{5}$$

a result of considerable practical importance and of wide applicability.

As the volume of a liquid is only a fraction of a per cent of the volume of vapour derived from it at ordinary pressures, it is often permissible to write simply V instead of $V-v$, which brings about a numerical simplification. For the gram-molecular volume of a gas we have $PV=RT$, where R is equal to $2J$ very nearly (see p. 30), so that $V=\frac{2JT}{P}$. We may therefore write equation (5) in the form

$$2JT\cdot\frac{dP}{P}=JQ\frac{dT}{T},$$

i.e.

$$\frac{dP}{PdT}=\frac{Q}{2T^2}, \tag{6}$$

or

$$\frac{d\log_e P}{dT}=\frac{Q}{2T^2}. \tag{7}$$

We may calculate from this result in the form of equation (6) the latent heat of vaporisation of benzene from the change of its vapour pressure with the temperature. At 5° the vapour pressure of benzene is 34·93 mm. of mercury, or 47·50 g. per sq. cm.; at 5·58° the pressure is 36·06 mm. or 49·04 g. per sq. cm. For dP then we have 1·54, for dT we have 0·58, for P we have the mean value 48·27, and for T the mean value 278·3. The value of Q is therefore

$$\frac{2T^2dP}{PdT} = \frac{2(278{\cdot}3)^2 \times 1{\cdot}54}{48{\cdot}27 \times 0{\cdot}58} = 8520 \text{ cal.}$$

The value of the heat of vaporisation actually found is 8420 cal., so that the agreement between calculation and experiment is fairly close, the difference not being greater than the error of experiment.

Equation (5) not only holds good for the liquid and gaseous phases, *i.e.* for vaporisation, but also for the equilibrium between any other pair of phases, for example, solid and liquid, or two solid phases such as the different crystalline modifications of sulphur. In the form

$$dT = \frac{T(V - v)}{Jq}\,dP \tag{8}$$

it is useful for ascertaining the effect of pressure on the temperature of equilibrium. V, v, and q may all refer either to molecular quantities or to unit weight of the substance considered, as the molecular factor cuts out in the right-hand member. If we consider the transformation brought about by supplying heat to the substance, q is a positive quantity, while J and T also are necessarily positive. Consequently dP will have the same sign as dT, or the opposite sign, according as $V - v$ is positive or negative, *i.e.* if the substance expands on being transformed by application of heat, dP and dT will have the same sign, whilst if it contracts dP and dT will have different signs. In the first case then the transition point will be raised by increase of pressure; in the second case it will be lowered. Rhombic sulphur on melting expands; $V - v$ is therefore positive and the melting point of rhombic sulphur is raised by pressure. Again rhombic sulphur expands on passing into monoclinic sulphur, and consequently the transition point is raised by application of pressure. Water, on the other hand, occupies a smaller volume than the ice from which it is produced; $V - v$ is therefore negative, and increase of pressure lowers the melting point.

As a numerical example of the application of formula (8), we may calculate the effect of one atmosphere increase of pressure on the melting point of ice. A cubic centimetre of water at 0° is obtained from 1·09 cc. of ice; the change of volume on liquefaction is therefore 0·09 cc. per gram of water. The latent heat of liquefaction per gram is 80 cal., and the temperature of liquefaction is $T = 273$. We have, therefore, if $dP = 1$ atm. $= 1033$ g. per sq. cm.,

$$dT = \frac{T(V - v)}{Jq}\,dP = \frac{273 \times (-0{\cdot}09) \times 1033}{42650 \times 80} = -0{\cdot}0075;$$

that is, the melting point of ice is lowered 0·0075° for each atmosphere increase of pressure. A corresponding diminution of pressure causes the same rise in the melting point. Thus ice which melts under atmospheric pressure at 0°, melts at 0·0075° under the pressure of its own vapour, so that the triple point (p. 105) lies at this temperature and not at 0°.

Dilute Solutions

When we dissolve a substance in any liquid, the process is not, under ordinary conditions, a reversible one, for we have not in general during dissolution a state bordering on equilibrium. In certain circumstances, however, it is possible to conduct the process reversibly. If we are dealing, for example, with the solution of a gas in a non-volatile liquid, we can proceed reversibly as follows. Let the gas and liquid be taken in such proportions that the gas will just dissolve in the liquid at the pressure p and the constant temperature of experiment t. Suppose the liquid and gas to be contained in a cylinder with a movable gas-tight piston. At first let there be a partition separating the gas and the liquid. Without removing this partition, expand the gas by gradually diminishing the pressure in such a way that at no instant during the expansion the condition of the gas differs sensibly from equilibrium. According to Henry's Law, the quantity of gas dissolved by the liquid is proportional to the pressure of the gas. Let the expansion be continued until the pressure of the gas is so small that practically none of it dissolves in the liquid when the separating partition is removed. After removal of the partition let the pressure on the gas be increased by insensible gradations. At no time does the state of the system deviate sensibly from equilibrium, and the pressure may be gradually raised until at the pressure p all the gas has dissolved. The solution of a gas in a liquid then may be made part of a reversible cycle if the process is carried out as here indicated.

The concentration of a solution of a non-volatile substance in any liquid can be changed reversibly by bringing the solution into contact with the solvent under equilibrium conditions, and then by an infinitely small alteration of the conditions determining a process of concentration or dilution. It is apparent at once that we cannot bring the solution into direct contact with the liquid solvent, either by mixing directly or allowing the dissolved substance to diffuse slowly into a fresh quantity of solvent as in the experiment described on p. 156, for no slight change in the conditions can at any stage make the action proceed in the reverse direction, *i.e.* make a solution separate into a more concentrated solution and the solvent. If the solvent is in the form of vapour or solid, however, the dilution or concentration may be effected reversibly. Suppose the solution to be in presence of its own saturated vapour at the constant temperature of experiment. An increase of external pressure, however slight, will cause part of the vapour to condense, *i.e.* will dilute the solution; while a slight diminution of the external pressure will cause part of the solvent to evaporate, *i.e.* will concentrate the solution. Similarly, if the solution is in equilibrium with the solid solvent, a very slight rise of temperature will bring about partial liquefaction of the solid solvent, and thus dilute the solution, and a correspondingly slight diminution of temperature will produce partial separation of solid solvent and thus concentrate the solution.

There is still another way of bringing the solution into contact with the pure solvent under equilibrium conditions, namely, through a diaphragm which is permeable to the solvent and not to the dissolved substance. If the solution is enclosed in a cylinder with a semipermeable end and a movable piston, it will be in equilibrium with the liquid solvent through the diaphragm when there is a certain pressure on the piston,—the osmotic pressure. If the pressure of the piston is increased ever so slightly, solvent flows outward through the semipermeable diaphragm and the solution becomes more concentrated; if the pressure on the piston is diminished, solvent flows inwards through the diaphragm, and the solution is thereby diluted.

All these methods of changing the concentration of a solution can therefore be adopted as parts of reversible cycles of operations, and we shall see that by removing a portion of solvent from a solution by one method, and by adding it to the solution again by another method, we obtain a series of results which are of great theoretical and practical importance.

In the first place we shall consider a cycle in which a gas is dissolved in a non-volatile liquid by the reversible process given on p. 348, and the system then brought back to its original condition by means of semipermeable diaphragms. We start with a volume v_o of the gas under pressure p_o, and with a volume V of liquid just sufficient to dissolve the gas under this pressure, and we propose to find what amount of work (positive or negative) must be done in order to bring the gas into solution reversibly at constant temperature. During the first stage contact between gas and liquid is prevented by a partition inserted at the surface of the liquid. If the cylinder in which the gas and liquid are contained have unit cross section, and the initial distance of the piston from the liquid surface is x_o, we have for this state $x_o = v_o$. At any stage of the expansion (x) the pressure p is given by the equation $p = \frac{p_o v_o}{x}$, and the work done by the gas during the expansion is represented by the expression

$$p_o v_o \int_{v_o}^{x} \frac{dx}{x} = p_o v_o \log_e \frac{x}{v_o},$$

x being a very large multiple of v_o. The partition is then removed, and the pressure on the gas increased. The pressure on the piston in a given position x is less than before, for the gas which was previously confined to the space x is now partly in solution. If s denote the solubility (p. 58), the available volume is practically increased in the ratio $x : x + sV$, so that the pressure in position x is now given by

$$p = \frac{p_o v_o}{x + sV},$$

and the work required to be done during the compression is

$$p_o v_o \int_o^x \frac{dx}{x + sV} = p_o v_o \log_e \frac{x + sV}{sV}.$$

On the whole, the work done on the system during the double operation is

$$p_o v_o \left\{ \log_e \frac{x + sV}{sV} - \log_e \frac{x}{v_o} \right\};$$

or

$$p_o v_o \left\{ \log_e \frac{x + sV}{x} - \log_e \frac{sV}{v_o} \right\}.$$

The quantity within the brackets of the second expression may be seen to be zero, since x is indefinitely great, so that $\frac{x + sV}{x} = 1$, and since by supposition the quantity of liquid is just capable of dissolving the gas, whence $sV = v_o$. The conclusion, then, is that there is no gain or loss of work in dissolving the gas reversibly in the liquid.

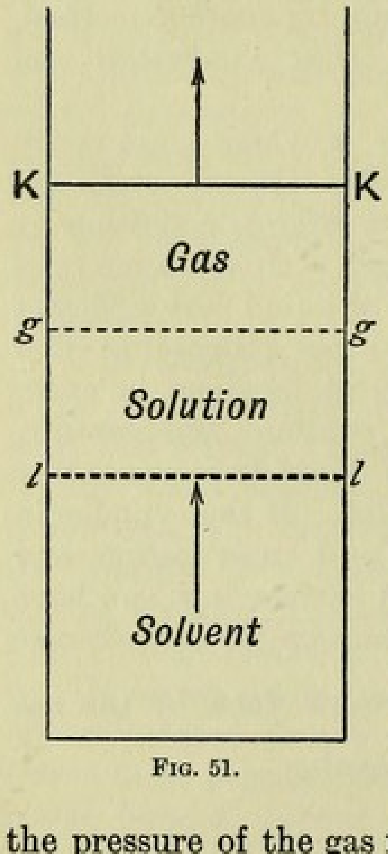

Fig. 51.

The gas may now be removed from solution and restored to its original state reversibly by means of semipermeable membranes arranged as in Fig. 51. One membrane gg permeable to gas but not to liquid, is introduced at the surface of the liquid, on which the piston KK rests at the commencement of the operation. A second membrane ll, permeable to liquid but not to gas, is substituted as a piston for the bottom of the cylinder, and is backed upon its lower side by the pure solvent. By suitable proportional movements of the two pistons, KK being raised through the space v_o, while ll is raised through the space V, the gas may be expelled, the pressure of the gas retaining the constant value p_o, and the solution which remains retaining a constant strength, and therefore a constant osmotic pressure P. When the expulsion is complete, *i.e.* when the two semipermeable membranes have come together, the work done upon the lower piston is PV, and the work done by the gas in raising the upper piston is $p_o v_o$.

The system is now in its original state, and all the operations have been conducted reversibly. A reversible cycle has therefore been performed, and the equation $Q - Q' = \frac{T - T'}{T} Q$ is applicable. The temperature has remained constant throughout, so that $T - T' = 0$, and therefore $Q - Q' = 0$, as in all reversible isothermal cycles. Since no heat has been converted into work, or *vice versa*, the work done on the system must on the whole be equal to the work done by the system. In the first stage, *i.e.* the process of solution, it has been shown that there is neither loss nor gain of work, so that for the second stage we must have

$$p_o v_o = PV.$$

If the gas which occupies the volume v_o at the pressure p_o, is made to occupy the volume V, its pressure will assume a new value p, and according to Boyle's Law we shall have $p_o v_o = pV$; combining this with the previous equation, we then obtain $pV = PV$ and $p = P$. The osmotic pressure then of the gas in solution is equal to the gaseous pressure which it would exert in absence of the solvent if it occupied the same space at the same temperature—a result in harmony with the calculation from experiment made on p. 170.[1]

The above result holds good only for ideal substances and for very dilute solutions, since in its deduction we have assumed that the gas is a perfect gas which obeys the laws of Boyle and Henry exactly, and that the volume of the solution is exactly the same as the volume of the solvent which it contains—an assumption which can only be justifiably made when the solution is extremely dilute. The solvent, too, was supposed to be non-volatile (although the proof may be extended to volatile solvents), and the reversible processes themselves are purely ideal. Notwithstanding all these assumptions the conclusion arrived at is practically important, and holds good with close approximation for all dilute solutions under ordinary conditions.

We shall now consider an isothermal reversible cycle performed with a solution of a non-volatile solute in a volatile solvent. Let the solution contain n gram-molecules of dissolved substance in W grams of solvent, and let the constant absolute temperature of all the processes be T. From the solution let there be removed by means of a piston and a diaphragm permeable only to the solvent, a quantity of the latter which in the solution contained one gram-molecule substance dissolved in it. This quantity is W/n grams, and the solution is supposed to be

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[1] The proof here given is taken from an article by Lord Rayleigh, *Nature*, vol. lv. p. 253, 1897.

present in such large proportions that the removal of this amount of solvent does not sensibly affect its concentration, the osmotic pressure thus remaining constant during the operation. Since the change in volume of the solution is the gram-molecule volume, the work done on the system in removing the solvent is the product of this into the osmotic pressure, and is therefore equal to RT, if the gas laws apply to dissolved substances. This quantity of liquid solvent is now converted into vapour reversibly by expanding at the vapour pressure of the liquid, which we shall call f. The vapour pressure of the solution is smaller than this and equal to f'. Let the vaporous solvent therefore expand reversibly till its pressure diminishes to this value. The gaseous solvent is then in equilibrium with the solution, and may be brought into contact with it and condensed reversibly at the pressure f', so that the whole system regains its initial state. We have now to consider the work involved in the expansion and contraction. The work done by the system on expanding from liquid to vapour under the pressure f, is equal to the work done on the system in condensing the gas to liquid under the constant pressure f', being equal in each case to RT for the gram-molecule, if we neglect the volume of the liquid (cp. p. 30). There remains then the work done by the gas on expanding from f to f'. For isothermal expansion we have the work $RT\frac{dv}{v}$ per gram-molecule of gas (equation 1a, p. 344). Now

$$-\frac{dp}{p}=\frac{dv}{v}$$

for a gas, since $pv=\text{const.}$, and therefore $pdv+vdp=0$. For the work done during the expansion of the gas then we have $-RT\frac{dp}{p}$, or $-RT\frac{f-f'}{f}$ per gram-molecule if the difference between f and f' is very small. For the actual amount of solvent considered we have consequently $-\frac{W}{Mn}RT\frac{f-f'}{f}$, where M is the molecular weight of the solvent in the gaseous state. Since in the whole cycle no heat is converted into work or *vice versa*, this work done by the system must be numerically equal to the work done on the system during the osmotic expulsion of the solvent, *i.e.*

$$RT=\frac{W}{Mn}.RT.\frac{f-f'}{f},$$

or

$$\frac{f-f'}{f}=\frac{Mn}{W},$$

which is identical with the result arrived at for very dilute solutions by the method of calculation given on p. 178. Thus by a direct thermodynamical proof we can arrive at the relation between the osmotic pressure and the lowering of the vapour pressure of liquids by substances which are dissolved in them.

If the solution considered be not very dilute, we cannot write $\frac{f-f'}{f}$ for $\frac{dp}{p}$. For greater concentrations we integrate this expression, and thus obtain $\log_e \frac{p}{p'}$. By the same process of reasoning as before, we then get

$$\log_e \frac{f}{f'} = \frac{Mn}{W}.$$

This expression holds good for all concentrations of solutions for which the total volume of the liquid does not change when the quantity of solvent considered is added to or removed from the solution. If this condition is not observed the result is only approximate, for in the deduction of the relation we assumed that the work done by the expressed liquid in expanding at the constant gaseous pressure of the solvent was equal to the work done on the vapour when it was condensed at the constant vapour pressure of the solution, an assumption which is only valid if the volume of the liquid is the same before and after the reversible mixing of the solvent with the solution.

The relation between the logarithmic and the usual expression may be obtained by writing the former as follows:—

$$\log_e\left(1 + \frac{f-f'}{f'}\right).$$

If we expand the logarithm in this second form, the first term of the expansion is $\frac{f-f'}{f'}$, practically identical with the usual expression.

Having thus obtained the formula for the lowering of the vapour pressure of a solvent, we may now proceed to deduce the formula for the corresponding rise in the boiling point. From equation (6) we obtain the expression

$$\frac{dP}{P} = \frac{Q}{2T^2}dT$$

to represent the concomitant variations of temperature and vapour pressure of a solvent. Consider now a solution containing n gram molecules of dissolved substance in W grams of solvent. Let this solution have the vapour pressure P at the temperature $T + dT$, T being the temperature at which the solvent has the same pressure. At the temperature $T + dT$ the solvent will have the pressure $P + dP$. Now $\frac{dP}{P+dP}$ is the lowering of the vapour pressure of the solvent, but since

dP is very small compared with P we may write instead of this the expression $\frac{dP}{P}$ for the lowering. But we found above that this lowering is equal to $\frac{Mn}{W}$, so that

$$\frac{Mn}{W} = \frac{Q}{2T^2}dT.$$

Now Q is the latent heat of a gram molecule of the solvent, and M is its molecular weight (both molecular quantities referring to the gaseous state), so that $Q/M = q$ the latent heat of vaporisation per gram. We thus obtain

$$\frac{n}{W} = \frac{q}{2T^2}dT;$$

or

$$dT = \frac{2T^2}{q} \cdot \frac{n}{W}.$$

$T + dT - T = dT$ is the elevation of the boiling point of the solvent caused by the substance dissolved in it, and we have now obtained an expression for this in terms of the boiling point of the solvent itself, its latent heat of vaporisation and the concentration of the solution, to which the elevation is proportional. The elevation of the boiling point caused by the solution of one gram molecule of substance in 100 grams of solvent is sometimes referred to as the "molecular elevation" (p. 193). For this concentration n becomes 1 and W becomes 100, so that the molecular elevation is $\frac{0{\cdot}02T^2}{q}$. For a solution containing one gram molecule per 1000 grams, *i.e.* very nearly one gram molecule per litre for aqueous solutions, the elevation is $\frac{0{\cdot}002T^2}{q}$.

Since both boiling point and heat of vaporisation vary with the pressure at which ebullition takes place, there is no definite "molecular elevation" for any one solvent unless the pressure is specified. For ordinary purposes the pressure is of course the atmospheric pressure, and the fluctuations to which this is subject have so little effect on the molecular elevation that it may be taken as a constant magnitude in the practical molecular weight determination by the boiling point method. In order to give an example of the agreement between the calculated molecular elevation and the same magnitude as determined experimentally, we may take the common solvent ether. The boiling point of ether is 35°, and therefore $T = 308$. The latent heat of vaporisation per gram at this temperature is 90. The expression $\frac{0{\cdot}02T}{q}$ has thus the value 21·1. The average molecular elevation observed in the case of nine different substances in moderately dilute ethereal solution was found to be 21·3, the extreme values being 20·0 and 21·8.

The expression for the molecular depression of the freezing point has a similar form, and may be deduced by means of a reversible cycle as follows. Let a solution containing n gram molecules of dissolved substance in W grams of solvent be contained in a cylinder provided with a semi-permeable end, and a movable piston. At $T-dT$, the freezing point of the solution, let such a quantity of the solvent freeze out as originally contained one gram molecule of substance dissolved in it, viz. $\frac{W}{n}$ grams. The quantity of solution is supposed to be so great that the freezing out of this amount of solvent does not appreciably affect its concentration, so that the temperature of equilibrium between solution and solid solvent does not change during the process of freezing. The solid is now separated from the solution, and the whole system is raised to the temperature T, the melting point of the solvent, and at this temperature the solid solvent is allowed to melt. In doing so it absorbs $\frac{W}{n}q$ calories, if q represents the latent heat of fusion per gram. The fused solvent is now brought into contact with the solution through the semipermeable diaphragm under equilibrium conditions, viz. with the pressure on the solution equal to the osmotic pressure P. By raising the piston under this constant osmotic pressure, the solvent passes through the diaphragm and mixes reversibly with the solution, the concentration as before remaining unchanged. The work done on the piston is equal to the product of the constant osmotic pressure P into the volume v which contains one gram molecule of solute. But this amount of work, according to the osmotic pressure theory, is equal to RT; or if we express the gas constant in thermal units, to $2T$. The system after mixing is finally cooled to the original temperature $T-dT$ so as to complete the cycle. By selecting the solution sufficiently dilute we may make the depression of the freezing point dT as small as we choose, and consequently the heat absorbed and evolved in warming and cooling the system through this small range of temperature may be made negligible in comparison with the finite amount of heat $\frac{W}{n}q$ absorbed by the solvent on melting. In the reversible cycle, then, we have the amount $\frac{W}{n}q$ absorbed at the higher temperature T, and the amount of this converted into work is $\frac{dT}{T}\cdot\frac{W}{n}\cdot q$. But the only work done by the system is the osmotic work, since the external work brought about by the volume-changes on freezing and melting are so small as to be negligible. We have consequently

$$\frac{dT}{T} \cdot \frac{W}{n} \cdot q = 2T;$$

or

$$dT = \frac{2T^2}{q} \cdot \frac{n}{W}.$$

The depression of the freezing point is thus seen to be proportional to the concentration of the solution, and if we make the concentration such that $n = 1$ and $W = 100$,—that is, if we dissolve one gram molecule in 100 grams of solvent,—we get the molecular depression equal to $\frac{0{\cdot}02T^2}{q}$. The expression is exactly the same as that for the elevation of the boiling point, q referring here, however, to heat of fusion instead of to heat of vaporisation.

The following table exhibits the nature of the agreement between the calculated and observed values of the molecular depression in various solvents :—

Solvent	$\frac{0{\cdot}02T^2}{q}$	Mol. Dep.
Water	18·5	18·7
Formic acid	28·4	27·7
Acetic acid	38·8	39
Benzene	51	49
Phenol	76	74
Nitrobenzene	69·5	70·7
Ethylene dibromide	119	118

Electrical and Chemical Energy

It is possible, as Helmholtz showed, to establish a relation between the energy of the chemical processes occurring in a galvanic cell and the electrical energy produced by the action. At one time it was supposed that all the energy which could be obtained under ordinary circumstances as the heat of the chemical reaction, could be converted into electrical energy and made available as an electrical current. Thus if Q were the thermal effect for one gram equivalent of the substances entering into chemical action in the cell, it was assumed that an amount of electrical energy equivalent to this could be obtained from the cell for each gram-equivalent of chemical transformation. In a Daniell cell, for example, where the reacting system is

$$\text{Cu, CuSO}_4 \text{ solution; ZnSO}_4 \text{ solution, Zn,}$$

the total chemical action is

$$\text{Zn} + \text{CuSO}_4 = \text{Cu} + \text{ZnSO}_4,$$

zinc being dissolved up at one pole of the battery and copper being deposited at the other. Now the thermal effect of this reaction is obtained by subtracting the heat of formation of the zinc sulphate from that of the copper sulphate, both numbers referring to aqueous solutions of the salts (cp. p. 128). We thus get $106,090 - 55,960 = 50,130$ cal. per gram molecule, or 25,065 cal. per gram-equivalent. That is, when 32·5 grams of zinc displace an equivalent amount of copper from a solution of copper sulphate, 25,065 calories are evolved. Now, if the displacement takes place indirectly in a galvanic cell with production of electric current, 96,500 coulombs of electricity will be obtained, according to Faraday's Law, for every 32·5 grams of zinc dissolved. To express the numerical equivalence of thermal and electrical energy we have the equation 1 volt-coulomb = 0·2391 cal. The electrical energy then equivalent to the heat of the chemical reaction is $25,065 \div 0{\cdot}2391 = 104,800$ volt-coulombs. If we now divide this number by 96,500, the number of coulombs produced, we get 1·08 for the electromotive force of the cell expressed in volts, on the assumption that all the chemical energy of the reacting substances has been converted into electrical energy. Direct measurement of the E.M.F. of the Daniell cell gives 1·09 to 1·10 volt. The assumption then that the chemical energy is wholly converted into electrical energy is in this case very nearly true, and several other cells are known to which a similar simple calculation for their electromotive force is applicable. These cells, however, are all of a special type, and we shall therefore proceed by means of a reversible cycle of operations to deduce a formula of more general application.

In the first place the cell considered must be, like Daniell's, of a completely reversible or non-polarisable type (cp. pp. 328, 333), so that if we pass a current through it in the reverse direction of the current which the cell would of itself generate, the chemical action in the cell will be exactly reversed. Thus when the Daniell cell is in action the positive current within the cell moves with the positive ions from the zinc electrode to the copper electrode. If we now by using an external electromotive force make the current pass from the copper pole to the zinc pole, the chemical action which occurs is

$$Cu + ZnSO_4 = Zn + CuSO_4,$$

which is the reverse of the primary action of the cell, copper being dissolved and zinc deposited.

Let the cell act at the constant temperature T, and generate the quantity $C = 96,500$ coulombs of electricity. If the electromotive force of the cell is E, the electrical energy afforded by the cell is EC, and this may or may not be equal to Q, the diminution in chemical energy, which under ordinary circumstances would be the heat of the chemical action. Suppose the electrical energy produced to be less than the fall in chemical energy, then the element on working will give out $Q - EC$ as heat at the constant temperature T. Let now the system be heated to the slightly higher temperature $T + dT$, and let the quantity C of electricity be sent through the cell in the reverse direction, the temperature being kept constant. If the electromotive force has diminished by the amount dE owing to the change of temperature, the work done on the cell will be $C(E-dE)$, and the amount of. heat absorbed will be $Q-C(E-dE)$ on the supposition that the heat of the reaction does not change appreciably with the temperature. The system is finally cooled to the original temperature T, so that everything regains its initial state, a reversible cycle having been performed. On the whole, the system has done the external electrical work $C(E-dE)-CE=-CdE$, which must be equal to the fraction dT/T of the heat given out at the lower temperature. Now the quantity of heat given out is $Q-CE$, so that the heat transformed into work is

$$\frac{dT}{T}(Q-CE);$$

and we have therefore the equation

$$-CdE=\frac{dT}{T}(Q-CE);$$

or

$$E=\frac{Q}{C}+T\frac{dE}{dT}.$$

From this relation we see that in order to ascertain the electromotive force of an element from the heat of the chemical action within it, we must know the rate of change of the electromotive force with the temperature. If the electromotive force does not vary with the temperature, *i.e.* if dE/dT be zero, then the simple formula

$$E=\frac{Q}{C}$$

may be used. The electromotive force of a Daniell cell has a very small temperature coefficient, so in its case the simpler formula gives a result closely approximating to the truth. The more accurate formula gives in this case a still closer approximation to the observed electromotive force, and has been experimentally verified in many other instances for which the temperature coefficient is larger.

If we write the expression in the form

$$EC=Q+CT\frac{dE}{dT},$$

we see at once that the electrical energy and the chemical energy of the process are equal if dE/dT is zero; that the electrical energy is greater than the chemical energy if the temperature coefficient is positive, *i.e.* if the electromotive force increases with rise of temperature; and that the electrical energy is less than the chemical energy if the temperature coefficient is negative, *i.e.* if the electromotive force falls with rise of temperature. If a cell with a positive temperature coefficient of electromotive force is allowed to act, it will make up for the difference between the electrical and chemical energies by abstracting heat from neighbouring bodies; or, if no external heat is available, it will cool itself by working. The student is apt to imagine that this is a contradiction of the Second Law of Thermodynamics; but, like the self-cooling of a freezing mixture, the process here involved is not a cycle of operations, and the system cannot regain its original state without work being done upon it. What the Second Law contradicts is the existence of a system which, working in a *cycle*, by repeated self-cooling, can convert into work the heat of neighbouring bodies.

Concentration Cells.—From the discussion of such a case as that of two silver electrodes immersed in a solution of a silver salt through which a current is being passed, it is apparent that a change of concentration round the two electrodes may be brought about by the passage of electricity through the system. Now such a process may be performed reversibly if the changes in concentration round the anodes are relatively very small, although the total amount of electrolyte transported may be large. But the concentration changes round the electrodes may also be executed reversibly in the other ways already referred to in the previous chapter, viz. by reversible evaporation or freezing of the solvent, or by the use of a semipermeable membrane. It is thus evident that we can obtain, for example, a thermodynamical relation between osmotic work on the one hand and electrical energy on the other by changing the concentration first by means of a semipermeable membrane, and then bringing the system back to its original condition reversibly by the passage of an electric current. The osmotic work and the electric energy will here be equivalent to each other, as mechanical energy and electrical energy are completely interconvertible, so that knowing one, the other may be calculated. Assuming the gas laws for dilute solutions, the osmotic work may be very simply determined, and thus the electrical energy, and from that the electromotive force of any concentration cell may be deduced.

For simplicity of calculation we shall as heretofore consider a binary electrolyte with univalent kation and univalent anion, say silver nitrate. Let there be two solutions of the salt of osmotic pressure P and $P + dP$ respectively. The number of cubic centimetres in which 1 gram molecule of the salt is dissolved may then be denoted by V and $V - dV$ respectively. If u and v are the rates of migration of the kation and anion, the passage of 96,500 coulombs through the solution will necessitate the passage of $\frac{u}{u+v}$ gram molecules of kation through the surface of separation of the solutions in one direction, and of $\frac{v}{u+v}$ gram molecules of anion in the opposite direction. Since the anode dissolves up to supply kation to replace that which leaves the anodic compartment and also to neutralise the anion which arrives, there will be on the whole (cp. p. 220) an increase of concentration of $\frac{v}{u+v}$ gram molecules of salt in the anodic compartment and an equal diminution of concentration in the kathodic compartment. The passage then of this amount of electricity is equivalent to the transference of $\frac{v}{u+v}$ gram molecules from the kathodic to the anodic compartment.

Let us now consider the osmotic work which would have to be done on the supposition that the solution in the anodic compartment is originally the more concentrated solution. Cut off from the more dilute solution of osmotic pressure P a portion containing $\frac{v}{u+v}$ gram molecules of the salt. This may be done by interposing a semipermeable membrane at the proper place. Concentrate the portion cut off by forcing water through the semipermeable membrane into the rest of the more dilute solution until the osmotic pressure in the separated portion reaches the value $P+dP$. It is assumed that the total bulk of the original solutions is so great that the addition or removal of the quantity of water containing $\frac{v}{u+v}$ gram molecules has no appreciable effect on their dilution or osmotic pressure. Since the degree of dilution of the solution of osmotic pressure P is V, and that of the solution of osmotic pressure $P+dP$ is $V-dV$, the process of concentrating one gram molecule of salt from the first to the second dilution would involve the removal of dV cubic centimetres of water, and so the concentration of $\frac{v}{u+v}$ gram molecules necessitates the expulsion of $\frac{v}{u+v}\cdot dV$ cubic centimetres through the osmotic membrane. This volume has been moved against an osmotic resistance rising uniformly from zero at the beginning of the compression to dP at the end. On the average the pressure difference is $\frac{1}{2}dP$. The osmotic work done during this part of the operation is therefore

$$\tfrac{1}{2}dP\cdot\frac{v}{u+v}\cdot dV.$$

The separated portion of solution being now of the same osmotic pressure as the more concentrated anodic solution may be mixed with it. To restore to the more dilute solution the $\frac{v}{u+v}(V-dV)$ cubic centimetres of water necessary to bring it back to the original volume we may force this quantity through the semipermeable membrane separating the solutions. The difference of osmotic pressure on the two sides of this membrane is and remains dP, so that the osmotic work done during this operation is

$$dP \cdot \frac{v}{u+v} \cdot (V - dV).$$

On the whole $\frac{v}{u+v}$ gram molecules of dissolved salt have now been transferred to the concentrated from the dilute solution at an expenditure of work equal to

$$\tfrac{1}{2} dP \cdot \frac{v}{u+v} \cdot dV + dP \cdot \frac{v}{u+v} \cdot (V - dV)\,;$$

or

$$dP \cdot \frac{v}{u+v} \cdot (V - \tfrac{1}{2} dV) \text{ gram centimetres.}$$

Since the difference in dilution dV is very small in comparison with V, the total work may be written

$$L = \frac{v}{u+v} \cdot dP \cdot V \tag{9}$$

without sensible error.

In order now to evaluate this expression in quantities accessible to measurement, we may make use of the gas laws for dilute solutions. For one gram molecule of dissolved salt, the van 't Hoff coefficient of which is i (p. 240), we have

$$\begin{aligned} PV &= iRT \\ dP &= d\left(\frac{iRT}{V}\right) \\ &= RT\left(-\frac{idV}{V^2} + \frac{di}{V}\right). \end{aligned}$$

Substituting this value of dP in (9) we obtain

$$L = RT.\frac{v}{u+v}\left(-\frac{idV}{V} + di\right).$$

If the same transference of one gram molecule from the concentrated to the dilute solution were carried out electrically, the electric energy expended would be CdE, dE representing the electromotive force (due to the difference in dilution dV) which must be overcome, *i.e.* the electromotive force of the concentration cell. The work and electric energy are equivalent, so that when R is expressed in electrical units,

$$dE = \frac{RT}{C} \cdot \frac{v}{u+v}\left(-\frac{idV}{V} + di\right). \tag{10}$$

If we are dealing with very dilute solutions for which i may be assumed to be constant and equal to 2, we obtain

$$dE = -\frac{2RT}{C} \cdot \frac{v}{u+v} \cdot \frac{dV}{V}.$$

For finite differences of dilution we may imagine a great number of concentration cells of the kind just considered arranged in series one after the other. The finite electromotive force between the first and last of these will then be obtained by integration between the extreme dilutions V_1 and V_2, and will be

$$E = -\frac{2RT}{C} \cdot \frac{v}{u+v} \cdot \log_e \frac{V_1}{V_2}.$$

If, as is usual, we substitute the inverse ratio of concentrations $\frac{c_2}{c_1}$, for the ratio of dilutions we obtain

$$E = \frac{2RT}{C} \cdot \frac{v}{u+v} \cdot \log_e \frac{c_1}{c_2}. \qquad (11)$$

When $u = v$, *i.e.* when the anion and kation have the same velocities, $\frac{v}{u+v}$ becomes $\frac{1}{2}$ and the expression for the electromotive force is

$$E = \frac{RT}{C} \cdot \log_e \frac{c_1}{c_2}.$$

In order now to obtain this expression in a form suitable for comparison with experimental determinations of electromotive force we must express R in electrical units, *i.e.* volt-coulombs or joules. In these units $R = \frac{84{,}678}{10{,}200} = 8{\cdot}3$ (cp. pp. 7 and 30). Substituting decadic for natural logarithms and taking $T = 273 + 15$, we obtain finally

$$E = \frac{8{\cdot}3 \times 288 \times 2{\cdot}30}{96{,}500} \log_{10} \frac{c_1}{c_2}$$

$$= 0{\cdot}057 \log_{10} \frac{c_1}{c_2} \text{ volts.}$$

Now if $c_1 = 10c_2$, $\log_{10} \frac{c_1}{c_2} = 1$, and $E = 0{\cdot}057$ volts. This is the difference between the electrode potential of a univalent metal in normal and decinormal solutions of the corresponding metallion (p. 330).

If the electrovalency of the ions of the binary electrolyte is n, then nC coulombs of electricity must be passed through the solutions for the transference of $\frac{v}{u+v}$ gram molecules from the kathodic to the anodic compartment, and equation (11) becomes

$$E = \frac{2RT}{nC} \cdot \frac{v}{u+v} \cdot \log_e \frac{c_1}{c_2}.$$

those derived from it experiencing the same division of the right hand member by n (cp. p. 330).

It is an easy matter to calculate from the osmotic theory the electromotive force subsisting at the junction of two differently concentrated solutions of the same electrolyte, the speeds of migration of whose kation and anion are u and v respectively. We will assume for simplicity that the ions are univalent and that the electrolyte is completely ionised. The osmotic pressure of each ion will be P_1 in one solution and P_2 in the other. Let C coulombs be passed through the solution so that the kation is transferred from the higher pressure P_1 to the lower pressure P_2. The amount of kation which will pass the junction from P_1 to P_2 will be $\frac{u}{u+v}$ gram molecules, and similarly the amount of anion passing from P_2 to P_1 will be $\frac{v}{u+v}$ gram molecules.

Applying now the gas laws, we find that when a gas is isothermally expanded, the work it does per gram molecule (cp. p. 344) is

$$L = RT \log_e \frac{V_2}{V_1};$$

or, since Boyle's Law here holds good,

$$L = RT \log_e \frac{P_1}{P_2}.$$

Consequently for the transference of $\frac{u}{u+v}$ gram molecules of kation from P_1 to P_2 we have

$$L_k = \frac{u}{u+v} \cdot RT \log_e \frac{P_1}{P_2},$$

and for the transference of $\frac{v}{u+v}$ gram molecules of anion from P_2 to P_1 we have

$$L_a = \frac{v}{u+v} \cdot RT \log_e \frac{P_2}{P_1}.$$

The total work during the passage of C coulombs when the kation moves from the higher to the lower concentration is therefore

$$L = L_k + L_a = \frac{u-v}{u+v} \cdot RT \log_e \frac{P_1}{P_2},$$

and since this work is equivalent to the electrical energy,

$$CE = \frac{u-v}{u+v} \cdot RT \log_e \frac{P_1}{P_2}.$$

so that
$$E = \frac{u-v}{u+v} \cdot \frac{RT}{C} \cdot \log_e \frac{P_1}{P_2}.$$

If finally we evaluate RT and C as before, and substitute the ratio of concentrations $\frac{c_1}{c_2}$ for the ratio of osmotic pressures we obtain

$$E = 0{\cdot}057 \, \frac{u-v}{u+v} \cdot \log_{10} \frac{c_1}{c_2} \text{ volts.}$$

If $u > v$ the expression on the right is positive, since we assumed $c_1 > c_2$, and if $u < v$ it is negative. In the first case the current due to the concentration difference will flow from the concentrated to the dilute solution, in the second it will flow from the dilute to the concentrated solution. For $c_1 = c_2$ or $u = v$ the expression vanishes, *i.e.* there is no electromotive force between two parts of the same solution, and none at the junction of two solutions of different concentrations when the speeds of anion and kation are equal.

The best modern work on Thermodynamics suitable for chemists is MAX PLANCK'S *Treatise on Thermodynamics*, London, 1903. The student may also consult the article by CAREY FOSTER in WATTS' *Dictionary of Chemistry*, original edition, 3rd supplement, pt. ii. pp. 1922-1951 (1881).

VAN 'T HOFF'S original paper on Osmotic Pressure and the Thermodynamic Deductions for Dilute Solutions will be found in the *Philosophical Magazine*, 5th series, **26**, p. 81 (1888), and also in *Zeitschrift für physikalische Chemie*, **1**, p. 481 (1887).

W. NERNST. The Electromotive Activity of the Ions, *Zeitschrift für physikalische Chemie*, **4**, p. 129 (1889).

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THE END

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