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AN INTRODUCTION TO PHYSICAL CHEMISTRY

BY

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WITH 4 PLATES, AND NUMEROUS DIAGRAMS IN THE TEXT

REVISED EDITION

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PREFACE TO REVISED EDITION

In preparing this edition it has been recognised that strong electrolytes must now be treated as completely ionised at all dilutions; that the student must at an early stage learn to deal with solid electrolytes as aggregations of ions; and that the way must be prepared for a treatment of the mechanism of chemical changes in terms of electrons and protons. Chapter X. has been almost entirely re-written, and the rest of the text has been thoroughly revised. Opportunity has also been taken to correct errors which had inadvertently found their way into the first edition. My thanks are due to G. E. M. Jones, Esq., of Balliol College, Oxford, for many helpful suggestions in connection with this revision, and to Professor E. J. Cohen of the University of Utrecht for the frontispiece.

F. B. FINTER.

CLIFTON COLLEGE,
April, 1933

PREFACE

Scope.—This book is intended to be sufficiently elementary for any boy to use when he has succeeded in passing the School Certificate or London Matriculation examination. It covers the ground required for Higher Certificate or University Scholarships, and should be sufficient for those first-year university students who are not reading for honours in chemistry. The ground plan of the book is outlined in the introduction, together with a note on the meaning of the term "physical chemistry." It is intended to supplement and not to replace the ordinary chemistry text-book. The latter must be retained for the sake of the details in it, but it does not usually contain an adequate treatment of general principles owing to the other demands on its space.

Mathematical Treatment.—Mathematics in large doses is repugnant to the boy reader of a chemistry book—it savours of powder without the jam. Hence mathematical treatment has been reduced to a minimum; but it is hoped that with the help of the numerical questions given at the end of nearly every chapter there will be sufficient mathematics to satisfy the boy who is gifted in that direction, and also the master who cannot avoid it when he is teaching!

I have endeavoured to show that general principles can be grasped by boys with little mathematical ability, and that those who are more favoured will have a good foundation on which to place a more detailed study.

Historical Treatment.—Historical details have been included whenever space has allowed, but the historical sequence has been deliberately abandoned in dealing with the atomic

theory in Chapter III. Clear ideas about atoms and molecules are so important that the confusion of the nineteenth century must not enter the student's mind. Hence the information is given from a present-day standpoint, and when the student has assimilated this, he will read with all the more interest the historical developments which helped to bring us out of darkness into the light.

Experimental Treatment.—The student must do as much **experimental work** himself as can possibly be managed, and masters will be able to choose suitable experiments from the lists given at the end of each chapter. No experimental details are given, for a book of this size cannot be practical manual and reader's handbook as well. If details are required they must be sought in books devoted to *Practical Physical Chemistry*,* for I have preferred discussing general principles to giving minute details of experiments which students are tempted to learn and to repeat in examinations without ever carrying them out. At the same time, the experimental basis for all principles must be made clear, and stress has been laid on this at all points.

Demonstrations.—A demonstration is invaluable when a new idea is being introduced. It does not remove the need for experimental work by the students, but it makes an enormous difference to the value of a lecture. Suggested demonstrations are indicated at the end of Chapters IV. to XIII. inclusive, from which a selection can be made as desired.

References.—References are in most cases to standard works which the student can consult with profit. The master can always indicate when he wishes an original paper consulted, and the reference to this is usually to be found in the authorities which I have cited. In most cases I consider that an original paper is far too full of detail for the average boy.

Cross References.—These are purposely very numerous. A reference to a page beyond the one being read may be left at a first reading, but references back should always be looked at. If masters, by judicious questioning, see that this is

* *E.g.* the work by Findlay having that title.

conscientiously done, they will find the "water-tight compartments" of the knowledge acquired tend to break down—a big step towards a mature outlook on the subject.

Omissions.—Many points will be found missing which one might expect to find in a book of this type. Allowing for the omission of work of an advanced nature owing to the limited space available (*e.g.* the quantum hypothesis, photochemistry, Werner's co-ordination hypothesis, etc.), there remain such topics as the phase rule, surface tension, viscosity, and the laws of thermodynamics, which find no place in these pages. These omissions are of two kinds:

(1) Certain branches of the subject (*e.g.* the phase rule, thermodynamics and its applications), which I consider are better left out altogether than nibbled at in an odd page or two. A proper understanding of the phase rule, for instance, cannot be obtained from five or six pages of an elementary book. The student will be able to assimilate these points at a later stage, and he will not be seriously handicapped by omitting them at present.

(2) Certain branches of the subject which are adequately dealt with in the physics books possessed by students taking this course. It is of course futile for a boy to read physical chemistry unless he is learning physics as well. Hence to save space for more important matter there is very little said here about the gas laws, the kinetic theory of gases, the liquefaction of gases, the determinations of specific heats or refractive indices, the theory of the voltaic cell, the elementary principles of viscosity and surface tension. While it is admitted that the chemist's treatment of these subjects is not identical with that of the physicist, I have thought it better to save space in this way, relying on chemistry masters to fill in gaps where necessary with the help of the students' text-books of physics

Symbols.—I have used those recommended by the International Commission (1914) for Unification of Physico-Chemical Symbols.

Acknowledgments.—My thanks are due to Prof. T. V. Barker and Prof J. W. McBain for revising the

sections dealing with "Crystals" and "Colloidal Solutions" respectively. Also to Brig.-Gen. H. Hartley, who has allowed me to make use of his methods of demonstrating the behaviour of indicators.

Mr. V. O. J. Hodgson, B.Sc., has carried out the onerous tasks of revising the MS. and correcting the proofs, and has assisted with much valuable criticism.

Sir Richard Gregory has kindly given me permission to reproduce quotations from his *Discovery, or the Spirit and Service of Science* (see pp. 1, 75, 112), and also passages from *Nature*. I have borrowed freely from standard works; notably those by Dr. J. W. Mellor, Prof. H. S. Taylor, and Prof. A. Findlay, and my thanks are due to both authors and publishers for the facilities they have granted. I have given the references in each instance by way of acknowledgment.

I have also to thank for the loan of blocks Prof. E. N. da Costa Andrade (Fig. 2), Messrs. F. E. Becker & Co. (Figs. 12, 21A, 23, 31, and 32), Messrs. Baird and Tatlock, Ltd. (Fig. 21); and for the use of plates Messrs. P. Spence & Co., Ltd. (Plate II.), Prof. Tilden, Messrs. G. Routledge & Sons, Ltd., and Messrs. Major & Co. (Plate III.). Several figures are derived from Messrs. Longmans' publications, the sources of which are acknowledged under the blocks. In the preparation of Plate IV. I was assisted by A. G. Statton and F. H. C. Higgs, of the Clifton College laboratory staff.

Last, but by no means least, I am indebted to my wife, without whose constant encouragement the work would probably never have been completed.

F. B. FINTER.

CLIFTON COLLEGE,
July, 1926.

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INTRODUCTION

The Growth of a Building.—To watch a large building being erected is of absorbing interest. Everything seems to fit exactly into a place made ready for it. Groups of men are occupied with all kinds of work, apparently disconnected, such as mixing mortar, controlling hauling gear, bricklaying or carpentering; foremen are keeping a watchful eye on the progress in their own particular departments; and fresh material is continually arriving at the building site, where it is not unceremoniously dumped, but placed where it can best be utilised when the workers are ready for it. And so the structure gradually rises, for behind it all is a plan.

The foundations have been well and truly laid and are strong enough to carry the weight above; the materials used have been selected with care and no flaws have been found; the scaffolding, though of a temporary nature, is strong enough for its particular duty, and it will be removed when this is finished; the girders which are to be the permanent supports for the building have been rigorously tested and found adequate. Thus, to a spectator the building almost seems to grow by itself without the knowledge of the individual worker, the chaos of the site giving place gradually to the order of a magnificent building.

The Growth of Scientific Knowledge.—The growth of a branch of science proceeds in a very similar manner, the individual workers, each in their several departments, adding slowly to the already existing accumulation. A large number are busy discovering new facts, the materials with which progress is to be made; some are at work on the foundations, the fundamental laws, and others are erecting scaffolding, the

hypotheses, which serve as temporary aids and allow the facts to be correctly placed in the growing framework. This framework consists of the general principles of the science which, like the girders in a building, serve to knit together the mass of miscellaneous material into one ordered whole.

The Work of the Individual.—What then is the task of the individual workman? He is ignorant of the plan prepared by the architect, and is simply concerned with collecting materials and so placing them amidst the apparent confusion of temporary supports that the edifice gradually rises giving glimpses here and there of the finished design.

The scientific worker similarly helps in the growth of the Temple of Knowledge, which, as it increases in size, reveals little by little the underlying plan prepared by the Founder of the Universe. At present it is far from completion, but by insisting on accuracy in our facts we ensure the use of good quality materials, and by testing our hypotheses, theories and laws in the light of new discoveries we ensure the soundness of our framework and can remove any sources of weakness likely to be a bar to future progress.

The Growth of Chemical Knowledge.—Let us see how progress is being made in the science of chemistry. The material which the chemist employs for this purpose consists of a knowledge of the properties of various kinds of matter: solids, liquids, gases, solutions, etc. The fundamental laws forming the foundations have so far proved adequate; the work of scaffolding is proceeding steadily, and from time to time a rotten member, a faulty hypothesis, is removed and replaced by a better one; the framework of general principles is making an appearance. These are the great generalisations and theories which are discussed in this book, for physical chemistry is but the main framework on which the whole science of chemistry is growing.

The Meaning of the Term "Physical Chemistry."—The adjective "physical" is employed, in the first place, because the changes in matter with which chemists are concerned are essentially dependent on physical conditions such as temperature and pressure. No reaction is adequately described

unless the conditions under which it occurs are specified. Secondly, it is used because the properties of the substances we deal with are largely physical properties, and for complete knowledge of their behaviour we must know their densities, thermal and electrical properties, etc. And thirdly, it is becoming apparent that the very nature of matter is electrical, and the forces which control its behaviour are electrical forces.

Hence it is necessary for physics and chemistry to co-operate, and the student must learn to apply his knowledge of physics to chemical problems. A course in the general principles of chemistry thus becomes an elementary course in physical chemistry, and a step forward has been taken towards co-ordinating the knowledge gained in the two great departments of natural philosophy—chemistry and physics.

AN INTRODUCTION TO PHYSICAL CHEMISTRY

PART I.—THE FOUNDATIONS

CHAPTER I

SCIENTIFIC METHOD

"I value in a scientific mind, most of all, that love of truth, that care in its pursuit, and that humility of mind which makes the possibility of error always present more than any other quality. This is the mind which has built up modern science to its present perfection, which has laid one stone upon the other with such care that it to-day offers to the world the most complete monument to human reason." (Prof. H. A. Rowland.)

1. Scientific Methods.—It is not only to the specialist or future chemist that a scientific training is of value. The study of science gives an outlook on life, and an alert, critical, orderly mind which will be of use in any walk of life. It is not the facts learnt, but the habits acquired while learning them, which are so valuable. There is no need for most people to know that the formula for sugar is $C_{12}H_{22}O_{11}$, but the student, while learning the meaning of this formula, is gaining a knowledge of scientific method.

2. Scientific Method.—Progress in science has not been made in a haphazard way, but has followed definite lines, very nearly "according to plan." This plan of campaign, known as scientific method, commences with the recording of observations or facts (the stuff text-books are made of). It goes on to try and find a cause for each effect, and to examine the why and wherefore of everything connected with that effect. The steps in the process are roughly as follows.

(a) *Recording of Facts.*—Observations must be accurately made and recorded, for other people will regard these statements as truth, having, worse luck, no time to verify them all for themselves.

But volumes of isolated facts would be useless (imagine trying to learn French with only a dictionary to help you !), so the next step is :

(b) *Classification.*—Similar facts are grouped together and their study is rendered easier, just as a collection of postage stamps is " classified " or sorted out into countries. This, remember, is solely for convenience ; a small child would probably classify a number of stamps according to colour—all the red ones together, and so on, or according to shape—square, oblong, triangular, etc. : in each case **some common property** forming the basis of the grouping.

(c) *Explanation of the Facts* is next attempted. This is not so easy. We can often find a cause for a given effect, such that it will always produce that effect, and we are apt to say that the fact is thereby " explained." We have really only deferred the explanation. Probably, we shall never be able to answer satisfactorily the question, " *Why* do the wheels go round ? " Any reply only indicates " *how*," or in what manner, they go round ; " steam pressure pushes them round " —yes, but why should it ? To say it pushes them round only states the fact and doesn't explain it. " *Explanation of a fact* (says Professor Fowler) *can mean no more than its correlation with and co-ordination among an existing body of other facts which can all be similarly related to the same general principles.*" *

Thus all we can hope for is to relate cause and effect, and, in the words of Aristotle, " let us first understand the facts, and then we may seek the cause."

(d) *Generalisation.*—If we have had bacon for breakfast every morning for a long period, and can never remember having had any alternative, it would be legitimate for us to " generalise " and remark that " we always have bacon for breakfast." It would be a true statement of the facts, and

* *Nature*, April 21, 1923.

from it we could tell what we had for breakfast on any particular date. But if after this remark we are given an egg one Sunday morning, and no bacon, the generalisation would evermore be incorrect. It would have to be qualified by saying " always, except on Sundays " or " nearly always."

A **generalisation** then is a general statement of a large number of facts, and it is arrived at by a mental process known as **induction** * (" leading up " from the particular cases to the general case). It is an economy. *E.g.* if we say that " all carbonates treated with hydrochloric acid evolve carbon dioxide," we know the action of this acid on the carbonates of copper, lead, calcium and all other metals. Some generalisations are of sufficient importance to be used as rules for future guidance. They are known as :

(e) *Natural Laws.*—These are the foundations of science, being simply statements of fact free from any guesswork or theory. For example, the law of constant composition (see Chapter III.) simply states that a particular compound has been analysed thousands of times and **has always been found** to have the same composition, and moreover that this **has been found to be true for all substances examined up to the present.**

Laws which merely state a numerical relation between varying quantities are termed :

(f) *Quantitative Laws.*—Thus, Faraday's first law of electrolysis (see Chapter X.) states that the quantity of an element liberated during electrolysis has always been found to be **directly proportional to** the quantity of electricity which has passed through the solution. Double one of these and the other is found to be doubled ; four times the quantity of electricity has always been found to liberate four times as much of the element ; and so on.

Quantitative laws are sometimes " exact " and sometimes " approximate."

(g) *Exact Laws* are those whose statements appear to be exact statements of the truth, inasmuch as increased experimental skill gives results nearer and nearer to the statements

* Latin, *in-duco* (I lead towards).

made in the law. Examples are Ohm's law, Faraday's laws of electrolysis, Snell's law of refraction,* and the laws of chemical combination (see Chapter III.).

(h) *Approximate Laws* are those which state an approximate relation between quantities. Thus Boyle's law states that PV is approximately constant; Dulong and Petit's law states that specific heat × atomic weight is approximately 6·4. In such cases rough work might show PV to be constant or sp.ht. × at.wt. = 6·4, but with increasing experimental skill the results would diverge more and more from these definite numerical relations, and so it is clear that ideal work (free from error) would show them to be only approximately realised (see p. 9).

(i) *Hypotheses* are now made in an attempt to find causes for the effects noted. These are **guesses,** and they must be in agreement with all the facts—any fact flatly contradicting a hypothesis is enough to cause its rejection. However, a leaky roof is better than no roof at all, and we sometimes find a faulty hypothesis retained, as something to work on, until a better can be found. A working hypothesis may, in fact, be retained **as long as it is useful to progress.**

(j) *The Testing of Hypotheses.*—For this purpose, the hypothesis is assumed to be correct, and by a mental process we "deduce" the consequences of this being the case. By **deduction** † we mentally "lead down" from the general statement to the particular cases (the exact opposite of induction). Thus, assuming the ionic hypothesis to be correct, we can deduce, among other things, that concentrated hydrochloric acid will precipitate solid salt if added to brine (see p. 232).

The deduction can as a rule be **verified** by experiment, and if the facts disagree with the deduction the hypothesis is pronounced faulty. Note that twenty or more verified deductions will not prove a hypothesis to be correct, but **one fact disagreeing is sufficient to show that it is incorrect.**

* It is interesting to note that Kepler made seventeen unsuccessful attempts to discover the relation between the angle of incidence and the angle of refraction

† Latin, *de-duco* (I lead away from).

Thus, a detective investigating a murder finds a blood-stained knife near the body (a clue). His hypothesis is that the man died from being stabbed. He draws the deduction that a wound should be found if looked for. This can be verified. Absence of wound proves the hypothesis incorrect; but if a wound **is** found it does not prove the hypothesis correct, for the cause of death might have been something else.*

(k) *A Theory* is a hypothesis of wide importance which has stood the test of time; *i.e.* after repeated testing it has never been found at variance with the facts. There is no hard line between hypotheses and theories—the atomic theory, for example, was originally Dalton's "hypothesis" and is often so called at the present day. Laws, on the other hand, are statements of fact. They are therefore of a totally different nature from theories, which must remain for ever open to doubt, even though the doubt may be continually decreasing.

CHAPTER II

LIMITS OF ACCURACY

1. Experimental Error.—All observations are liable to be inaccurate, for we are but mortal, and must work with hands, eyes, and instruments which are far from perfect.

Yet "accuracy of facts is essential"! Let us rather say "greatest possible accuracy is essential," and if we can state the possible amount of error in our recorded facts then at least no one will be deceived into regarding them as absolute truth. A knowledge of the limits of accuracy attainable in experimental work is therefore as important as the work itself.

2. Avoidable Errors.—Leaving out gross carelessness, there remain certain sources of error which can be removed, or at any rate minimised: *e.g.* impurities in material, variations in temperature and pressure during an experiment,

* A novel in which this situation arises is *The Mystery of Norman's Court* by John Chancellor.

incorrectly calibrated apparatus, etc. In general, **repetition of an experiment in different ways using different forms of apparatus and different samples of material** will show, by the agreement in the results, to what extent these errors are present (see also paras. 3 and 6). In some cases the error can be estimated and allowed for. *E.g.* a **"correction" can be applied** to calorimetric measurements to allow for heat lost by radiation.

Experiments should always be designed to avoid sources of error such as transference of material from one vessel to another, **or difficult measurements** such as gaseous volumes or small temperature changes.

Large quantities of material should be used whenever possible **to reduce the relative error.** It is relative error which matters, for the absolute error is usually fixed by the nature of the apparatus. *E.g.* if a balance can weigh correctly to ·01 gm. the possible error in weighing 1·000 gm. is $\frac{5}{1000}$ or ·5 %, but in weighing 100·000 gms. the possible error is only $\frac{5}{100000}$ or ·005 %.

3. Unavoidable Errors.—The sum total of the errors made in carrying out an experiment is termed the "experimental error." Assuming that all possible precautions have been taken, this error is due to the observer, handicapped by his senses and his apparatus, and is sometimes called the "personal error" of the observer. Hence a more accurate result can be obtained by taking a mean value from repetitions of the experiment by different observers. There always remains, however, the possibility of some **constant error** affecting every result in the same way and thus remaining unsuspected.

Thus, all measurements of the density of atmospheric nitrogen were in agreement, and no error was therefore suspected, but there was a constant error due to the presence of argon in the nitrogen, which was making each value greater than the true density of nitrogen.*

4. Mean Values.—Assuming that some results will be

* See Freund, *Study of Chemical Composition*, p. 89, Camb. Univ. Press, for an account of Lord Rayleigh's work in this connection.

too big and others too small, *i.e.* some errors +ve and others −ve, the law of probability leads us to the arithmetic mean as the value nearest to the correct one, and the greater the number of individual readings the nearer the mean will be to the truth. (NOTE.—Any reading widely divergent from the others is neglected in taking the mean, it being assumed that some unique error has been made in this case.)

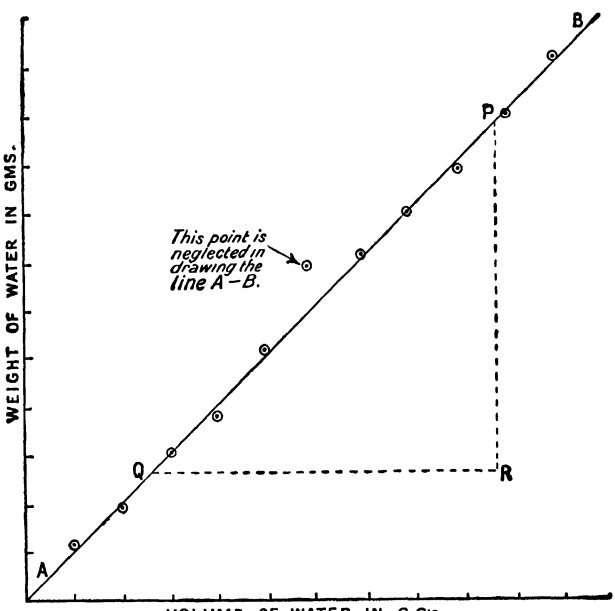


FIG 1.—Graph showing the most probable value of the weight of 1 c.c. of water obtained from a series of measurements. The points P and Q may be taken anywhere on the line AB, and $\frac{PR}{QR}$ gives the required value.

A very accurate method of obtaining the mean of a series of readings is the **graphical method**, and Fig. 1 shows clearly the "probability" that the curve represents the correct values—some readings being above it and an equal proportion below.

5. Calculation of Results.—The strength of a chain is governed by its weakest link. If in an experiment involving many measurements, there is an error of 1 % in **any one measurement,** then, however carefully the others are made, the final result is bound to be liable to a 1 % error. Moral: (1) Don't waste time by making the other measurements to an unnecessary degree of accuracy. (2) Don't waste time in arithmetic by working to many places of decimals when you know that only three significant figures are worth keeping in your answer. (3) Find out before you start work the limits of accuracy possible and so avoid the waste of time just mentioned.

NOTES.—(1) To state the weight of a body as 1 gm. means that its weight lies somewhere between ·5 gm. and 1·5 gms., and that for some reason or other it is not known more accurately. If you had been working to an accuracy of 1 % this would have been recorded as 1·00 gms., meaning something between ·995 gm. and 1·005 gm. (2) To obtain "3 figure" accuracy, the fourth figure must be roughly determined. Thus ·9956 would be recorded as ·996, and ·9954 as ·995.

EXAMPLE.—The density of a liquid is required and its volume is found to be 49·8 c.c. There is, therefore, bound to be a possible error of 5 in 4980, or ·1 % in the density, however carefully it is weighed. The weighing must, however, be correct to 1 part in 1000, so that if it weighs about 100 gms. we must be correct to the nearest $\frac{1}{10}$th gm. If it is recorded as 102·5432 gms., time has been wasted; the "4" is required to decide between 102·5 and 102·6 and that is all. The density will then be $\frac{102{\cdot}5}{49{\cdot}8}$ gms. per c.c. $=2{\cdot}058 \pm {\cdot}002$. To have carried the arithmetic to 2·05823 would have been absurd.

6. Limits of Accuracy.—If the same observer repeats the same operation with his utmost skill, the results he obtains will differ from the mean by small amounts representing his personal error or limit of accuracy in this operation. Thus the density of oxygen obtained from potassium chlorate was measured by *Morley* * with the following results:

* Freund, *Study of Chemical Composition*, p. 88.

Density in gms. per c c.	Mean value.	Differences from the Mean.	Average or Mean Error.
1·42920		+·00002	
1·42860		−·00058	
1·42906		−·00012	$\frac{\cdot 00158}{7}$ or
1·42957	1·42918	+·00039	
1·42910		·00008	
1·42930		+·00012	·00023
1·42945		+·00027	

His limits of accuracy are therefore known, and the density value is seen to be reliable to not more than 4 figures; *i.e.* 1·4292 ± ·0002. If now he obtains a mean value 1·42908 for the density of oxygen from another source, the only conclusion to be drawn is that these values are identical—the difference being within the "**limits of experimental error.**" This frequently used term is, therefore, seen to have a very definite meaning. (*The student should determine his own limits of accuracy in some simple operation so as to make this quite clear* (*see experiment* 1, *p.* 10).)

We can therefore gauge the accuracy of experimental work, and it is interesting to note how this is increasing as our laboratory resources increase.

	Weight of Silver Chloride obtained from 100 gms. Silver	Experimental error.*
Berzelius, 1820	132·757	±·019
Stas, 1865	132·8445	±·0008
Richards and Wells, 1905 . .	132·807	±·0005

And in 1910, in a list of atomic weights published by *Clarke*, the value for silver is given as 107·880 ± ·00029; *i.e.* correct to 3 parts in 1,000,000. The exactness or approximate nature of a quantitative law can obviously be put to the test when the limits of accuracy can be defined in this way. Thus,

* From Freund, *Experimental Basis of Chemistry*, p. 376, Camb. Univ. Press

Landolt has verified the law of conservation of matter, working to an accuracy of 1 part in 10,000,000. He has not "proved" the law. It is impossible to "prove" laws. But he has found no deviations from it greater in magnitude than 1 part in 10,000,000, and if deviations do exist they are beyond the limits of accuracy so far attainable.*

PRACTICAL WORK: *Experiment* 1.—Find the weight of 1 c.c. of water by successive weighings of a stoppered bottle containing 0, 1, 2, 3, etc. c.c. of distilled water delivered from a burette (use the same portion of the burette throughout). Determine your personal error in carrying out this operation.

QUESTIONS.—1. Write a short detective story to show the meaning of the terms "hypothesis" and "deduction," and the method of verifying hypotheses.

2. Calculate the value of PV correct to 4 figures if $P=3757{\cdot}18$ and $V=101{\cdot}216$.

3. If $\alpha=0{\cdot}00019$ show that if $(1+\alpha)^3$ is taken to be $1+3\alpha$ the error is negligible.

4. If 969·355 gms of silver yield 1287·72 gms of silver chloride, and the equivalent weight of chlorine is 35·5, what is the equivalent weight of silver?

CHAPTER III

FUNDAMENTAL LAWS. THE ATOMIC THEORY

This chapter is mainly revision of work done in previous terms, and it is therefore somewhat condensed. It is recommended that historical books should be read to supplement it (*e.g.* Lowry, *Historical Introduction to Chemistry;* Freund, *Study of Chemical Composition;* or the *Alembic Club Reprints*).

1. The Fundamental Laws.—(a) *The law of conservation of mass* (or indestructibility of matter) states that:

"The mass of a system† is not affected by any chemical change within the system."

* For fuller discussion the student should read Freund, *Study of Chemical Composition*, Chapter III.

† A "system" is formed by one or more substances occupying a space with definite boundaries.

This was apparently taken for granted in the past, for we find nearly 2000 years ago *Lucretius* remarking that "out of nothing, nothing ever comes," and yet up to the end of the eighteenth century nobody seems to have produced any experimental evidence for such a statement. In 1785, however, *Lavoisier* showed by his experiments on fermentation that (mass of sugar+mass of water) was always equal to (mass of alcohol+mass of carbonic acid), and generalising from this and from some of his earlier quantitative work (on the calcination of metals), he stated the law * and remarked that "equations" could in consequence be written such that:

mass of reacting substances=mass of products.

This law has since been verified to a high degree of accuracy (see p. 10).

(b) *The law of conservation of energy* (or first law of thermodynamics) is of great importance in chemistry since all chemical changes involve changes in energy. The "activity" of a person depends upon his *energy or capability of doing work.* A stone at the top of a hill possesses energy by virtue of its position, for it can roll down and "do work" on anyone in the way. Similarly a chemical system possesses chemical energy capable of being transformed into other forms of energy. We should find the winters chilly if it were not so, for in burning coal we are obtaining *heat energy from chemical energy.* Other examples of energy changes are:

(1) Chemical energy to light energy (in burning magnesium).
(2) Light energy to chemical energy (carbon assimilation by green plants in sunlight). (See p. 191.)
(3) Chemical energy to electrical energy (in accumulators and all voltaic cells).
(4) Electrical energy to chemical energy (in electrolysis).

The ease with which a substance reacts (its reactivity), and the converse (its stability or inertness), are dependent on the amount of chemical energy it possesses.

* For his actual words, see Lowry, *Historical Introduction to Chemistry*, p. 389.

The law states that:

"The total energy of any system cannot be altered by any action between its parts, though it may be transformed from one form to another."

Thus, whenever Q units of heat energy are produced, an equal amount of some other form of energy is always found to have been used up. In other words, **one gets no work for nothing** (as most employers of labour know only too well). (See p. 215 for further notes on "Chemical Energy.")

(c) *The law of constant composition* (or definite proportions) states that:

"A definite chemical compound always contains the same elements combined in the same proportions by weight."

This is our main guide when deciding whether a substance is a compound or a mixture. *E.g.* the variable composition of the atmosphere is taken as proof that it is a mixture. (See also p. 38.)

The first statement of this law appears to have been due to *Proust* in 1799, but some doubt as to its validity existed until the work of *Stas* in 1865 verified it to an accuracy of ·004 %. The figures on p. 9 give some idea of the exactness with which it has been established at the present day.

By analysis of compounds, the combining proportions of the elements can be determined. These are referred to a standard for convenience and are then known as **equivalent weights.** Thus:

"The equivalent weight of an element is that weight of it which will react with 8 parts by weight of oxygen."

Originally 1 part by weight of hydrogen was taken as the standard, but so few elements will react directly with hydrogen that the oxygen standard has been substituted as more suitable.

(d) *The law of multiple proportions* recognises that elements can combine in more than one proportion (*e.g.* there are 5 different compounds of nitrogen and oxygen), but that in all such cases:

"The weights of one of the elements which are combined with a fixed weight of the other are simply related."

EXAMPLE.—In the 5 oxides of nitrogen, if we take weights of each containing 1 gm. of nitrogen the weights of oxygen are found to be $\frac{8}{14}$, $2\times\frac{8}{14}$, $3\times\frac{8}{14}$, $4\times\frac{8}{14}$, $5\times\frac{8}{14}$ which are in the simple proportion 1 : 2 : 3 : 4 : 5.

It follows that **an element can have several equivalent weights, but that these will all be simply related.**

(e) *The law of reciprocal proportions* (or combining weights). The laws above mentioned do not cover the majority of chemical changes which are "interactions" between two or more substances:

E.g. simple replacement—$Zn+CuSO_4=Cu+ZnSO_4$,
or double decomposition—$AgNO_3+NaCl=AgCl+NaNO_3$,

but the work of *Richter* (*circa* 1795) and *Berzelius* (1811) showed that a statement could be made which would include all these cases.

"Things which are equal to the same thing are equal to one another," says Euclid.

"Weights of elements which are equivalent to the same thing (viz. 8 gms. of oxygen) are equivalent to one another," says the chemist.*

EXAMPLES.—(1) 12 gms. magnesium ≡ 1 gm. hydrogen
8 gms. oxygen ≡ 1 gm. hydrogen.
and 12 gms. magnesium ≡ 8 gms. oxygen.

(2) 32·5 gms. zinc ≡ 1 gm. hydrogen.
31·75 gms. copper ≡ 8 gms. oxygen ≡ 1 gm. hydrogen.
and 31·75 gms. copper are displaced from copper sulphate by 32·5 gms. of zinc.

NOTE.—In the case of an element possessing more than one equivalent weight, the law does not tell us which one is

* There are several long statements of this law, one of which must be learnt for examination purposes, but the essential meaning of them all is given above. The least confusing statement appears to me to be as follows: "To every element can be assigned a 'combining weight' (one of its equivalent weights) In any reaction, the relative weights of the elements taking part are simple multiples or submultiples of these combining weights."

to be considered here, but as they are simply related we can cover this complication as follows:

w gms. of nitrogen $\equiv$ 1 gm. H.
8 gms. of oxygen $\equiv$ 1 gm. H.

then $w \times \frac{m}{n}$ gms. of nitrogen will react with 8 grms. of oxygen, where m and n are small whole numbers.

3. The Atomic Theory.—

"The Atomic Theory has triumphed. Its opponents, which until recently were numerous, have been convinced and have abandoned one after the other the sceptical position that was for a long time legitimate and no doubt useful. Equilibrium between the instincts towards caution and towards boldness is necessary to the slow progress of human science: the conflict between them will henceforth be waged in other realms of thought." *

The atomic theory is in satisfactory agreement with known chemical facts. It has helped us to build up the system of chemistry as we know it to-day with its formulæ, indicating in "shorthand" the composition of substances, and its equations which enable us to calculate reacting quantities; and it even assists us in this way to predict to a certain extent the possibility of reaction between substances and the probable nature of the products.

(a) *Present State of the Theory.*—(1) In Dalton's time no one believed that it would ever be possible to demonstrate **the existence of atoms,** but this has actually been done. Single atoms have not been "seen," but they have been made to reveal their presence in several ways. Thus, when an electric discharge passes through a gas, under certain conditions, the atoms may move at such high speeds that on striking a screen of suitable material a visible effect is produced,—a flash of light. If this is hard to understand, remember that a rifle bullet is invisible in flight, but it reveals its presence when it strikes a target.

Again, *C. T. R. Wilson* has devised a very beautiful

* Perrin, *Atoms* (1916 ed.), p. 257, Constable.

experiment by which **the track of a moving atom can be made visible.** Fig. 2 shows some typical "atom tracks." Each fork indicates that a moving atom has collided with another atom in its path and been deflected, at the same time setting the other in motion. Further evidence will be given in Chapter XIV., so that the speculative nature of the hypothesis has clearly been very much reduced. We can in fact deal with invisible atoms to-day with as much confidence as we can deal with the invisible gases forming the atmosphere. "To-day (says Millikan *) we are counting the number of atoms in a given mass of matter with as much certainty and precision as we can attain in counting the inhabitants of a city."

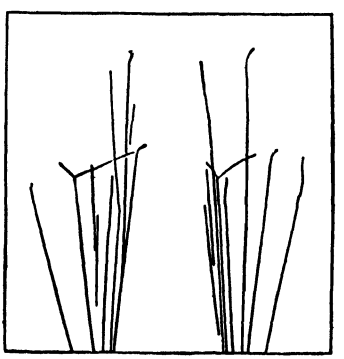


FIG. 2.—Atom tracks. (*By kind permission of Prof. E. N. da Costa Andrade.*)

(2) *Dalton* supposed that the atom was indivisible, but this is unnecessary if we decide to define **the atom as the smallest particle of an element which can take part as a whole in a chemical change.** Let us admit that the atom is a complicated system of electrically charged particles (see Chapter XIV.), yet we cannot divide it into these by any "chemical" process; *i.e.* by any of the methods by which elements can be caused to combine or compounds to decompose. Hence, as a hypothesis designed to account for the experimental facts which we call "chemical changes," we can regard the atom simply as a particle.†

(b) *Atomic Weights.*—Assuming the correctness of the atomic theory we can determine the **relative weights of**

* Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1. 754.

† Even if we attempt to "explain" chemical reactions in terms of electrons instead of atoms, the validity and use of the atomic hypothesis remains unchanged. We are only superimposing an additional "electronic hypothesis" in an attempt to get still nearer the truth.

different atoms—their so-called "atomic weights." A knowledge of these is of great importance, for they are needed in determining the formulæ for substances (see para. 5), and are used in all calculations based on formulæ and equations. If the zinc atom weighs 65 units and the chlorine atom 35·5 units, then the fact that zinc chloride contains 65 gms. of zinc combined with every 71 gms. of chlorine fixes the empirical formula for this substance as $ZnCl_2$.

What is the "unit" referred to here? We have stated that the zinc atom weighs 65 units and this unit must be incredibly small, for it would take millions of these atoms to weigh as much as a grain of sand. As a matter of fact it weighs about ·00000000000000000008 gm. (8×10^{-21} gm.)! **The unit chosen is $\frac{1}{16}$th of the weight of an oxygen atom** and the zinc atom weighs 65 times as much. Hence, the **atomic weights are really relative weights,** or numbers indicating how many times the atoms are as heavy as $\frac{1}{16}$th of an oxygen atom.

Originally the weight of one hydrogen atom was chosen as unit (*cf.* p. 12), but the oxygen standard has now been adopted and on this basis the atomic weight of hydrogen = 1·008. This can be taken as 1 for most purposes, when great accuracy is not required.

The same unit must of course be employed when referring to weights of "molecules." **A molecule is the smallest particle of a substance which can lead an independent existence** (see p. 22), and **molecular weights** are therefore numbers indicating how many times the molecules of substances are as heavy as $\frac{1}{16}$th of an oxygen atom.

It is useful in practice to base our calculations on the gram as the unit of mass, so we **imagine that the oxygen atom** could be magnified until it **weighed 16 gms.** If all the other atoms changed in the same proportion we should find for the atomic weight of zinc 65 GRAMS, and for the molecular weight of a compound such as sulphuric acid, H_2SO_4, (2+32+64) or 98 GRAMS. The molecular weight expressed in grams is referred to as the GRAM MOLECULAR WT. or MOLAR WT. (shortly 1 MOL).

(c) *Atomic Weight Determination.*—Analysis of compounds

gives us the combining proportions or equivalent weights of the elements, and IF one atom always combined with one atom and no more, these would be the relative weights of the atoms. Thus, analysis of red copper oxide would give

$$\frac{\text{wt. of copper}}{\text{wt. of oxygen}} = \frac{127}{16} = \frac{\text{wt. of so many million copper atoms}}{\text{wt. of an equal number of oxygen atoms}} = \frac{\text{wt. of one copper atom}}{\text{wt. of one oxygen atom}}$$

so that the atomic weight of copper would be 127.

Unfortunately for us **this is not always the case** (*vide* the law of multiple proportions). There are two oxides of copper, so if one is CuO the other cannot be! It might be Cu_2O, Cu_3O, etc. Which is the red one? Unless we know, then

$$\frac{127}{16} \text{ might be } \frac{\text{wt. of 1, 2, 3 or more copper atoms}}{\text{wt. of 1 oxygen atom}}$$

and 127 might be a multiple of the atomic weight of copper. In other words the **atomic weight is some multiple of the equivalent weight** and the difficulty is to decide what multiple! The equivalent weight of copper is 31·75 or 63·5 according to which oxide we analyse, but its atom cannot weigh 31·75 units in one compound and 63·5 in another.

(d) *Valency.*—Atomic Weight $= n \times$ equivalent weight where n is a small whole number, and if we define the **valency of an element** as:

The number of hydrogen atoms which the atom of the element is worth (*valoir* = "*to be worth*") *in combining capacity,*

then the value of n is equal to the valency so defined. Thus, in ammonia the equivalent weight of nitrogen is $4\frac{2}{3}$. If nitrogen is trivalent in this compound (*i.e.* its atom will combine with 3 hydrogen atoms giving a compound $N\langle H, H, H$) then we should have

$$\frac{\text{wt. of 1 nitrogen atom}}{\text{wt. of 3 hydrogen atoms}} = \frac{4\frac{2}{3}}{1},$$

and therefore $\frac{\text{wt. of 1 nitrogen atom}}{\text{wt. of 1 hydrogen atom}} = \frac{3 \times 4\frac{2}{3}}{1} = \frac{14}{1}$;

i.e. atomic weight = 3 × its equivalent IF it is 3 valent.

This notion of valency can be extended to include compounds not containing hydrogen, for things which are equivalent to the same thing are equivalent to one another. Hence if oxygen is bivalent $\left(\text{its compound with hydrogen being } \begin{matrix} H \\ H \end{matrix}\!>\!O\right)$, then its compound with trivalent nitrogen will be

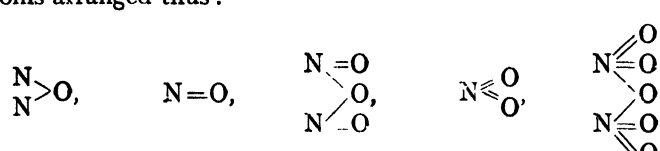


the 2 nitrogen atoms being worth 3 oxygen atoms in combining capacity.

Unfortunately there is a snake in the grass! If we apply this idea of valency without care we shall be led into error, for we have arrived at the conclusion that

$$\text{valency} = \frac{\text{atomic weight}}{\text{equivalent weight}}.$$

Now there are 5 oxides of nitrogen giving us on analysis 5 equivalent weights for nitrogen! Has this element then 5 different valencies? This would mean molecules with the atoms arranged thus:

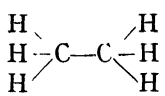


and we have good reasons to suppose that certain of these arrangements do not exist. Again, consider the compound known as red lead: analysis gives the equivalent weight of lead $= \frac{3 \times 207}{8}$, and the atomic weight of lead is 207. Is the valency $\frac{8}{3}$? This is absurd!

We conclude that if the **valency of an element really**

means the combining capacity or "saturation capacity" of its atom (its original meaning), and is not merely the quotient $\frac{\text{atomic weight}}{\text{equivalent weight}}$, then we must get to know how the atoms forming a molecule are linked together before their valencies can be determined.

EXAMPLE.—We have good reason to suppose that in the molecule of ethane the hydrogen atoms are symmetrically arranged in relation to each carbon atom. We may depict the molecule as follows:

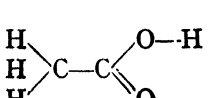


but must remember that in the actual arrangement of the atoms in space they are not all in one plane. In this case, then, each carbon atom is saturated by 4 hydrogen atoms or their equivalent (the quadrivalency being depicted by means of the four valency "bonds"). But if we had divided the atomic weight of carbon by its equivalent weight in this compound we should have obtained a number $\frac{12}{4}=3$. This is certainly not the value of the carbon atom in the ethane molecule and has no right to be called its valency.

Again, it will be noticed that on p. 17 we had to assume the constitution of the ammonia molecule in establishing that the valency of nitrogen was numerically equal to $\frac{\text{atomic weight}}{\text{equivalent weight}}$

In a compound containing more than two elements the valencies of the elements in it cannot be determined from the $\frac{\text{atomic weight}}{\text{equivalent weight}}$ quotient alone.

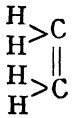
EXAMPLE.—Acetic acid has the formula $C_2H_4O_2$, but unless we know that the atoms are arranged thus in its molecule:



how are we to determine the valencies of carbon and oxygen in this compound? It cannot be done until, by studying the reactions of this compound, we have discovered how the atoms are linked together; *i.e.* determined the **structure of the molecule** as depicted by the graphic or structural formula above.

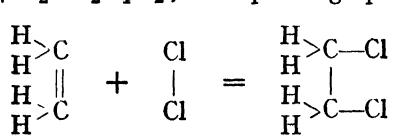
Indeed, the difficulty is not yet fully presented, for it appears that atoms sometimes keep some of their valencies "**latent**" or unsatisfied. The compounds in such cases are said to be "**unsaturated**" because they still have some ability to combine with other elements.

EXAMPLE.—In the molecule of ethylene the atoms are believed to be arranged



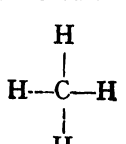
and the carbon atoms are not saturated. By virtue of the **residual valencies** this compound can form **additive compounds** by combining with other elements.

E.g. $C_2H_4+Cl_2=C_2H_4Cl_2$; or depicted graphically

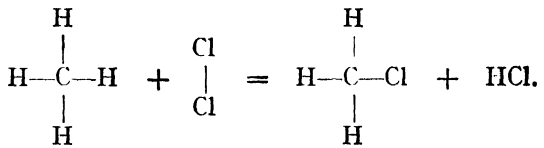


This compound (ethylene dichloride) is "**saturated,**" for its molecule cannot add on any more atoms. Any reaction with this compound (other than decomposition) must be a "**substitution**" where one atom can replace or be substituted for another.

EXAMPLE.—Methane is a saturated compound,



and its molecule cannot take on any other atoms without losing some of its hydrogen atoms, *e.g.*



Hence we may find compounds of an unsaturated nature like nitric oxide or carbon monoxide, and $\frac{\text{atomic weight}}{\text{equivalent weight}}$ would give us no idea of the saturation capacities or valencies of the atoms in such cases.*

4. Methods of Determining Atomic Weights.—Since atomic weight $= n \times$ equivalent weight, we must

(1) Find the equivalent weight **as accurately as possible ;**
(2) Find the value of n approximately ; take the nearest whole number to this and
(3) Multiply by it the accurate equivalent weight.

(*E.g.* if eq. wt. $=107{\cdot}88$ and the value of n is found to be approximately ·96 then the at. wt. is $107{\cdot}88 \times 1$.)

The first method of finding "n" which was really satisfactory was due to *Cannizzaro* (1858) and was based upon the work of *Gay Lussac* (1808) and *Avogadro* (1811), to which we must therefore refer.

Gay Lussac's Law states that "*the volumes of interacting gases are always simply related to one another and to the volumes of the products* (*if gaseous*), *assuming that all measurements are made at the same temperature and pressure.*"

This, like all "laws," is simply a statement of observed facts, but it is only an "approximate law" (see p. 4). Probably under ideal conditions, which can never be realised in practice (*e.g.* very small pressures and very high temperatures), the law would be "exact," but under existing conditions we find slight deviations. Thus, for the ratio by volume in which

* Further notes on valency will be found in Chapter XIV.

hydrogen and oxygen combine at N.T.P. we find from the most accurate work a mean value 2·003 : 1.

Avogadro's Hypothesis was put forward to account for this law, and his suggestion was that

" Equal volumes of all gases contain equal numbers of molecules when at the same temperature and pressure."

The term " molecule " was introduced by Avogadro because attempts to explain Gay Lussac's law in terms of atoms had led to failure. Thus it had been suggested that reacting gases contained equal numbers of atoms per c.c., but this led to an absurdity in the case of hydrogen and chlorine combining to form hydrochloric acid, for experiment showed :

hydrogen	+	chlorine	→	hydrochloric acid gas
1 vol.		1 vol.		2 vols.

and if this was

1 atom + 1 atom → 2 atoms (compound atoms)

then the hydrogen and chlorine atoms would have had to break in half ! If anyone accused you of dancing with two partners at once you would probably think he had gone mad, and the hydrogen atom is just as incapable of being simultaneously in two different " atoms " of hydrochloric acid gas ! Suppose that hydrogen gas consists of particles which are already complex, then **during the chemical action** these particles might break up into their constituent atoms (compare definition of atom, p. 15). Avogadro decided to *call the smallest particle of a substance* (*element or compound*) *capable of independent existence a* **molecule,** admitting that this might contain atoms but that without chemical action the atoms would remain combined. Bubbles of oxygen then contain millions of molecules, and the contents of these molecules are never set free unless the oxygen is chemically reacting with something else. We can now write

hydrogen	+	chlorine	→	hydrochloric acid gas
1 vol.		1 vol.		2 vols.
as 1 molecule (consisting of 2 atoms or more)	+	1 molecule (consi ting of 2 atoms or more)	→	2 molecules. (each containing at least 1 hydrogen atom and 1 chlorine atom).

Inexactness of Avogadro's Hypothesis.—Since Gay Lussac's law is inexact the hypothesis which accounts for it must be approximate also. It should read "equal volumes contain **approximately** equal numbers," etc., but the error introduced by treating it as exact is usually so small as to be negligible.

Unit Volume.—The density of hydrogen is ·0899 gm. per litre at N.T.P. Hence 2·016 gms. of hydrogen (1 gm. mol.—see below) occupies 22·4 litres at N.T.P., and by Avogadro's hypothesis the molecular weight in grams of any gas would occupy this volume. Hence 22·4 litres is called the gram molecular volume of a gas (or sometimes, for short, 1 volume).

This argument is important, so we must understand it clearly.

(*a*) 1 molecule of hydrogen has an inconceivably small volume.

(*b*) Suppose it were magnified until the hydrogen atom weighed 1·008 gms., and its molecule 2·016 gms., it would now occupy 22·4 litres at N.T.P.

(*c*) 1 molecule of any gas according to Avogadro's hypothesis occupies the same volume (actually very minute, but with our imaginary magnification 22·4 litres), and hence the gm. mol. wt. occupies (at N.T.P.) the gm. mol. vol. (22·4 litres).*

(a) *Cannizzaro's Method of Determining Atomic Weights.*—We have seen that the hydrogen molecule contains at least 2 atoms and there is evidence that it contains only 2 (see p. 25). On this assumption the molecular weight of hydrogen = 2·016, which can be taken as 2·0 when a high degree of accuracy is not required.

Now the vapour density of a substance is defined as

$$\frac{\text{density of vapour at N.T.P.}}{\text{density of hydrogen at N.T.P.}} = \frac{\text{weight of 1 volume of vapour}}{\text{weight of 1 volume of hydrogen}}$$

* It is essential that the student should see where the mystic figure "22·4" comes from. If the density of hydrogen is ·0899 gm. per litre, then 2·016 gms. would occupy $\frac{2\cdot016}{\cdot0899} = 22\cdot4$ litres.

and by Avogadro's hypothesis this

$$\frac{\text{weight of 1 molecule of vapour}}{\text{weight of 1 molecule of hydrogen}} = \frac{\text{molecular weight of vapour}}{2 \cdot 0}$$

$$\therefore \textbf{Molecular weight of a substance} = 2 \times \textbf{vapour density}$$

Hence if a number of volatile compounds be taken, all containing the element whose atomic weight is to be determined, we can proceed as follows:

(1) Find the vapour density of each compound (details of the methods employed are given in Chapter IX.).

(2) Double the vapour densities and get the molecular weights of these compounds.

(3) Analyse each compound and calculate the weight of element contained in the gram molecular weight of it.

(4) If we have taken enough compounds, one at least will **probably** contain in its molecule only one atom of that element which is present in all of them (*e.g.* in the thousands of carbon compounds used in this way surely at least one will have only one carbon atom in its molecule!). We are not certain, but we hope so! Assuming this to be correct, the smallest weight of the element in any of these gram molecules is the weight of one gram atom. Table I. shows how this method of determining atomic weights (often referred to as the "many compound method") works in practice.

Assuming that at least one of these compounds contains not more than one carbon atom in its molecule, the atomic weight of carbon = 12.

We may, with confidence, believe this to be the correct atomic weight until a smaller weight of the element is found in a molecule containing it, or unless other methods of atomic weight determination give a different value.

(5) We have here obtained only an **approximate value** for the atomic weight, since vapour density measurements are not capable of a high degree of accuracy. But this will settle for us the value of n, and $n \times$ *the accurate equivalent weight is the accurate atomic weight.*

TABLE I.

THE ATOMIC WEIGHT OF CARBON BY CANNIZZARO'S METHOD.

Compound used.	Vapour density.	Molecular weight.	Weight of carbon in gms. in the gram molecular weight.
Carbonic oxide . . .	14	28	12
Carbonic anhydride . .	22	44	12
Carbon bisulphide . .	38	76	12
Marsh gas	8	16	12
Ethylene	14	28	24
Propylene	21	42	36
Formic acid	23	46	12
Acetic acid	30	60	24
Acetic anhydride . . .	51	102	48
Alcohol.	23	46	24
Ether	37	74	48

The Atomicity of Hydrogen.—Evidence in favour of diatomicity:

(1) It must be at least diatomic (1 vol. hydrogen→2 vols. of hydrochloric acid gas).

(2) Hydrochloric acid is monobasic and hence **probably** contains **only one** atom of hydrogen in its molecule. But 2 molecules of hydrochloric acid contain 1 molecule of hydrogen (or 1 molecule contains $\frac{1}{2}$ molecule); so that 1 atom of hydrogen is contained in half a molecule of hydrogen.

(3) In every gaseous hydrogen compound we find at least 1 gm. of hydrogen per 22·4 litres. Presumably one or more of these will have only one H atom per molecule, in which case the 22·4 litres will contain 1 gm. mol. of compound. Hence 22·4 litres must (by Avogadro's hypothesis) be the gm. mol. vol. But 22·4 litres of hydrogen weigh 2 gms. (approx.), which is the weight of 2 gm. atoms.

(4) Physical measurements of the properties of a gas, such as the velocity of sound in it and the ratio of its specific heats give us information with regard to its atomicity (see p. 67). When applied to hydrogen, the results are in agreement with the above conclusions, viz. that it is diatomic.

Extension of Cannizzaro's Method.—There are several other methods of determining molecular weights of compounds (see Chapter IX.), and these can all be employed. Atomic weight determination therefore resolves itself into finding by analysis:

"*The least weight of an element present in the molecular weight of any of its compounds.*"

(b) *Dulong and Petit's Law applied to Atomic Weight Determination.*—In spite of the unreliable nature of the atomic weight values assigned to the elements before 1819, *Dulong and Petit* in that year were able to show that:

"*For solid elements, specific heat* $\times$ *atomic weight* $=$ *approx.* 6·4."

(The product at. wt. $\times$ sp. ht. is termed the atomic heat and is the heat capacity of 1 gm. atom.) Hence if we determine the specific heat of an element and divide it into 6·4 we get the **approximate atomic weight.**

Now, atomic weight $=n\times$ equivalent weight, so that in this way we can determine n and so calculate the atomic weight accurately.

This method has to be used with care, however, for the specific heats of many elements vary with the temperature.

E.g. equivalent weight of beryllium $=4{\cdot}6$

$$\text{specific heat} = {\cdot}47 \text{ and } \frac{6{\cdot}4}{{\cdot}47} = 13{\cdot}6$$

Hence $n=3$ $\left(\frac{13{\cdot}6}{4{\cdot}6}=3 \text{ nearly}\right)$, and therefore atomic weight of beryllium would be $3\times4{\cdot}6$ or 13·8. This was later found to be incorrect (see p. 29), for $n=2$ and the atomic weight $=2\times4{\cdot}6=9{\cdot}2$. The weakness of the method is thus revealed, for the specific heat of beryllium varies rapidly with the temperature.

At 100° C. sp. ht. $={\cdot}47$
„ 200° C. „ $={\cdot}54$
„ 400° C. „ $={\cdot}62$

The method is valuable as a check on other methods, especially

in the case of solid elements or of those which form few volatile compounds (sodium, calcium, aluminium, etc.), for in these cases Cannizzaro's method is inapplicable.

(c) *Mitscherlich's Law applied to Atomic Weight Determination.*—This was of great value a hundred years ago in checking atomic weights based on untrustworthy data, but is nowadays of less importance. This remark applies equally to all the methods here described since for all existing elements the value of "*n*" is known, and **redeterminations of atomic weights amount to nothing more than more accurate measurements of the equivalent weights.** Only when a new element is discovered will methods of finding "*n*" have to be employed.

The law of isomorphism * (1820) states that:

"*Crystalline form is independent of the nature of the atoms forming the molecule of a compound and depends solely on the number and the arrangement of them.*"†

The law is based on facts such as these:

(1) The acid phosphates and arsenates of potash are isomorphous, and are similarly constituted; *e.g.* KH_2PO_4 and KH_2AsO_4 (a phosphorus atom in one and an arsenic atom in the other, but the number of atoms and their arrangement identical).

(2) Sodium sulphate and sodium selenate are isomorphous and their molecules are $Na_2SO_4.10H_2O$ and $Na_2SeO_4.10H_2O$ respectively.

(3) Many double sulphates exist isomorphous with potash alum ($K_2Al_2S_4O_{40}H_{48}$). This terrifying formula for potash alum becomes less so when we depict how the atoms are arranged in the molecule, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, and all these isomorphous "alums" as they are called are **similarly constituted.** Thus the general formula for an alum is $R_2SO_4,M_2(SO_4)_3,24H_2O$, where R is a univalent metal or

* Isomorphism, ἴσος (equal), μορφή (form), refers to the existence of different substances with the same crystalline form.

† It may be noted that the univalent ammonium radical (NH_4) will have to be considered as behaving like a single atom, because of the existence of isomorphous potassium and ammonium salts.

basic radical (Na,K,NH_4, etc.), and **M** a trivalent metal (Fe, Al, Cr, etc.).* (See Plate II.)

Use of this law.—If two substances are found to be isomorphous, it follows that they are similarly constituted, and if we know the formula of one we can write down that of the other. Thus, potassium sulphate is known to have the formula K_2SO_4, so that potassium chromate, being isomorphous with it, must have the formula K_2CrO_4. Accordingly we can find by analysis the atomic weight of chromium, as that weight which is combined with 4×16 gms. of oxygen in this compound.

Difficulty in the use of this method.—

How can we tell that two substances are isomorphous?

This is not so easy as it sounds. It is unfortunately not sufficient to show similarity of crystalline form (there are too many exceptions; *e.g.* iron pyrites, FeS_2; sodium chloride, NaCl; and sodium chlorate, $NaClO_3$; all crystallise in cubes!). On the other hand absolute identity of corresponding angles in the crystals of isomorphous substances is not often found (*e.g.* calcite ($CaCO_3$) has one angle of 105° 5′ and Smithsonite (mineral form of $ZnCO_3$) which is isomorphous with it has a corresponding angle of 107° 40′).

The following are regarded as tests for the isomorphism of two substances:

(1) Close similarity of crystal form as shown by measurements of corresponding angles.

(2) Capability of forming **mixed crystals**; *i.e.* they must be able to crystallise out together, each crystal so formed being a mixture of the two substances in various proportions—(not a compound, as the composition is variable).

(3) Capability of forming **isomorphous overgrowths**; *i.e.* a crystal of one will continue to "grow" in a saturated solution of the other, an outer layer forming round the inner crystal (not forming a homogeneous crystal as in the last paragraph). Some beautiful examples of this can be seen at the Natural History Museum, South Kensington, showing an outer layer of a different colour from the inner crystal.†

* For further examples of isomorphism, see Lowry, *Historical Introduction to Chemistry*, or Freund, *Study of Chemical Composition*, or Briggs, *Study of Crystals*.

† See Instructions for Practical Work at end of this chapter.

(d) *The Periodic Classification applied to Atomic Weight Determination.*—It is assumed that the student is familiar with the outlines of the periodic classification—Mendeléeff's table which shows similar elements grouped into "families" when the elements are arranged in order of increasing atomic weight. Some further remarks on this classification will be found in Chapter XIV., but we are here only concerned with its use in checking atomic weights. Examples will make the method clear.

1. **Beryllium** has an oxide resembling alumina (Al_2O_3) and was therefore regarded as trivalent (oxide Be_2O_3). Its equivalent weight was found to be 4·6 so that its atomic weight was written down as $4{\cdot}6 \times 3 = 13{\cdot}8$, and we have seen that application of Dulong and Petit's law apparently confirmed this value (p. 26). But there was no place in Mendeléeff's table for an element of this atomic weight. A space between lithium and boron, however, was vacant, the element to fill which would probably resemble magnesium, calcium and zinc and be bivalent. If beryllium were bivalent its atomic weight would be $2 \times 4{\cdot}6 = 9{\cdot}2$, which would agree well with this "vacancy," as also would the properties of the element. Hence **the periodic table suggested a revision of the atomic weight determination.** It was proved later that it really was bivalent and had an atomic weight 9·2; for the vapour density of beryllium chloride = 40·05, therefore molecular weight = 80·1, which agrees with $BeCl_2$ ($9{\cdot}2 + 2 \times 35{\cdot}5$), but not with $BeCl_3$ ($13{\cdot}8 + 3 \times 35{\cdot}5$).

PORTION OF PERIODIC TABLE SHOWING THE POSITIONS OF BERYLLIUM AND TITANIUM.

He 4	Li 7	Be 9	B 11	C 12	N 14	O 16
Ne 20	Na 23	Mg 24	Al 27	Si 28	P 31	S 32
A 40	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52
	Cu 63·5	Zn 65	Ga 70	Ge 72.5	As 75	Se 79

(2) **Titanium.**—Analyses of the tetrachloride were first employed in order to fix the atomic weight of this element. Very discrepant values were obtained and 50·25 was regarded as the most trustworthy figure. *Mendeléeff* in 1869 pointed out that this was at least two units above the value to be expected from the position of the element in the periodic table. In 1885 some careful analyses of specially purified titanium tetrachloride showed that Mendeléeff was correct, and that the atomic weight was 48·1.*

(d) *Special Method for Volatile Elements.*—If the atomicity of the element is determined by the physical method described on p. 68, and the vapour density determined and doubled, we have:

$$\text{wt. of 1 atom} = \frac{\text{wt. of 1 molecule}}{\text{number of atoms in the molecule}}, \text{ and so}$$

$$\text{atomic weight} = \frac{\text{molecular weight}}{\text{atomicity}}.$$

This is the *only method available in the case of the inert gases (helium, neon, argon, krypton and xenon), for these form no compounds and thus have no equivalent weights.*

5. The Fixing of Formulæ.—(a) *For a compound:* (1) Find by analysis the percentage composition. (2) Divide the percentage of each element by its atomic weight and so get the **relative number of atoms** of each present (working on the principle that the number of marbles in a bag

$$= \frac{\text{weight of all the marbles}}{\text{weight of one marble}}\Big)$$

This gives us the **empirical formula**; *e.g.* CH_2O for acetic acid. (3) Find the molecular weight of the compound and the **molecular formula** is that multiple of the empirical formula which corresponds to the molecular weight.

EXAMPLE.—Acetic acid: empirical formula CH_2O. Molecular weight=60. Now $CH_2O = 12+2+16 = 30$, therefore molecular formula $= 2(CH_2O)$ or $C_2H_4O_2$.

(b) *For an element:* (1) Find its molecular weight.

* *Nature*, February 24, 1923.

(2) Divide by its atomic weight and so find the number of atoms in the molecule (or alternatively find the atomicity by the physical method).

EXAMPLE.—Phosphorus: vapour density=62, therefore molecular weight=124. But atomic weight=31, therefore there are 4 atoms in the molecule, or formula=P_4. For helium, the physical method shows it to be monatomic, and therefore its molecular formula=He.

Practical Work.—(1) Experiments should be carried out in illustration of the laws of combination, and of the different methods of determining equivalent weights.

(2) Determine the atomic weight of some metal by measurements of (*a*) its equivalent weight, (*b*) its specific heat.

(3) Grow some crystals of the various alums; suspend a crystal of chrome alum in a saturated solution of potash alum; grow some "mixed crystals" by evaporation of solutions containing potash alum and chrome or ferric alum. Note the differences in colour. A very useful exercise would be to estimate the percentage of ferric alum in some of these crystals by volumetric analysis.*

QUESTIONS.—1. Write an account of the experimental evidence on which Gay Lussac's law is based. Show how this led to Avogadro's hypothesis.

2. Summarise the methods by which the atomic weights of the elements can be determined. Which method would you employ for (*a*) sulphur, (*b*) lead, (*c*) chromium? Give reasons

3. State briefly the evidence on which the following formulæ are based: $CuSO_4.5H_2O$; N_2O; He; CH_4; O_3.

4. Write an essay on "isomorphism."

5. Distinguish between the terms "valency" and "atomicity." Why is it so important that we should have a knowledge of the atomicity of hydrogen?

6. The two oxides of titanium contain respectively 66·7 % and 60·0 % of the metal. Its specific heat is ·131. What conclusions can be drawn from these data?

7. 1·620 gms. of indium yielded 1·962 gms. of oxide on oxidation.

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* For useful hints on practical work and demonstrations in connection with isomorphism, see Barker, *The Study of Crystals* (Murby & Co.). This book includes the matter from Professor Barker's earlier pamphlets (now out of print) besides giving a very readable account of many other phenomena relating to crystals.

The sulphate of this metal forms an alum with ammonium sulphate. What is its atomic weight ?

8. 3·183 gms. of the chloride of an element were mixed with excess of silver nitrate and 7·00 gms. of silver chloride were precipitated. The vapour density of the chloride is 133. What is the probable atomic weight of the element ? (Ag=108, Cl=35·5.)

PART II.—THE MATERIALS

CHAPTER IV

DIFFERENT FORMS OF MATTER. PHYSICAL AND CHEMICAL CHANGES

1. The Chemist's Materials.—The chemist must have an adequate knowledge of the materials he is going to handle if he is to produce good work. His object is to investigate the nature of all kinds of matter, from the colouring matter in a green leaf to the smoke which passes up a chimney. His materials are not only the refined "chemicals" which fill the bottles in his laboratory, but the thousands of different substances which are to be found on the earth.

2. States of Matter.—In this terrific assortment we can recognise two main divisions—fluids and solids, literally things which flow and things which do not. Attempts to define these terms are not very satisfactory, for substances like pitch and butter are hard to place—they are border-line cases—so that there is no boundary between the two classes but a gradual transition:

typical solids—soft solids and viscous * fluids—typical fluids.
(soft solids and viscous * fluids: border-line cases.)

In this instance our definition really defines the two extremes, and we may leave the border-line cases to those who love argument.

We find a similar difficulty in trying to define many other pairs of terms, *e.g.* metals and non-metals (with elements like

* A viscous fluid is one which does not flow readily; *e.g.* treacle or glycerine.

arsenic "between the two"), physics and chemistry, plants and animals, transparent and opaque; but the use of a definition is to describe **briefly** and **accurately** the meaning of a term, and if it is impossible to do this, then framing a definition is a waste of time. "Definitions," it has been said, "are the most accursed of all things on the face of the earth." *

A **typical solid** is a substance which can support a small steady pressure without lateral support, whereas a **typical fluid** cannot withstand any pressure unless its sides are supported by a containing vessel. It is now considered that the term "solid" should only be applied to substances in the crystalline state (see pp. 40–43), and that matter should be divided into crystalline and non-crystalline substances instead of into solids and fluids as defined above. This would mean that substances like glass and rubber would cease to be regarded as solids. This will be referred to again presently. It follows that a solid will have a **definite shape and size**, but a fluid will have no shape for it must conform to the outline of the containing vessel. If a fluid has a definite size (*i.e.* volume), it is called **a liquid**; if it has not, but fills the space in which it is placed, it is termed **a gas.**† A gas near its point of liquefaction is termed **a vapour.** By altering the conditions, however, most substances can be obtained in any of these three states; *e.g.* mercury can be vaporised or solidified by changing the temperature.

3. Differences between Solids, Liquids, and Gases.—All matter is thought to be made up of small particles‡ in constant motion and separated by spaces. Hence we can imagine the differences between solids, liquids, and gases to be connected with the closeness with which these particles are

* Mellor, *ibid.* I. 386.

† Under certain conditions it is not easy to distinguish gases from liquids (see p. 66), so here again there is no sharp boundary between the two terms.

‡ In the case of gases these are the molecules (see p. 62), but in many solids *Bragg* has proved by X-ray analysis that electrically charged atoms (called "ions") lead an independent existence. No "molecule" can be distinguished, for example, in common salt, but only equal numbers of sodium and chlorine atoms. That is what the formula NaCl indicates and nothing more. Cohesive forces are probably electrical in nature.

packed. We know little of the forces which hold them together (cohesive forces), but at any rate these must be strongest in solids (which show **cohesion** to a marked extent) and least in gases. For example, a solid, like a lump of iron, does not fall to pieces under the influence of its own weight, whereas a column of unsupported liquid would break up into drops, and a bubble of gas rapidly "diffuses" into space—its particles becoming widely separated from each other. The correctness of this view is supported by the peculiar behaviour of "surfaces" of solids and liquids where the particles have free play in one direction. Thus we find evaporation and sublimation occurring at surfaces—the particles diffusing into the space above, and also surface tension effects at the surface of liquids.

4. Recognition of Different Kinds of Matter.—How do you know Brown from Smith? By certain characteristic features—Brown is fair and has blue eyes, Smith is dark and has brown eyes. How do we distinguish gold from silver? By certain characteristic properties—gold is reddish, silver is white; gold is denser than silver; gold will not dissolve in nitric acid, but silver will. So each kind of matter is known by its specific or characteristic properties, and these are of two kinds—**physical properties** which concern the substance alone, and **chemical properties** which concern its action with (or effect upon) other substances. *E.g.* the density of gold is a physical property, but its behaviour with nitric acid is a chemical property.

A Complication.—If two or more substances are found to have identical chemical properties, the chemist regards them as varieties of the same substance, although they may differ in physical properties (see Polymorphism and Allotropy). Even so, **each variety can be recognised by its characteristic properties.** *E.g.* rhombic sulphur has a specific gravity of 2·06, and monoclinic sulphur a specific gravity of 1·96.

5. Physical Properties.—The following are the physical properties of most importance to the chemist (details will be found in later pages).

(1) The **Density** * (mass per unit volume).

* Specific gravity = density compared to the density of water; *e.g.*

(2) The **Melting Point** and **Boiling Point.**

(3) The **Crystalline Form.**

(4) **Thermal Properties : Specific Heat** and **Latent Heat.**

(5) **Optical Properties : Refractive Index, Rotatory Power** (effect on polarised light), **Emission** and **Absorption Spectra,** and **X-ray Spectra.**

(6) **Electrical Properties : Conductivity,*** and **Dielectric Capacity.**

(7) **Viscosity** and **Surface Tension** (of liquids).

(8) **Solubility in Water** (usually included in a list of "physical" properties, but see p. 73).

(9) **Colour** and **Odour.** These cannot be "measured" and are therefore less valuable, for slight variations would pass unnoticed. (Such properties as thermal conductivity, coefficient of expansion, magnetic properties, and "metallic" properties like hardness, ductility, elasticity and rigidity are from the chemist's point of view comparatively unimportant.)

6. Pure Substances.—Determining the properties of a substance is like taking its "finger-prints," for it can be recognised by these in future. If a substance is "**impure,**" **it must be a mixture** of the **pure substance** with other ingredients called "**impurities,**" and the presence of the latter is betrayed by their physical properties, just as the presence of salt in sea water is betrayed by its taste.

Quite small quantities of impurities sometimes produce a marked effect on properties. *E.g.* $\frac{1}{1000}$th part of bismuth in copper reduces its electrical conductivity to such an extent that, Lord Kelvin stated, it would be fatal to the success of a submarine cable.

Hence, the most efficient test for purity is an accurate determination of physical properties ; *e.g.* for gases, the density ; for solids, the melting point ; for liquids, the boiling point. Sharpness of melting point or boiling point often indicates

iron has a density of 7·9 gms. per c.c. Its specific gravity is 7·9. Remember that vapour density = density of a vapour compared to the density of hydrogen at the same temperature and pressure.

* Conductivity $= \frac{1}{\text{resistance}}$ (see p. 169).

purity * since **the presence of dissolved impurities causes a gradual change in temperature during change of state,** but only soluble impurities are detected in this way. *E.g.* the melting point of ice is not affected by the presence of sand, but it is by the presence of salt. It follows that the determination of only one physical property is not always sufficient.

7. Methods of Purification.—These depend as a rule on differences in the physical properties of the pure substance and the impurities mixed with it.

Thus: (a) *Crystallisation* separates substances whose solubilities in a given solvent are different.

(b) *Distillation* separates liquids whose boiling points differ.

(c) *Diffusion* separates gases whose densities differ.

(d) *Liquefaction* separates gaseous substances which condense at different temperatures.

(e) *Ether Extraction* separates substances whose solubilities in ether are different.

8. Elements, Mixtures and Compounds.—By analysis, 90 kinds of matter have been found which have (up to the present) † defied all attempts to subdivide them by chemical means into anything different. These have therefore been termed " elements," and all other substances are mixtures or compounds of these.

If elements "**combine**" together, forming a "**compound,**" a new kind of matter is formed, as recognised by its properties, and in addition an energy change of some kind occurs.‡ On the other hand a "**mixture**" retains the

* The converse is not true—many pure substances have no sharp melting point; *e.g.* amorphous solids, or crystals containing much water of crystallisation.

† This is the number of elements identified up to date, but there are reasons for believing that at least 92 exist (see Chapter XIV.). The term " element " is further discussed in that chapter.

‡ Evolution or absorption of heat, for example, is often taken as evidence that a chemical change has occurred, *e.g.* nitrogen and oxygen can be " mixed " to form air without heat change, but when these gases " combine " to form nitric oxide, heat is absorbed. But heat of solution does not always indicate chemical change, and during changes of state latent heat is absorbed or evolved when there is definitely no chemical change. Hence thermal change *by itself* must not be considered as conclusive evidence of chemical change.

independent properties of its constituents, so a new kind of matter is not formed.

Thus a **mixture** of iron and sulphur still shows the properties of iron and of sulphur: magnetic properties of the iron, solubility of the sulphur in carbon disulphide, etc. A **compound** of iron and sulpnur does not show these properties.

(a) *Separation of mixtures* depends on the fact that the constituents are present side by side and retain their individual properties (see para. 7). It follows that the properties of a mixture (such as density) will depend upon the proportions of the constituents present (*e.g.* 100 % iron, density=7·9; 100 % sulphur, density=2·1; 40 % iron and 60 % sulphur, density $=\frac{40\times 7\cdot 9+60\times 2\cdot 1}{100}=4\cdot 4$). Hence

(b) *The properties of a mixture are a function of its composition.*

(c) *The composition of a compound cannot vary.* In other words, if the composition of a substance is found to vary according to the conditions, it is not regarded as a compound (see, for example, Cryohydrates, p. 91; Constant Boiling Mixtures, p. 100; Reasons for believing Air to be a Mixture, p. 12; Mixed Crystals, p. 28; and Hydrates, p. 90).

(d) *A Compound must be homogeneous;** *i.e.* every part identical † with every other part. **Mixtures** can be **sometimes homogeneous**; *e.g.* any gas mixture, and some liquid mixtures, and **sometimes heterogeneous**; *e.g.* a mixture of salt and sand, or of chalk and water.

It is not always easy to decide if a given substance is a mixture or a compound, and mistakes have been made in the past (*e.g.* cryohydrates and constant boiling mixtures). The above gives some idea of the tests which can be applied in trying to solve such a problem, but the difficulties should be readily apparent if they are applied to " solutions."

* ὁμός (the same), ἕτερος (other), and γένος (kind).

† We are not considering sub-microscopic features. *E.g.* the atoms in a crystal may be so arranged as to make neighbouring portions dissimilar, but the crystal as a whole under the most powerful microscopes is homogeneous.

9. Phases.—*Any portion of a heterogeneous system which is itself homogeneous, physically distinct, and capable of mechanical separation from the remainder, is termed* **a phase.**

Thus in a tank containing a solution of various salts and some sand, if we consider the system bounded by sides, bottom, and lid, we can distinguish three phases:

(1) A gas phase (the air above the solution—a mixture of gases).

(2) A liquid phase (the aqueous solution).

(3) A solid phase (the sand).

If some iron filings, chalk, sulphur and lead were now dropped into the tank there would be 5 solid phases present altogether, for each kind of solid could be collected to form a homogeneous mass.

NOTE.—(*a*) A mixture of gases is 1 phase only.

(*b*) A solution is 1 phase only.

(*c*) A mixture of n solids is n phases.*

(*d*) A mixture of n immiscible liquids is n phases.

EXAMPLES.—(1) A sealed flask containing calcium carbonate at high temperatures contains 3 phases: 2 solid phases (lime and calcium carbonate), and 1 gas phase.

(2) If silver nitrate solution be added to a solution of sodium chloride, the vessel will contain 2 phases: 1 liquid phase—the solution, and 1 solid phase—silver chloride.

10. Some Common Forms of Matter.—Certain forms of matter are conveniently grouped together by virtue of common properties. Thus we distinguish metals, non-metals, crystalline and amorphous solids, alloys, solutions, and colloidal solutions.

(a) *Metals and Non-metals.*—This distinction is purely arbitrary, and is based primarily on the characteristics tabulated overleaf. The terms are relative, and elements like arsenic have many metallic properties and many non-metallic properties. In the opinion of the chemist an element must have at least one basic oxide in order to be regarded as a metal, and he pays comparatively little attention to physical properties.

* Immiscible solids are here understood. Solutions of solids in solids are uncommon (see p. 105), but these are of course 1-phase systems.

	Metals.	Non-metals.
Physical properties	"Metallic" properties such as lustre, hardness, high melting point, good thermal and electrical conductivity	Comparative absence of "metallic" properties.
Chemical properties	Basic oxides	Acidic oxides.
	Comparatively stable chlorides	Chlorides hydrolysed by water.
	Unstable hydrides	Comparatively stable hydrides.
	Liberated at the cathode since they form positive ions Hence called electropositive elements.	Liberated at the anode since they form negative ions. Hence called electronegative elements.

(b) *Crystalline and Amorphous Solids.*—The solid state can be reached either by cooling a liquid or vapour, or from a solution by evaporation of the solvent. The atoms or ions (see p. 34) generally arrange themselves in a regular manner forming a kind of lattice work * (see Fig. 3), and as a result the solid assumes definite shapes, being bounded by plane faces which meet at fixed angles. Thus sodium chloride separates from a solution in the form of cubes; sodium nitrate forms rhombs and alum octahedra (Fig. 4A)

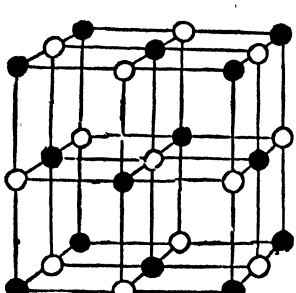


FIG. 3—Diagram of simple cubic lattice.

(From Houston's *Light and Colour.*)

Such plane-faced particles are termed **Crystals.**† These can increase in size or "grow," provided that they are surrounded by a saturated solution (or by

* The evidence for this is beyond the scope of this book. The student should consult Bragg, *X-rays and Crystal Structure*, or Sutton, *Natural History of Crystals*, for further information.

† κρύσταλλος (ice). The name was first given to quartz (rock

cooling liquid or vapour), and under favourable conditions will do so in a perfectly regular manner without change of shape. But in many cases, as crystallisation proceeds, separate crystals come into contact and interfere with each other's development, so that they will cease to have a

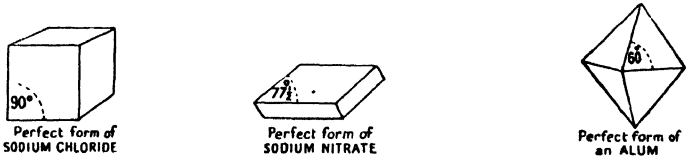


FIG. 4A.—Diagram of perfect forms of cube, rhomb (77½°), and octahedron.

characteristic shape, and may become matted together into a coherent cake as in loaf sugar. Such masses of crystals are termed **Crystalline Aggregates,** and blocks of ice or pieces of iron form familiar examples. Even a single crystal may become "distorted" during growth, since the rates at which solid is deposited on the different faces will probably be unequal. *E.g.* a perfectly cubical particle may develop into the forms illustrated (Fig. 4B), but it is easily

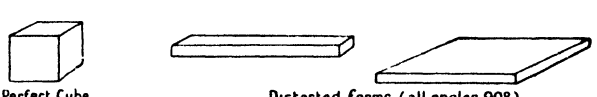


FIG. 4B.

seen that all such forms could be broken up into little cubes of perfect form by removing layers of solid parallel to the external faces. Conversely, if we suppose that the crystal is made up of bricks of perfect form, we can imagine that the growth of a crystal proceeds by the addition of successive layers of bricks to its faces, and the reason for the distorted forms is then clearly due to the excessive rate at which bricks are added to a particular face (or faces). A glance at the space-lattice (Fig. 3) will serve to remind us that our "bricks"

crystal) as it was thought to have obtained its ice like appearance owing to intense cold.

are really hollow, being, in fact, imaginary shells round the particles forming the lattice, but the analogy of " building bricks " can still be used with advantage.

The diversity of external form of crystals of the same substance is partly due to this kind of distortion, and partly to **twinning** or the joining together of crystals during growth (beautifully illustrated by the feathery forms of frost or ammonium chloride crystals) ; but there is yet another cause to be mentioned, namely the appearance of " facets " or planes cutting across two or more faces as shown in Fig. 5.

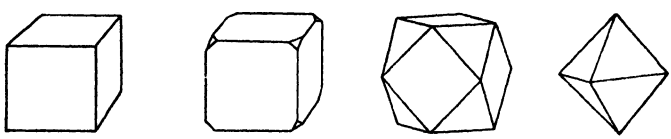


FIG. 5.—Octahedron developed from a cube by increasing the size of facets at the corners.

Using our analogy we can suppose that bricks are being economised. The effect of omitting rows of bricks when building a wall is illustrated in Fig. 6, and the last diagram shows

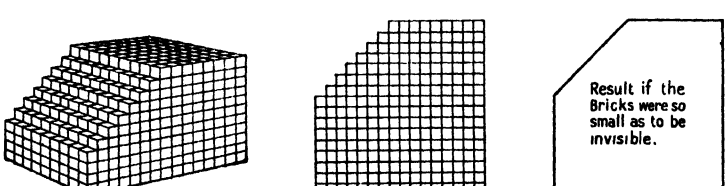


FIG. 6.

the appearance which the wall would have if the bricks were too small to be seen individually (as is the case with our " crystal bricks "). Solid angles or corners can obviously be truncated in a similar manner. In fact, the only external characters common to these distorted forms are the angles between corresponding faces, and it is therefore on angular measurement that the crystallographer pins his faith.

Since external form is apt to be so variable, it is important

to notice that " crystalline " solids have certain other properties by which they can be recognised. In these respects they differ essentially from **amorphous** * solids such as glass. Amorphous solids have no power to assume any shapes other than those of the moulds into which they are poured in a fused or liquid condition. They are in fact regarded as supercooled liquids and not as true solids, for they have no sharp melting point, but when heated pass through a treacly condition into liquids with gradual rise in temperature. The belief that they are in the metastable † condition of supercooled liquids is strengthened by the fact that, under certain conditions, they may change into crystalline solids. *E.g.* glass may become " devitrified." The mobility of the molecules of an amorphous solid has been reduced to the value it would have in a true solid, but the regular " pattern " arrangement which confers crystalline properties is lacking.

The properties of crystalline solids are the outward expression of their orderly internal structure. Thus we find that the majority of crystals break or " cleave " easily along one or more directions parallel to the external faces,‡ whereas glass breaks into irregular splinters. This shows that the cohesive forces inside a crystal must vary with the direction, being smallest in directions perpendicular to the planes of cleavage. Further, many other physical properties of crystals are found to vary with the direction of measurement. *E.g.* when heated, many crystals expand unequally in different directions. Again, the thermal conductivity of some crystals varies with the direction in which the heat is flowing relative to the faces; and the velocity of light is not always the same in every direction and hence they are doubly refracting and give characteristic effects when examined in polarised light. Substances are said to be **isotropic** if their properties are the same in all directions; **anisotropic** if the properties vary with the direction of measurement; and the existence of anisotropy is

* ἄμορφος (without shape).

† See p. 52 for the meaning of this term " metastable."

‡ There are some crystals which show no planes of cleavage; notably alum, quartz and copper sulphate ($CuSO_4.5H_2O$).

conclusive evidence that a substance is crystalline and not amorphous.*

(c) *Alloys.*—Metallic substances which are either mixtures or compounds of two or more metals (with occasional non-metallic constituents, such as carbon in steel and phosphorus in phosphor-bronze) are termed **alloys**; *e.g.* brass (containing copper and zinc), solder (containing tin and lead). If mercury is one ingredient the alloy is termed an **amalgam**; *e.g.* sodium amalgam, or amalgamated zinc.

Alloys are most commonly prepared by mixing the molten ingredients and allowing the whole to solidify, and their great value lies in this possibility of manufacture, for by adjusting the composition we can so vary the properties as to give us metals suited for particular purposes. Thus, we have specially hard steels containing nickel, tungsten, or manganese; light but strong alloys of aluminium, magnesium, and copper for aeroplane parts, etc. The effect on properties of a slight change in composition is amazing. *E.g.* $\frac{1}{500}$th part of carbon will convert pure iron into mild steel.

Classes of Alloys.—Alloys can be:

(*a*) *True Compounds.* Homogeneous and of composition corresponding to a simple formula; *e.g.* $CuAl_2$ or Fe_3C. These will have a definite melting point. Examples are not numerous.

(*b*) *Mixtures* which may be:

(1) *Solid Solutions.* Homogeneous mixtures of varying composition and melting point; *e.g.* the various alloys of copper and zinc, or gold and silver.

(2) *Eutectic Alloys.*—Particular types of alloy whose melting points are lower than those of their ingredients.† They are apparently homogeneous, but a microscopic examination shows them to be conglomerates; *i.e.* heterogeneous. They have a

* Most crystals are anisotropic, but the "cubic" crystals form an exception to this. Certain liquids such as cholesteryl benzoate are found to be anisotropic and have therefore been termed "crystalline liquids" or "liquid crystals."

† They are often called "lowest melting alloys" for this reason: εὔτηκτός (easily melted).

fixed composition and melting point (in these respects resembling compounds—*cf.* cryohydrates, p. 91); *e.g.* the alloy containing 63 % tin and 37 % lead; the alloy containing 55 % bismuth and 45 % tin.

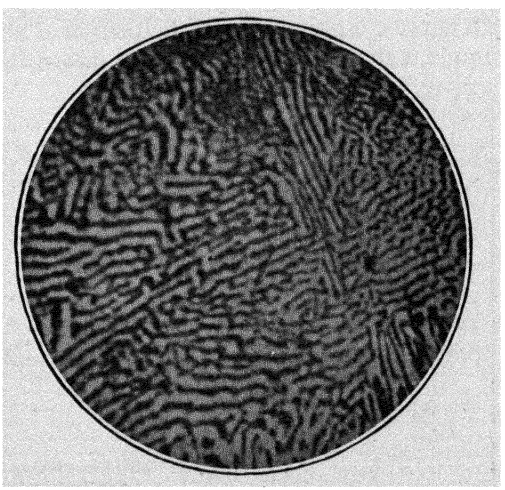


FIG. 7.—Photomicrograph of a eutectic alloy.
(From Mellor's *Crystallisation of Iron and Steel.*)

(3) *Heterogeneous Mixtures* of compounds, eutectics, or solid solutions, with other metals or with each other; *e.g.* several alloys of tin and copper, antimony and silver.

The Study of Alloys.—The nature of an alloy is determined by several methods.

(1) *Microscopic examination* of thin slices which have been polished and then etched with some reagent such as aqua regia.

(2) *X-rays* are transmitted through thin slices and allowed to fall on a photographic plate. If one ingredient absorbs these rays more than another the result will be seen in the photograph.

(3) The *rate of cooling* of the molten alloy is studied (see below).

(4) The *freezing points* of mixtures of the molten ingredients in varying proportions are determined. The results are plotted graphically giving a *freezing-point composition curve*, and much information can be obtained by an examination of such curves, especially with the help of the phase rule.

An example is shown in Fig. 8, and the discontinuity in the

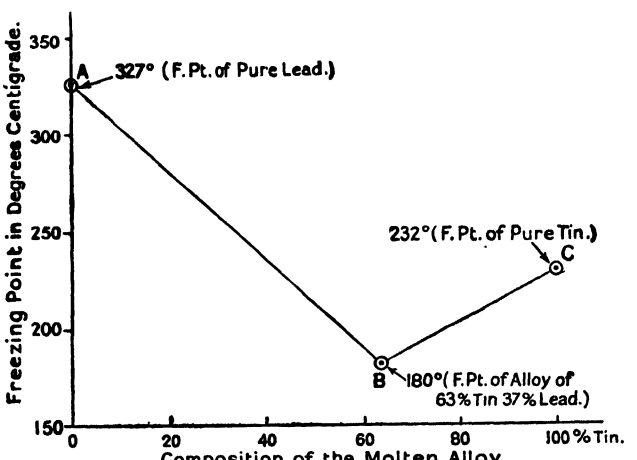


FIG. 8.—Freezing-point composition curve for tin-lead alloys.*

curve at B indicates the formation of a eutectic alloy containing 63 % tin and 37 % lead solidifying at 180° C.

The Cooling Curve of an Alloy.—The **rate of cooling of a pure substance** is uniform until the freezing point is reached. It then abruptly changes, and the temperature remains constant until all is solid, when cooling recommences (see AB, BC, CD in (*a*) Fig. 9).

NOTE.—*In any curve connecting two variable quantities, a* **discontinuity** *or abrupt change indicates a sudden change in one of the variables* (*cf.* Fig. 17, on p. 89).

* The curves AB and BC are diagrammatic, and are not plotted from experimental data.

A **mixture when cooled** will behave differently, since any dissolved ingredient lowers the freezing point of the solvent, and as solid separates out the composition changes, with consequent effect on the freezing point (lowering of freezing point is proportional to concentration of dissolved substance, see

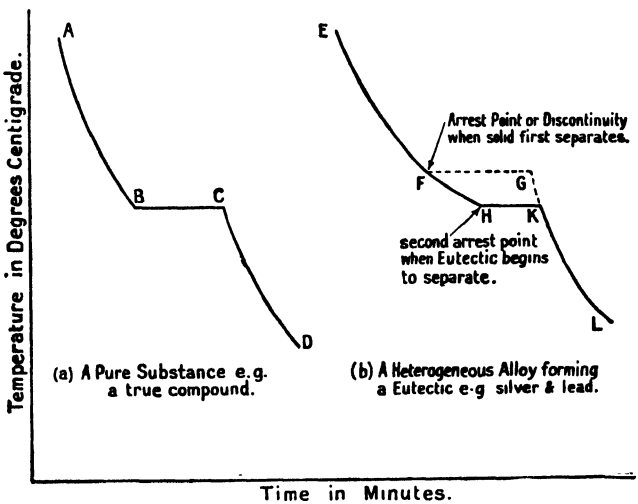


FIG. 9.—Cooling curves of alloys.

p. 91). Hence, for example, a heterogeneous alloy of silver and lead will have a cooling curve similar to (*b*) Fig. 9. If pure lead had been cooled, EFGL would have been its cooling curve, and the effect of the dissolved silver is clearly marked. The point H indicates the separation of a solid mixture (eutectic) which has all solidified at point K.

(d) *Solutions.*—Every one knows what is meant by a "solution" of sugar in water. Sugar is the **solute** which has dissolved in the **solvent** water. The solution looks just like water, but taste it—it is not water! And it is not sugar, for it is liquid (the sugar has not melted, the temperature being below its melting point). The sugar and water have simply been mixed, and the result is **a homogeneous mixture.** There is a limit to the amount of sugar we can mix with a given amount

of water, beyond which any additional sugar will remain in the solid phase, so that the mixture would become heterogeneous; the solution having this limiting concentration is said to be "**saturated.**" Hence we may have homogeneous mixtures of sugar and water containing **any proportion** from 0 % sugar up to the concentration which will produce a saturated solution.

Again, if we mix ether and water we find **two limits.**

(1) From 0 % to 9 % ether will give us homogeneous mixtures.

(2) From 98·9 % to 100 % ether will give us homogeneous mixtures.

Between 9 % and 98·9 % ether we shall have two layers, (*a*) a saturated solution of ether in water, and (*b*) a saturated solution of water in ether.

(Note the arbitrary nature of the terms "solute" and "solvent." If the water is in excess the ether is the solute and the water the solvent, but the terms are usually reversed if the ether is in excess—it then becomes the solvent.)

Hence the mixture is only homogeneous within certain limits, and so:

A solution is a homogeneous mixture whose composition can be continuously varied within limits.

We can, therefore, have solutions of solids in solids (*e.g.* mixed crystals, certain alloys, iodine in solid benzene); solids in liquids, liquids in liquids, gases in liquids, gases in gases, and gases in solids.

If solutions are true mixtures (as we have stated) their properties will vary in proportion to their composition, but this is not always the case, and we are driven to the conclusion that **after the mixing process or physical act of solution chemical actions may sometimes occur in the solution,** such as combination between solute and solvent:

$$E.g.\ SO_2+H_2O=H_2SO_3$$

or "dissociation" * of solute molecules:

$$E.g.\ NaCl+H_2O=Na^{\bullet}+Cl'+H_2O$$

* See p. 154.

or changes in the solvent molecules themselves. But in every case we can imagine that the physical process of mixing occurs first, and this is probably the process to which the name "solution" should be applied. Further discussion of solutions will be found in Chapters V. and VI.

(e) *Colloidal Solutions.*—Some solutions, which even under the most powerful microscopes appear homogeneous, are found to consist of solute particles, larger than molecules, floating about in the solvent. This has been demonstrated by means of the ultramicroscope (described in Chapter VIII.), which is not an ordinary microscope at all, for it does not magnify the particles, but only shows us that they are present. It does not give us any direct information as to their size or shape; but indirectly it has been found that particles as small as 5 millionths of a millimetre can be detected in this way.

The human eye can detect particles as small as	0·1 mm.
The most powerful microscopes can detect particles as small as	0·0001 mm.
The ultra microscope can detect particles as small as	0·000005 mm.
Molecules have a diameter of about . . .	0·0000005 mm.
Atoms have a diameter of about	0·0000002 mm.

These figures are inconveniently large, so special units have been adopted:

1 micron $= \frac{1}{1000}$ mm. (written as μ)
1 millimicron $= \frac{1}{1000000}$ mm. or $\frac{1}{1000}\mu$ (written as $\mu\mu$).

Hence apparently homogeneous solutions may by means of the ultra microscope be found to have particles of sizes between $\cdot 1\mu$ and $5\mu\mu$ dispersed through the solvents. They are therefore referred to as **disperse systems,** and there can obviously be all degrees of dispersion between true solutions, where **molecules** are dispersed, and coarse suspensions, where **visible particles** are dispersed (*e.g.* water containing fine particles of clay or sand which are too small to settle quickly). A true solution is often regarded as one which will pass through filters, but as our apparatus improves we shall get smaller and smaller particles retained by the filter, so the distinction is

unreliable. The influenza germ is at present a filter-passer, but we hope one day to be able to catch it, and the term "filter-passer" will then be reserved for still smaller particles.

We should not classify disperse systems or colloidal solutions separately if it were not for their peculiar properties, but these are of sufficient importance to merit the existence of a distinct branch of scientific investigation known as "Colloid Chemistry."

The term "colloid," which has become established in chemical literature, is unfortunately liable to be confused with Graham's use of it (see p. 108). Graham thought that "colloids" were a distinct group of substances, and used the term "colloid" as a noun. This idea has been abandoned, for we now consider that any substance can exist in the colloidal condition. Hence the term "Colloid Chemistry" really stands for the study of matter in the colloidal state, and "colloid" is used as an adjective.

Most of the organic matter composing our bodies is in the colloidal state, and medical progress in recent years has been largely due to our increasing knowledge of the behaviour of matter in this state. Again, many important industries involve the use of colloidal material, and technical advances have resulted from a recognition of this fact. Space will only allow a few to be mentioned, such as dyeing, tanning, soap making, and the manufacture of bread and photographic materials, but as Wolfgang Ostwald once stated:

[We] "see colloids everywhere. . . . We begin the day with a colloid practice—that of washing—and we end it with one in a bedtime drink of colloid tea or coffee. Even if you make it beer, you still consume colloid." *

11. Physical Changes.—Physical changes are those which affect the physical properties of a substance but do not alter its chemical properties. A chemical change, on the other hand, will convert a substance into a different kind of matter

* From Wolfgang Ostwald's *Introduction to Theoretical and Applied Colloid Chemistry*, translated by Martin H. Fischer, second and enlarged American edition, page 194, John Wiley and Sons, Inc., New York, 1922; or *Introduction to Theoretical and Applied Colloid Chemistry*, Wolfgang Ostwald, translated by Martin H. Fischer, first edition, page 180, John Wiley and Sons, Inc., New York, 1917.

with a resulting change in its chemical properties (*cf.* para. 4).

EXAMPLES.—When lead melts, the resulting liquid still has the chemical properties of lead—it still **is** lead But if lead is heated in air, it is changed to a yellow or red powder which has not the chemical properties of lead ; the lead has in this case suffered a chemical change—the powder is a compound of lead and oxygen.

12. Changes of State. Transition Points.—Typical physical changes are the changes from the solid state to the liquid or gaseous state, or vice versa, known as "changes of state."

CHANGES OF STATE.

Solid	Fusion or Melting ⟶ ⟵ Solidification or Crystallisation	Liquid
Liquid	Evaporation or Boiling ⟶ ⟵ Condensation or Liquefaction	Vapour
Solid	Sublimation ⟶ ⟵ Condensation	Vapour

We will in this paragraph discuss the change from solid to liquid, in para. 16 the change from solid to vapour, and in Chapter VI. the change from liquid to vapour.

The **melting point** of a substance is the temperature above which it is stable in the liquid state, and below which it is stable in the solid state. It is, therefore, a **transition point** between two regions : (*a*) a region where the liquid phase is stable, (*b*) a region where the solid phase is stable.

It is only at the transition point that both forms can coexist in equilibrium. *E.g.* when the pressure is 76·0 cms. we can have a mixture of ice and water at 0° C., but raise the temperature and all the ice will melt ; lower the temperature and all the water will solidify.

13. The Notion of Equilibrium.—Anything which is not moving is said to be in **equilibrium**. Humpty Dumpty

was in equilibrium **until** he began to fall—**unstable equilibrium** in this case because the slightest movement made further motion inevitable (see Fig. 10). Similarly the chemist regards a system which is not changing (chemically or physically) as in a state of equilibrium. *E.g.* silver in water, or ice in water under a pressure of 76 cms. and at 0° C. constitute systems in **stable equilibrium**—there is no tendency to change. Sodium



FIG. 10.

in water, or ice in water at 76 cms. pressure but above 0° C., would not be systems in equilibrium—change is inevitable; nitrogen iodide is an unstable substance because the slightest touch causes it to decompose with explosive violence: until touched, it was, like Humpty Dumpty, in unstable equilibrium.

It is to be noted that two equal and opposite motions would give the appearance of equilibrium. We shall refer to this again on p. 72.

If a change takes place very slowly, a system may appear to be in equilibrium. Many a snail at top speed is probably thought to be " at rest " ! Hence an unstable system, changing to the stable condition so slowly as to give no indication of the change occurring, will masquerade as a stable system. Such systems are termed **metastable** to distinguish them from those whose changes are rapid or **labile.**

EXAMPLE.—Tin in the winter is in the metastable condition. The stable form of tin below 18° C. (its transition point) is a grey powder, but it changes into this form so slowly that during an ordinary winter, although the temperature may be several degrees below the transition point, no apparent change takes place. In 1867, however, an extremely severe winter

in Russia accelerated the change to such an extent that blocks of tin stored in the Customs House at St. Petersburg (as it was then called) crumbled to a grey powder. See Plate I. (frontispiece). This change can also be accelerated by the presence of tin ammonium chloride and the true state of equilibrium thus reached more quickly. Evidently a metastable system is in a state of **suspended transformation,** like a chrysalis kept in cold storage.

It is frequently possible to obtain metastable systems, for **a transition point marks the boundary between two regions : (1) where A is stable, (2) where B is stable,** and we can often cool B a little below the transition point, as in the case of tin, or warm A a little above it, without the change to the stable form occurring. Thus, water can be **supercooled** nearly 6° C. without solidification if due precautions are taken,* and it is easily **superheated.** As a result it does not boil until the temperature is well above its true boiling point and " bumping " occurs, a large bubble suddenly forming as the system changes to the stable condition of vapour. Note that in all such cases, as soon as solidification does commence, up jumps the temperature at once to the true freezing point ; and as soon as ebullition occurs, down falls the temperature to the true boiling point—the metastable systems have changed to stable systems. For further examples of metastable systems see supersaturated solutions (p. 83), and yellow mercuric iodide (p. 56).

14. The Effect of Pressure on a Transition Point.—Experiment shows that :

(*a*) If a liquid expands on freezing (*e.g.* water) increase of pressure lowers its freezing point (see Fig. 11). In the case of water the change is ·0075° C. per atmosphere.

(*b*) If a liquid contracts on freezing (*e.g.* mercury) increase of pressure raises its freezing point. In the case of mercury the change is ·03° C. per atmosphere.

(*c*) All liquids expand on vaporising and increase of pressure raises their boiling points.

* It has never been found possible to heat a solid above its melting point without liquefaction occurring.

(*d*) All transition points are altered by changes in pressure (see paras. 15 and 19).

These results can also be deduced from the laws of thermodynamics since they are due to the work done against external pressure by an expanding substance, and heat energy is used up in doing this work.

Two of the factors controlling the nature of chemical

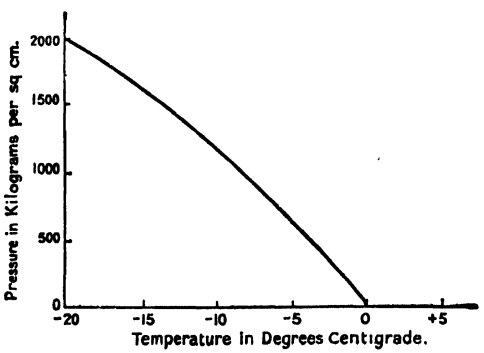


FIG. 11.—The effect of pressure on the melting point of ice.

and physical systems are thus seen to be temperature and pressure. Other factors will be considered in Chapter XI.

15. Le Chatelier's Rule.—The donkey is regarded as a nuisance when he tries to go the opposite way to that in which he is pulled. He seems to do so out of sheer cussedness. A well-known French scientist named le Chatelier came to the conclusion that this type of perversity is widespread in Nature. He laid down as a guiding rule what might well have been called the " law of pure cussedness " :

If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, then the displacement will occur **in such a direction as to oppose** *the constraint.*

If you try to compress a piece of ice in contact with water at 0° C., it will object to the compression—it shrinks away or contracts to avoid the increase in pressure. How does it do this? By melting! (for ice occupies a larger volume than the water it produces). We could, therefore, have deduced from

le Chatelier's rule the effect of pressure on the melting point of ice, for if under compression the ice is going to liquefy at 0° C. its freezing point must be below 0° C. This rule is extremely useful and many examples will be found later.

Try to apply it yourself to the following cases:

(1) A liquid contracts on freezing. How does pressure affect its freezing point?

(2) The reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$ causes volume changes
1 vol. 3 vols. 2 vols.
to occur. What will be the effect of pressure on this system?

(3) The reaction $N_2 + O_2 \rightleftarrows 2NO$ proceeds in the direction → with absorption of heat. What change will occur if this system is heated?

(NOTE.—If it wants to keep cool, it must not evolve heat, for this evolved heat would raise its temperature. Paradoxical as it sounds, it keeps cool by absorbing heat from its surroundings, whereby these are cooled and the temperature of the whole system falls.)

16. Sublimation.—Solids have a surface from which molecules are continually becoming detached and passing into the space above, so that at all temperatures vaporisation is slowly occurring. The effect is so small that in most cases it cannot even be detected, but with some solids (such as iodine) it is large enough to produce a measurable vapour pressure.

Temperature.	Vapour pressure of iodine.
30	·47 mm.
55	3·1 mms.
85	20 mms.
113	83 mms. (The melting point.)
137	200 mms.
161	400 mms.
185	760 mms. (The boiling point.)

If the pressure over some solid iodine is kept below 83 mms., its temperature can never reach the melting point. Hence on heating it will completely vaporise or sublime without liquefying. Conversely the cooled vapour will condense to

the solid state. At higher pressures iodine if heated will melt, like the majority of solids whose sublimation pressures are smaller.

17. Polymorphism and Allotropy.—If a substance can exist in the solid state in more than one form—the differences being in physical properties only—it is said to be **polymorphous.** Chemical identity of these forms is proved by their identical composition and behaviour with reagents, *i.e.* chemical properties. Thus mercuric iodide is **dimorphous ;** a red variety forms tetragonal crystals stable below 126° C. ; and a yellow variety forms rhombic crystals stable above this temperature, which is obviously a transition point (*cf.* p. 53). The yellow form if cooled below 126° C. is metastable and will change into the red form on rubbing. Calcium carbonate is another example of dimorphism, calcite and aragonite crystallising in hexagonal and rhombic forms respectively. Titanic oxide is **trimorphous,** and ammonium nitrate has 5 modifications with transition points at 16° C., 32° C., 84° C., and 125° C., the last form melting at 170° C.

In the case of elements, different modifications are termed **allotropes,*** well-known examples being carbon, sulphur, and phosphorus. In this case identity does not always mean identical molecules ; thus oxygen is O_2 and ozone O_3 ; phosphorus is probably P_4 in the white form and P_8 in the violet : the various forms of solid sulphur (S_8) probably vary owing to different arrangements of the atoms in their molecules. Hence different terms are sometimes employed, such as :

(a) *Polymerism,* when one molecule is a multiple of the other. This term is usually applied to compounds only ; *e.g.* water, which consists of molecules of H_2O and of its polymers $(H_2O)_2$, $(H_2O)_3$; or aldehyde (C_2H_4O) and its polymer paraldehyde $(C_2H_4O)_3$; and it is restricted to cases in which the complex molecules are directly obtainable from the simpler ones.

(b) *Isomerism,* when the arrangement of the atoms in the molecule is the cause of the differences ; *e.g.* in the soluble and insoluble forms of sulphur. This term is usually restricted to molecules whose differences in structure (or atomic arrange-

* ἄλλος—τρόπος (another habit).

ment) are revealed by the differences in their chemical properties. *E.g.* alcohol and dimethyl ether both have molecules of formula C_2H_6O, but the atoms are known to be differently arranged—C_2H_5OH in the alcohol molecule and $CH_3.O.CH_3$ in that of ether. In elements, however, the chemical properties of the various forms usually differ, if at all, in degree only.

(c) *Polymorphism,* when differences in crystalline form are due to changes in the space-lattice or " pattern " arrangement of the particles making up the crystal.

Liquid Allotropes.—Two different forms of liquid sulphur exist and these are both thought to be present in molten sulphur, the proportions varying with the temperature. Thus, the vicosity and colour variations can be explained if we suppose that one form S_λ is limpid and pale yellow, the other form S_μ viscous and dark brown, and the system $S_\lambda \rightleftarrows S_\mu$ in equilibrium at any given temperature. A rise in temperature might then shift the equilibrium in the direction $S_\lambda \rightarrow S_\mu$ and vice versa, so that on heating, the liquid would become darker and more viscous. This has been termed **dynamic allotropy,** and is similar to **dynamic isomerism** (or **tautomerism**) in which two mutually convertible compounds exist in equilibrium, the composition of the mixture being dependent on conditions; *e.g.* acetoacetic ester,

$$CH_3.CO.CH_2.COO_2H_5 \rightleftarrows CH_3C(OH) : CH.COO_2H_5.$$

18. The Properties of Allotropes.—Detailed accounts of the allotropic forms of many of the elements, etc., will be found in text-books of inorganic chemistry. An examination of these will reveal the following general principles:

(1) Under given conditions one form is always more stable than the other. *E.g.* rhombic sulphur is more stable than monoclinic below 95·6° C.; yellow phosphorus is always less stable than red.

(2) The less stable form can always be transformed into the more stable; *e.g.* yellow→red phosphorus; but we cannot always transform the stable form into the less stable by reversing the conditions. Thus, $S_{monoclinic} \rightarrow S_{rhombic}$ can be reversed by altering the temperature, but $P_{yellow} \rightarrow P_{red}$ cannot be

reversed in this way. In order to obtain yellow phosphorus from red we have first to vaporise the red, and then to condense the vapour to obtain the metastable system yellow phosphorus.

If the change is reversible (as in the cases of sulphur, tin and oxygen) it is termed **enantiotropic.**

If it will only go one way and cannot be reversed it is termed **monotropic** ; *e.g.* the forms of phosphorus and arsenic.

NOTE.—*These terms are applied with the same meaning to all dimorphous substances, not only to allotropes. Thus, mercuric iodide is enantiotropic*: HgI_2 (*yellow*) $\underset{\text{transition point 126° C.}}{\rightleftarrows}$ HgI_2 (*red*) *; but iodine monochloride and benzophenone are monotropic, one form being always less stable than the other. This is also the case with phosphorus, there being no transition point and the unstable form only existing in a state of suspended transformation. It has been suggested that there would be a transition point if the solid did not melt first, but that since it melts below the transition point the form stable above this temperature can never be obtained in the solid state.*

All the transition points referred to can be altered by pressure (*cf.* para. 14). Applying le Chatelier's Rule to the case of sulphur, for example, we can deduce that increase of pressure will cause monoclinic sulphur to contract to the rhombic form. Hence, in order to keep the two forms in equilibrium we shall have to raise the temperature if the pressure is increased ; *i.e.* increase of pressure raises this transition point.

(3) The **least stable form is always deposited first** from condensing vapour or on precipitation from solution. Thus, phosphorus vapour on cooling gives yellow phosphorus, mercuric iodide when precipitated by the action of mercuric chloride on potassium iodide comes down yellow.

This is in accordance with a general rule known as the **law of successive reactions** which states that a system does not pass from the state of least stability to that of greatest stability in one jump, but if intermediate stages are possible it will pass through them. It behaves, in fact, like a ball

rolling downstairs and reaching a slightly more stable condition on each stair as its potential energy decreases, instead of bounding from top to bottom and missing out the intermediate steps. Thus, chlorine water decomposes in two stages:

(*a*) $Cl_2+H_2O \rightarrow HOCl+HCl$ followed by (*b*) $2HOCl \rightarrow 2HCl+O_2$.

NOTE.—If the second reaction is very rapid the intermediate products will never accumulate, so they may never be detected experimentally, but in cooling a vapour the fall in temperature slows down further reaction and the intermediate or metastable form of the solid may possibly be obtained.

(4) The differences in stability are indicated by differences in energy content. We find, for example, that:

Heat of combustion of 62 gms. yellow phosphorus = 369,100 cals.,
heat of combustion of 62 gms. red phosphorus = 326,800 cals.,

so that converting 62 gms. yellow phosphorus into red causes an evolution of heat of 42,300 cals. In other words, **the least stable form has the largest heat of combustion.**

(5) Differences in crystalline form, and other physical properties such as density, solubility in solvents, melting point, vapour pressure, colour, etc., serve to distinguish the different forms and

The least stable form has always the lowest melting point.
" " " " *highest vapour pressure.*
" " " " *largest solubility.*

At the transition point, when both forms are equally stable, their vapour pressures and solubilities must obviously be the same.

19. Determination of Transition Points.—The methods usually adopted depend upon the change in properties which a substance undergoes if it is heated from below its transition point until this temperature is passed. Volume changes, heat evolution, solubility changes, vapour pressure changes, etc., will occur as form A changes to form B, and if the value of the physical property in question be plotted against the temperature, a discontinuity (see p. 89) will be apparent at

the transition point; *e.g.* the points B in Fig. 8, and the point B in Fig. 17.

Demonstrations in connection with the foregoing paragraphs are suggested as follows:

Paras. 2 and 3. Properties of viscous fluids or soft solids. The filling of a space by a gas may be shown by a drop of liquid bromine in a flask, cohesion by means of clay or putty.

Paras. 8 and 9. Illustrations of the terms homogeneous, heterogeneous, and phase.

Para. 10 (*b*). Nature of amorphous and crystalline solids. Cleavage, sharpness of melting point, etc. Show a model "space lattice" and illustrate the growth of a crystal from unit "bricks" (leading to distortion).

Para. 10 (*c*). A display of alloys and, if possible, some photomicrographs.

Para. 10 (*d*). The partial miscibility of ether and water.

Para. 10 (*e*). Some simple illustrations of disperse systems.

Para. 13. Mechanical notions of equilibrium illustrated by a wooden egg and other solids with high or low centre of gravity; instability illustrated by nitrogen iodide.

Paras. 17 and 18. Formation and properties of the yellow and red forms of mercuric iodide or the allotropic forms of sulphur.

PRACTICAL WORK.—

(1) Measurements of density or specific gravity should be made; and also of melting point and boiling point. Other physical properties can be measured at a later stage in the course.

(2) A cooling curve should be plotted for (*a*) a pure substance, (*b*) an alloy.

(3) Further experiments on crystals might be carried out on the lines suggested in the footnote on p. 31.

(4) Prepare allotropes of sulphur or forms of mercuric iodide and examine their properties. More advanced students should, if possible, determine a transition point.

QUESTIONS.—1. How would you determine the purity of a sample of (*a*) silver, (*b*) water, (*c*) oxygen, (*d*) iodoform?

2. What are "mixed crystals"? Give as completely as possible your reasons for believing them to be mixtures and not compounds.

3. Write a short essay on either (*a*) crystals, (*b*) disperse systems, or (*c*) allotropy.

4. How would you investigate the nature of the alloy of tin and lead known as solder ?

5. Explain the meaning of the term " equilibrium " as applied to chemical systems. What is a metastable system ? Illustrate your answer by reference to mercuric iodide.

6. What is the effect of pressure on the freezing point of (*a*) water, (*b*) alcohol ? Show how these effects could be deduced by le Chatelier's Rule.

CHAPTER V

GASES

1. The Kinetic Theory.—Gases differ in some respects from solids and liquids. *E.g.* they have no definite volume, are very easily compressed, and diffuse rapidly into surrounding space. A possible reason for these differences has already been suggested;—the molecules are more widely separated in gases and comparatively free from cohesive forces. To account for other phenomena, such as the pressure which fluids exert on the walls of containing vessels and the effects of heat energy on their temperatures, some additional assumptions are necessary: (1) that the molecules are in rapid motion, the pressure on the side of a vessel being due to their impacts with it; (2) that the temperature of a substance is determined by the mean kinetic energy of its molecules, so that increase in energy would be manifested to us as an increase in temperature; (3) that the molecules are perfectly elastic, the average momentum of the molecules being unaltered by collisions. **The Kinetic Theory of Matter** (which embodies these assumptions) is in harmony with all known facts, but it is in explaining the properties of gases that it has proved most useful. In dealing with solids and liquids its application is very limited owing to the complicating effects of cohesive forces, and the comparatively restricted motions of the molecules resulting from frequent collisions.

The Kinetic Theory of Gases originated nearly 200 years ago when *Daniel Bernouilli* suggested that Boyle's law might be thus explained. Extended by *Clausius* (1857), *Clerk-Maxwell* (1860), *Boltzmann* (1868) and others, it has become a most valuable aid to progress, and coordinates a large number of independent facts. (See summary on p. 79.) Its hypothetical nature has been largely reduced by our increasingly intimate knowledge of molecules.* For example, the actual number of molecules in a litre of a gas has been determined by several *widely different methods* and there is a remarkable agreement between the results: so remarkable, in fact, that it would be hard to suggest an alternative hypothesis to account for it. In the words of *Perrin*, "The real existence of the molecule is given a probability bordering on certainty."†

2. The Gas Laws.—Applying the kinetic theory of gases quantitatively it can be proved ‡ that if a volume of gas V, at a pressure P, contains n molecules, each of mass m, then

$$PV = \tfrac{1}{3}mn\,C^2$$

where C^2 is the mean of the squares of their velocities.§ It follows that:

(1) **If the temperature is constant** (*i.e.* the kinetic energy $\frac{1}{2}mnC^2$ constant), **PV will be constant—which is Boyle's law.**

(2) **If the pressure is constant** $V \propto \frac{1}{2}mnC^2$ (the kinetic energy) and so the **volume will be proportional to the absolute temperature** ¶**—which is Charles' law.**

* Some idea of our knowledge of molecules may be gained from the information given in the Appendix (p. 80).

† Perrin, *Atoms*, 1916 ed., p. 207.

‡ For this proof, and further details in connection with paragraphs 1–5 of this chapter, reference should be made to text-books of physics.

§ C is often called the root mean square velocity. It is not identical with the mean or average velocity, but is proportional to it.

¶ Temperatures reckoned from −273° C. as zero are termed absolute temperatures, since this is the temperature at which the molecules will be at rest, or $\frac{1}{2}mnC^2 = 0$.

(3) If two gases are **at the same temperature and pressure** then **equal volumes will contain equal numbers of molecules—which is Avogadro's hypothesis.**

If the temperature and pressure of a gas vary simultaneously their effect on the volume of a gas can be deduced by applying Boyle's law and Charles' law, and the result can be expressed in the form $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$, or more simply, $\frac{PV}{T}$=a constant. This constant is symbolised by R, so that we may write PV=RT, and *if we consider* 1 *gram molecule of gas*, then, applying Avogadro's hypothesis, V is the same for all gases, and hence R *will have the same value for all gases.* It is termed the universal gas constant.

We can calculate R once and for all (since it is constant) by substituting in the equation PV=RT the values found for any particular gas. Thus V becomes 22·4 litres when P is 76×13·59 gms. per sq. cm. and T is 273° absolute, so that

$$R=\frac{22{,}400\times 76\times 13\cdot 59}{273}=84{,}760 \text{ gm. cms. per } 1^\circ \text{ C.}$$

This is measured in units of energy, and since 1 calorie of heat is equivalent to 42,650 energy units expressed in gm. cms.,* we can if we choose express R in thermal units. Thus $R=\frac{84{,}760}{42{,}650}=2$ calories per 1° C., nearly, or **PV=2T.** This form of the equation is frequently used in physical chemistry, and it must be remembered that the "2" is an approximate value for R when expressed in calories.

3. Ideal Gases. Deviations from the Gas Laws.—Boyle's law is only an approximation to the truth, and the same must be said about the other gas laws. Hence the previous paragraph refers to an ideal state which is never realised in practice. Is this a blow to the kinetic theory? On the contrary, we should expect to find deviations from the gas laws, for the expression $PV=\frac{1}{3}mnC^2$ was arrived at on

* Joule's equivalent is $4\cdot2\times10^{-7}$ calories per erg, and 1 erg or dyne cm.=981 gm. cms.

two assumptions which cannot possibly be correct in actual practice: (1) that the molecules themselves occupy no volume; (2) that the molecules move independently without attracting or repelling each other. Now the molecules must occupy some volume, though it may be negligible in comparison to the volume of the gas (*i.e.* of the spaces between the molecules), and cohesive forces though small are not entirely absent. Hence, in order to express the behaviour of gases more exactly we shall have to modify the equation $PV=RT$ and substitute $V-b$ for the volume of the gas which can be compressed (b being the incompressible volume of the molecules themselves), and $P+p$ for the pressure (the attractive force between the molecules will tend to reduce the volume of the gas and so behaves like an additional pressure p). *Van der Waals* assumed that this attractive force would vary inversely as the square of the volume, so he wrote the following equation as a nearer approximation to the truth than $PV=RT$

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \text{ (Van der Waals' equation).}$$

This is in very fair agreement with experimental results, but it is still only approximately correct. Note that at very low pressures or high temperatures when V becomes large in comparison to P and b, this reduces to $PV=RT$, for both $\frac{a}{V^2}$ and b will then be negligible. We can therefore regard this as expressing an ideal state of affairs. A **perfect gas** is defined as one which is ideal in this sense; *i.e.* that its behaviour agrees exactly with the expression $PV=RT$, both b and $\frac{a}{V^2}$ being zero.* Under ordinary conditions hydrogen is not very far from being a perfect gas.

Reference should at this stage be made to the work of *Amagat*, who by plotting PV against P at various temperatures,

* It is because the deviations from the gas laws are not the same for all gases that Gay Lussac's law and Avogadro's hypothesis are found to be inexact when working with gases under the same temperature and pressure conditions (see p. 21).

showed clearly the deviations from Boyle's law for various gases; and also to the work of *Andrews*, who made a series of experiments in 1863, from which he plotted the pressure of

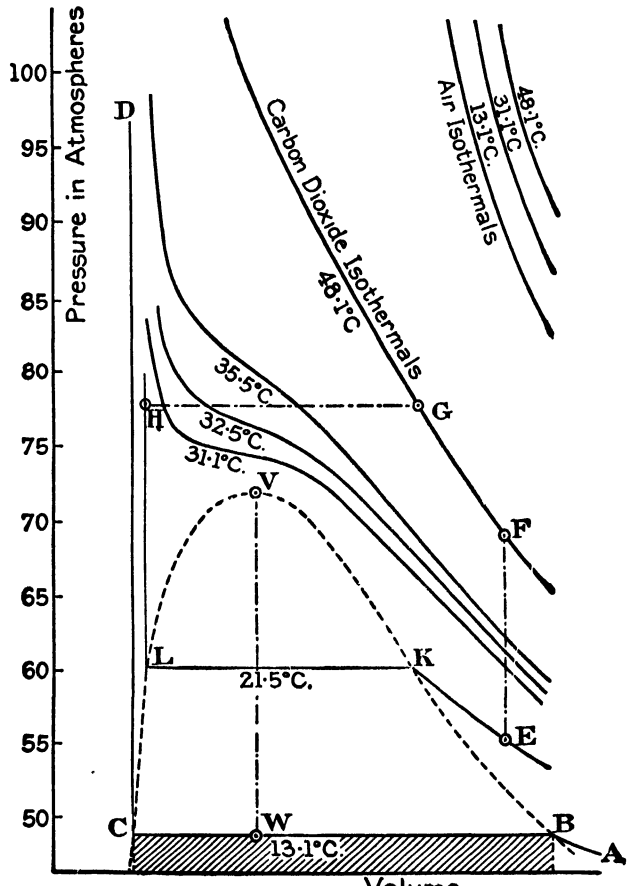


FIG. 12.—Carbon dioxide isothermals.
(From McEwen's *The Properties of Matter.*)

carbon dioxide against its volume (Fig. 12), and made important deductions from the shape of the curves.

4. Critical Temperature. The Liquefaction of Gases.—*Andrews* was able to explain why *Faraday* had failed to liquefy the "permanent gases"—hydrogen, oxygen, nitrogen, etc. As a result, renewed efforts were made and all gases have now been liquefied, the last to succumb being helium.

Kammerlingh Onnes succeeded in liquefying helium in his Leyden laboratory in 1908. In attempting to solidify it by rapidly evaporating liquid helium at very low pressures he claimed in 1920 to have reached a temperature only ·82° above absolute zero.*

The key to the problem was shown by Andrews to lie in the fact that a gas must be cooled below a certain definite temperature before liquefaction becomes possible. This temperature is a constant for a particular gas (30·92° C. for carbon dioxide) and is called its **critical temperature.** Above this temperature it is impossible to liquefy it; below this temperature it is easily liquefied by pressure. At the critical temperature it is impossible to distinguish gas from liquid, for by changing the pressure it can pass from one state to the other without any perceptible break or discontinuity in properties, no sudden decrease in volume or separation into two layers occurring. The value of the pressure required to liquefy a gas at its critical temperature is called the critical pressure.

Detailed accounts of the methods used in liquefying gases should be referred to in other books, but the underlying principles may be briefly summarised:

(1) Preliminary external cooling to a temperature below the critical temperature; *e.g.* by contact with rapidly evaporating liquids. This is followed by compression.

(2) Compressing the gas (followed by external cooling to remove the heat generated by compression), and then allowing the compressed gas to expand. Cooling is here due to heat energy being used in doing external work when the gas expands.

(3) The modern method due to *Linde and Hampson* in which a gas issuing from a nozzle under pressure is cooled

* *Nature*, November 4, 1922.

owing to "free expansion." In this case no external work is done, but heat energy is used for the work done against the intermolecular forces.*

By an ingenious arrangement the cooled gas *from* the nozzle is used to cool the next supply of gas *to* the nozzle, so that the effect is cumulative and the issuing gas finally liquefies. It is this regenerative method which has made large-scale liquefaction of air a commercial success.

The uses of liquid air are numerous, varying from the large-scale production of oxygen, nitrogen, and helium, to the production of high vacua.† Cryogenic laboratories have now been installed at Leyden and in America, and investigations of the properties of matter at very low temperatures are likely to produce important results.

5. The Nature of the Molecule. Atomicity.—In the preceding paragraphs we have considered the molecule as though it were a solid particle and have taken no account of the atoms of which it is composed. But these will have to be taken into account when we consider the amount of heat energy required to raise the temperature of a gas. If we measure the molecular heat ‡ of a gas at constant pressure, C_p, we find that this is greater than its molecular heat at constant volume, C_v. Now the difference $C_p - C_v$ is sometimes greater than the heat used in performing the external work which is done when the gas expands at constant pressure. There must in such cases be some heat used up in other ways, and we may assume that this is utilised in altering the positions or velocities of the atoms inside the molecule. If we write Q as the heat used in performing external work we shall have $C_p = C_v + Q$ when no internal work has to be done, as would be the case if there were only one atom in the molecule, and it can be proved that $Q = \frac{2}{3}C_v$, so that $C_p = C_v + \frac{2}{3}C_v$ or $\frac{C_p}{C_v} = \frac{5}{3}$. Experiment shows that $\frac{C_p}{C_v}$ is very nearly 1·67 (*i.e.* $\frac{5}{3}$)

* Hydrogen must be cooled below −80·5° C. before this effect is obtained. Above this temperature, it is heated by "free expansion," and not cooled.

† See p. 68.

‡ Molecular heat = specific heat × molecular weight.

for helium, neon, mercury vapour and a few other gases, but that for most gases lower values are obtained; *e.g.* about 1·41 for hydrogen, nitrogen, and oxygen; and about 1·29 for carbon dioxide and steam. Helium, neon, and mercury vapour would therefore appear to be monatomic; but for the other gases $C_p+x=C_v+Q+x$, where x is heat used up in doing internal work. If we assume 2 atoms in the molecule for hydrogen, nitrogen, and oxygen, and 3 atoms in the molecule for carbon dioxide and steam, the values for $\frac{C_p}{C_v}$ will be less than 1·67 to different extents: $\frac{5+x}{3+x}=1{\cdot}41$ and $\frac{5+x}{3+x}=1{\cdot}29$ respectively. These atomicities are in agreement with chemical evidence as to the structure of the molecules, so the assumptions are justified. We can therefore determine the atomicity of any gas by experimental measurement of the ratio $\frac{C_p}{C_v}$ (or γ), for if this approximates to 1·67, 1·41 or less, then the gas has probably 1, 2 or more atoms in its molecule. It is not easy to measure C_p and C_v separately, but the ratio γ can be determined by two distinct methods, details of which are to be found in text-books of physics.

6. The Density of a Gas.*—This is a most important physical property, for, if accurately determined, it serves as an indication of purity, and moreover it leads directly to the molecular weight and hence to the formula for the gas. Gases are not so easy to manipulate as solids and liquids, and until recently, accurate density measurements were not possible. There were two main reasons. (1) It was difficult to fill a space with pure gas without impurities such as air or moisture being present; (2) accurate weighing was difficult with substances so light compared to their containing vessels. The difficulties have been largely solved by the use of charcoal cooled in liquid air, together with improved apparatus and more powerful pumps, for producing high vacua. Charcoal at

* The densities of vapours produced by the action of heat on substances which are normally liquid are not referred to in this paragraph but in Chapter IX.

such low temperatures has been found to have the amazing property of absorbing all gases. With the exception of hydrogen, helium, and neon the absorption is almost complete, so that good vacua can be obtained with comparative ease in this manner. The gas to be examined can then be introduced. Moreover, the ease with which gases can now be liquefied has rendered their purification a comparatively simple problem.

The density determination consists of three processes:

(1) Weighing a vacuous globe, counterpoised by a similar globe to avoid errors due to variations in buoyancy (*i.e.* the upthrust due to the weight of air displaced) during the experiment.*

(2) Weighing the same globe full of gas.

(3) Weighing the same globe full of hydrogen, for vapour densities are always compared to the density of hydrogen.

Of course the temperature has to be kept constant during the experiment, and the two gases must be at the same pressure, so that several precautions have to be taken in order to obtain accurate results. To indicate the degree of accuracy attained *Gray* and *Burt's* results may be quoted: 10 determinations of the density of hydrogen chloride were made in 1908 with values varying from 1·64069 to 1·63950 (mean value, 1·64016).

7. Mixtures of Gases. Dalton's Law of Partial Pressures.—The constituents of a mixture are as independent as the birds in an aviary, and this is particularly noticeable in the case of gaseous mixtures where the molecules have plenty of space in which to move about. If gases exert pressure owing to their molecules bombarding the walls of their containing vessels, then each gas in a mixture should exert its own pressure, and experiment has shown this to be so.

Dalton's law of partial pressures (1802) states that:

The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases.†

* The error due to buoyancy changes may be quite large if no counterpoise is used. If the surrounding air temperature falls by 1° C. the increase in upthrust on a 300 c.c. flask will be about 1 milligram.

† This is only an approximate law owing to the intermolecular forces preventing complete freedom of movement.

EXAMPLES.—(1) If a moist gas exerts a pressure of 740 mms. and the pressure due to the water vapour is 10 mms., then the gas itself is exerting a pressure of 730 mms.

(2) In air at 760 mms. pressure, the partial pressure of the oxygen is about $\frac{1}{5} \times 760$ mms. and of the nitrogen $\frac{4}{5} \times 760$ mms.

The constituents of a gas mixture can be separated by any method based on differences in their properties; *e.g.*

(1) By liquefaction (or distillation of the liquefied mixture), as in the separation of oxygen from other gases in the air.

(2) By diffusion (see next paragraph).

(3) By solution (frequently termed absorption) in water or other solvents. Thus in gas analysis the constituents are removed one by one when the mixture is shaken with various absorbents. The contraction in each case shows the volume of the constituent removed.

8. Diffusion.*—Since the molecules of gases move freely in all directions, a small mass of gas will rapidly diffuse until its molecules are dispersed throughout the space in which it is placed. The gas is said to "fill" or "occupy" the space, but the molecules only fill it in the same sense that flies are said to fill a room on a summer's day. We say that they "fill it," because they are to be seen everywhere, and if holes be made in the wall they will diffuse through into the next room and "fill" that also. As a result of this diffusion process, a mixture of gases will always become homogeneous in time, even if the denser gases be underneath, for diffusion is quite independent of gravitational forces. This can be easily demonstrated by placing a little bromine vapour at the bottom of a jar containing air.

Diffusion can also occur through porous material (*i.e.* through the holes or pores), and by allowing different gases under the same conditions of temperature and pressure to diffuse through plaster of Paris *Graham* established in 1832 that:

* For diffusion of liquids, see p. 107.

*Their rates of diffusion are inversely proportional to the square roots of their densities.**

Thomas Graham was born in Glasgow on December 21st, 1805, and is stated to have been "a quiet, studious boy, conscientious and diligent in his work, but not otherwise remarkable among his fellows." † Yet he became the first president of the Chemical Society of London when it was founded in 1841, and he carried out much original work of great importance.

We may write Graham's law as $\text{Rate} = K\sqrt{\frac{1}{\text{density}}}$, and it is then clear that light gases diffuse more quickly than denser gases.

EXAMPLE.—Vapour density of ammonia $= \frac{17}{2}$ and of carbon dioxide $= \frac{44}{2}$.

$$\frac{\text{Rate of diffusion of ammonia}}{\text{Rate of diffusion of carbon dioxide}} = \sqrt{\frac{22}{8{\cdot}5}}$$

When dealing with such small holes, the molecules in a mixture of gases move through independently, so that a partial separation occurs—the lighter gas diffuses through more rapidly than the denser one. Methods of separating gaseous mixtures based on this principle have been employed, the name **Atmolysis** ‡ being given to the process. The existence in neon of atoms of mass 20 and atoms of mass 22 was confirmed by the partial separation produced in this way.

When the holes are larger, *e.g.* holes cut in a metal plate, there is no separation brought about by diffusion—the mixture passes through as a whole. This is therefore not regarded as true diffusion, but is termed **effusion.** Also if the length of the hole is large compared to its diameter (forming a narrow tunnel), the rate of flow is not in accordance with Graham's law but depends upon the viscosity of the gas, so that this again is not true diffusion, but is termed **transpiration.**

All the above phenomena are easily explained by the kinetic

* Note that rate of diffusion means the *volume* of gas passing through in unit time.

† Thorpe, *Essays on Historical Chemistry.*

‡ ἄτμος (a vapour); λύω (I loosen).

theory, and Graham's law follows directly from the equation $PV=\frac{1}{3}mnC^2$; for C is proportional to the rate of diffusion (or average velocity of the molecules) and $C^2=\frac{3PV}{mn}$, so that if P is constant $C\propto\sqrt{\frac{v}{mn}}$ or $C\propto\sqrt{\frac{1}{\text{density}}}$.

Practical Importance of Diffusion.—Apart from the mixing of gases in our atmosphere, two examples may be quoted to show the importance of this phenomenon. (1) The interchange of gases in the leaves of plants (whereby carbon dioxide is absorbed and oxygen returned to the air) is carried out through small holes known as stomata. These may be as small as ·0006 mm. in diameter, but they are so numerous that diffusion can occur quite freely. A sunflower leaf possesses about 13 million stomata. (2) Building materials such as bricks are porous, and hence houses are ventilated to a certain extent even when doors and windows are tightly closed.

9. Meaning of the Term "Solubility."—If a substance is shaken up with a solvent, some of its molecules may enter the latter and form a homogeneous mixture or solution. Experiment shows that there is a limit to the weight of a particular substance which a given quantity of solvent can dissolve under specified conditions. The kinetic theory accounts for this without difficulty, for the molecules in the solution are still moving, and some will be continually leaving the solution. This process, of course, increases as the number of dissolved molecules increases. Hence there will always be two things happening:

(*a*) Dissolved molecules leaving the solution←.

(*b*) Molecules dissolving→.

As the substance dissolves (*a*) ← will increase; and → (*b*) will decrease in rate, until the two operations are proceeding at equal rates when

rate of solution=rate of leaving the solution.

No further change in the concentration of the solution can now occur, for a state of **dynamic equilibrium** has been reached.

i.e. two equal and opposite motions producing an appearance of rest. At this stage the solution is said to be **saturated,** and the weight (or volume) of solute which has dissolved in a specified weight (or volume) of solvent to produce this saturated solution is termed its **solubility.**

We can therefore define *a saturated solution as one which can remain in stable equilibrium with excess of solute,* for the amount of solute it contains cannot be exceeded without the solution becoming metastable. Thus, **supersaturated solutions** contain more solute than saturated solutions, but they are metastable, and if a particle of solute is introduced they will lose all their excess of solute and revert to the stable condition of saturation. Also **unsaturated solutions** are not stable in contact with more solute, for the latter will start to dissolve.

Notes on the measurement of solubility :

(1) Since this varies with temperature, the conditions of measurement must be stated. *E.g.* the solubility of sodium chloride is 35·7 gms. per 100 gms. of water at 10° C. ; the solubility of carbon dioxide is 1·713 c.cs. per c.c. of water at 0° C.

(2) Unless otherwise stated the solvent is considered to be water, and either weights or volumes can be used, according to convenience. Thus, for gases, volumes are usually referred to ; for solids it is customary to refer to weights dissolved ; and sometimes the concentration of the saturated solution or weight of solute per unit weight (or volume) of solution is given. There is no confusion if the units are always stated.

(3) If anything happens to the solute molecules **after solution,** such as combination with the solvent molecules or with each other, there will be more solute in the saturated solution than the amount in equilibrium with the dissolving solute. *E.g.* when sulphur dioxide, SO_2, dissolves in water, the state of saturation is reached when sulphur dioxide molecules are dissolving as fast as the dissolved molecules of the gas are leaving the solution, but the experimentally determined solubility measures not only this quantity of sulphur dioxide, SO_2, but also a great deal more which is now in the form of

sulphurous acid, H_2SO_3. Hence it must be remembered that the experimental solubility is a measure of the total amount of solute which has entered the solvent, and it is not always all there in the same form as before it dissolved.

10. The Solubility of Gases.—This depends upon the nature of the gas, the nature of the solvent, the temperature, and the pressure. Examples: Under the same conditions oxygen is more soluble in water than nitrogen. Solubilities are not the same in water as in alcohol. Water containing dissolved salts usually has a smaller solvent power for gases than pure water. Rise in temperature decreases the solubilities of gases in water (with the exception of helium). *E.g.* we can expel air from water by warming it, and can collect nitrous oxide over hot water although it is fairly soluble in cold water.

The Effect of Pressure on Gas Solubilities.—This was studied experimentally about 120 years ago and the results, expressed as **Henry's Law,** state that:

*At a given temperature the weight of a gas which will dissolve in a given volume of a solvent is directly proportional to the pressure.**

Thus, double the pressure and twice the weight of gas dissolves —another triumph for the kinetic theory, for this means that twice as many molecules dissolve, a result which this theory would have predicted. For rate of solution depends upon the rate at which gas molecules hit the liquid surface, and this is directly proportional to their concentration. If the pressure is doubled, rate of solution is therefore doubled, and when a state of equilibrium is again reached this must be balanced by a doubled rate of vaporisation (see Fig. 13). The concentration of dissolved molecules must have been doubled to bring this about, so that the doubled pressure has caused twice the weight of gas to dissolve.

11. Solubility of Gas Mixtures.—If a mixture of gases is shaken up with a solvent, each dissolves as though the

* Applying Boyle's law, it follows that the *volume* of dissolved gas will be the same at all pressures; *e.g.* twice the pressure causes twice the weight to dissolve, but the volume which this would have occupied under the original pressure conditions has been halved.

others were not present. The weight of each dissolving will therefore depend upon its solubility, and also (in accordance with Henry's law) upon its pressure. Now the pressure of each constituent of the mixture is its partial pressure (*vide* Dalton's law of partial pressure), so that if as an example we

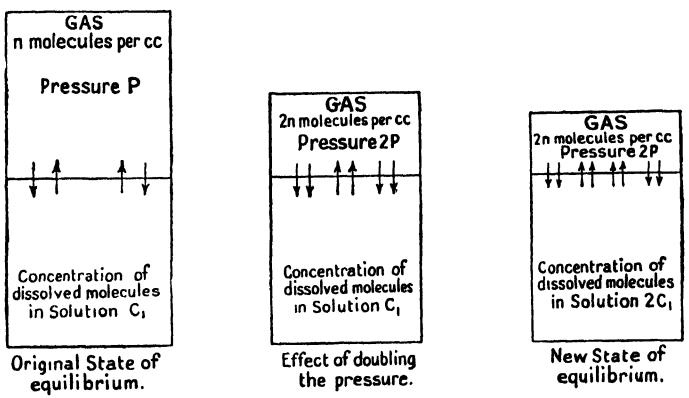


FIG. 13.—Kinetic explanation of Henry's law. The number of arrows indicates the number of molecules crossing the boundary of gas and liquid in a given time.

consider air being shaken up with water, the partial pressure of oxygen $=\frac{1}{5}$ atmosphere, the partial pressure of nitrogen $=\frac{4}{5}$ atmosphere; and the solubilities of these gases are respectively ·034 c.c. and ·018 c.c. per c.c. of water at 15° C., so that

$$\frac{\text{weight of oxygen dissolved}}{\text{weight of nitrogen dissolved}} = \frac{\cdot 034 \times 1}{\cdot 018 \times 4} = \frac{17}{36}$$

Hence " dissolved air " contains a greater proportion of oxygen than ordinary air—a fact of which the fish (who make use of it) are probably unaware !

12. Meaning of the term " Abnormal."

" Experiment is the interpreter of the artifices of Nature. It is never wrong; but our judgement is sometimes deceived because we are expecting results which experiment refuses to give."

(LEONARDO DA VINCI.)

If a law is established from a series of facts, we can deduce from it the results to be expected in some case which has not itself been examined experimentally. Thus, from Boyle's law we could calculate the effect of pressure on the volume of some gas which was not actually investigated by Boyle when formulating the law. If the experiment were then carried out, we should say that the results were quite normal if they agreed with our calculations. If the results of experiment do not agree with deductions from a law we have two alternatives: (1) to regard the law as an incorrect generalisation; (2) to regard the experimental results as "abnormal," *i.e.* deviating from the normal owing to causes which have escaped notice. A search for the cause of such abnormalities has in many cases proved a most fruitful line of research (*cf.* p. 146).

13. Deviations from Henry's Law.—When we are dealing with only slightly soluble gases (*e.g.* oxygen or nitrogen), Henry's law is an accurate statement of the facts as long as we do not alter the pressure by more than a few atmospheres. At higher pressures the solubility does not increase, when further compressed, as much as it would if Henry's law was applicable, but such deviations are quite comparable with the deviations from the gas laws (p. 64), and are thus easily comprehended.

An entirely different and much more serious type of deviation is found, however, when very soluble gases (*e.g.* hydrogen chloride) are employed.* In such cases the solubility is not even approximately proportional to the pressure. Is Henry's law to be abandoned in consequence? No; but it must be restricted to cover the less soluble gases only. Why do the others behave abnormally? It will be shown later (p. 154) that in these cases some of the dissolved molecules may have split up into smaller parts called "ions." † Since *the equilibrium with which Henry's law is concerned is between identical molecules in the two phases*, we have here a plausible explanation of the

* Similarly with ammonia at room temperatures, but at 100° C. (when it is much less soluble) Henry's law is nearly true. The solubility of carbon dioxide is also abnormal, but to a much smaller extent. This agrees with our belief (p. 175) that carbonic acid is only slightly ionised.

† Combination between the molecules and the solvent may or may not precede ionisation; *e.g.* $SO_2+H_2O=H_2SO_3$, but this alone would not affect the validity of Henry's law.

abnormalities, and, moreover, one which is in accordance with the other properties of the solutions.

Henry's law is a particular case of a general **law of distribution** * which concerns the partition (or distribution) of a solute between two solvents and states that:

$$\frac{\text{concentration in solvent A}}{\text{concentration in solvent B}} = \text{a constant}$$

provided the temperature is constant and the molecules of dissolved solute are identical in the two solvents. In the case of Henry's law solvent A is the liquid, and solvent B the space above.

14. Determination of the Solubilities of Gases.—Two methods are employed: the first if the gas is not very soluble; and the second for very soluble gases.

First Method.—A known volume of gas is shaken with solvent and the contraction noted by means of graduated apparatus (see Fig. 13A). This gives the volume of gas dissolved in a given volume of solvent directly, but it is not suitable for use with very soluble gases. The temperature and pressure of the gas above the solution must be recorded.

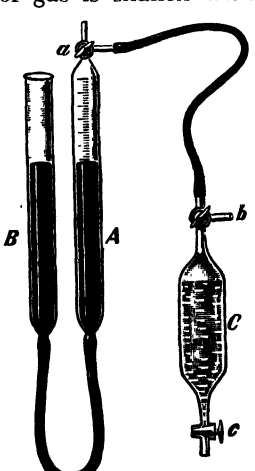


FIG. 13A. — Heidenhain and Meyer's absorptiometer.

Second Method.—A saturated solution is first prepared by bubbling gas through some of the solvent kept at a constant temperature by immersing the containing vessel in a constant temperature bath or **thermostat** (see Fig. 13B). The gas pressure must be recorded, and after sufficient time has been allowed the vessel is sealed up and weighed, so that the weight of saturated solution is known. This has now to be analysed by any suitable method and so the amount of dissolved gas determined; *e.g.* for ammonia, the

* See p. 159.

vessel is opened under standard acid and the ammonia estimated by volumetric analysis. Hence we arrive at the weight of gas dissolved in a definite weight of saturated solution.

15. The Solubility of Gases in Solids.—Gases do not as a rule dissolve in solids in a manner similar to that in which they dissolve in liquids, but they **are absorbed** in various ways, and if the results are homogeneous mixtures they are referred to as "solutions of gases in solids." The process of absorption may consist of (1) chemical combination between gas and solid; *e.g.* the absorption of carbon dioxide by lime. (2) Diffusion of gas molecules into the solid. This is true solution, and may of course precede the act of combination just mentioned. (3) Condensation of gas molecules on the surface of the solid (this is known as **adsorption**) *followed by* a slow diffusion into the interior; the whole process being termed **sorption.** It has been shown by *McBain* to be by sorption that hydrogen passes into charcoal, the adsorption being rapid compared with the subsequent diffusion.

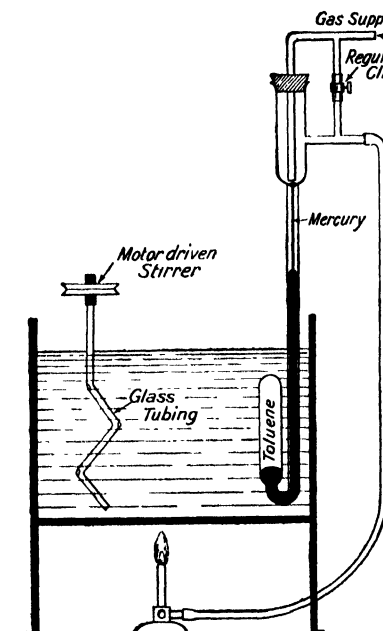


FIG. 13B.—A thermostat.

It is by considering the effect of pressure on the absorption of gases by solids that information is obtained as to the process which is occurring, but very few cases have up to the present been fully investigated.*

* See Findlay, *Phase Rule*, on hydrogen and palladium for further details.

16. Deductions from the Kinetic Theory.—A brief summary may show the large number of independent facts which are brought within the scope of this theory.

I. As applied to gases: qualitative explanations of pressure, temperature changes, diffusion, and solubility. Quantitative deduction of the gas laws, Avogadro's hypothesis, Graham's law and Henry's law. Explanation of the deviations from the gas laws leading to Van der Waals' equation, etc., and the cooling of gases owing to "free expansion." Explanation of the fact that gases have two specific heats. Explanation of deviations from Henry's law.

II. As applied to liquids: (details will appear in later chapters) qualitative explanations of hydrostatic pressure, comparatively slow rates of diffusion, cooling due to evaporation, surface tension, viscosity and the osmotic pressure of solutions. The laws of osmotic pressure and their similarity to the gas laws together with the deviations from these laws help to show that the kinetic theory of matter is not applicable to gases only, although it is only to gases that it can be applied in a strictly quantitative manner.

Demonstrations.—In illustration of paragraphs in this chapter, Dalton's law of partial pressures might be verified by introducing air, water vapour, etc., into the space above mercury in a barometer tube. Rates of diffusion of gases can be compared in several ways, most of which are only qualitative. The methods of gas analysis form a useful illustration of the differences in the solubilities of gases in various solvents, and the composition of "dissolved air" also introduces the solubility of gaseous mixtures. The distribution law should be illustrated when mentioned for the first time by shaking iodine with water and chloroform (or carbon disulphide), but the full discussion of this leading to the partition coefficient may be left for a later chapter.

Practical Work.—1. Measurements of $\frac{C_p}{C_v}$ might be carried out by the more advanced students.

2. The densities of air, ammonia, hydrogen chloride and carbon dioxide can all be determined by methods more approxi-

mate than those indicated in this chapter. A discussion of the sources of error and limits of accuracy is very valuable.

3. Determining the solubilities of the more soluble gases gives good practice in volumetric analysis, though the making of the saturated solutions may be troublesome. As an exercise in illustration of the method, let the student determine the weight of dissolved gas in a given weight of a solution which is not necessarily saturated; *e.g.* sulphur dioxide and hydrogen sulphide by iodine titration; ammonia, hydrogen chloride and carbon dioxide by acidimetry.

QUESTIONS.—1. To what extent do you consider that the kinetic theory gives an adequate explanation of the behaviour of matter?

2. Write an essay on *either* (*a*) liquefaction of gases *or* (*b*) diffusion.

3. Describe in detail how the atomicity and vapour density of argon could be determined. How will these data lead to the atomic weight of the element?

4. Outline the methods by which mixtures of gases can be separated. How would you proceed to analyse a sample of coal gas? Draw the apparatus required.

5. What is a saturated solution? Describe how you would determine the solubilities in water at room temperature and pressure of (*a*) ammonia, (*b*) oxygen.

6. State Henry's law. Account for the fact that the behaviour of many gases is not in accordance with this law.

APPENDIX TO CHAPTER V

Our Knowledge of Molecules.—A few examples are given.

(*a*) "Each molecule of the air we breathe is moving with the velocity of a rifle bullet; travels in a straight line between two impacts for a distance of nearly $\frac{1}{10{,}000}$ mm.; is deflected from its course 5,000,000,000 times per sec. . . ." (Perrin, *Atoms*, p. 82).

(*b*) Value of N, the number of molecules per gm. mol. of a gas at N.T.P.

62×10^{22}	by method	involving	measurements	of gas viscosity.
68×10^{22}	,,	,,	,,	brownian movement.
$60\ (?) \times 10^{22}$	,,	,,	,,	blueness of the sky.
64×10^{22}	,,	,,	,,	spectra of black bodies.
68×10^{22}	,,	,,	,,	charged spheres in a gas.
64×10^{22}	,,	,,	,,	radioactivity.

(Abridged from Perrin's *Atoms*, p.206.)

(*c*) Velocity of the hydrogen molecule $= 1{\cdot}8 \times 10^5$ cms. per sec.

Mean path of the hydrogen molecule $= 16 \times 10^{-6}$ cm.

Number of collisions per sec. of the hydrogen molecule $= 10{\cdot}6 \times 10^9$

(counting 3 per sec. for 24 hours a day it would take more than 100 years to reach this figure ! !).

Number of hydrogen molecules per c.c. $= 2{\cdot}70 \times 10^{19}$

Mass of hydrogen molecule $= 13{\cdot}3 \times 10^{-24}$ gm.

Diameter of hydrogen molecule $= 2{\cdot}4 \times 10^{-8}$ cm.*

These examples are given to show the extraordinary precision with which the scientist can now deal with particles too small to see or feel, and almost too small to imagine.

CHAPTER VI

SOLUTIONS

(*Introductory remarks on "solutions" will be found on p. 47, and the meaning of the terms "saturated solution" and "solubility" on p. 73.*)

1. The Solubility of Solids in Liquids.—The weight of solid which will dissolve in a given weight of solvent so as to produce a saturated solution, depends upon the nature of the solid, the nature of the solvent, the temperature, and to a smaller extent on the size of the grains of solid. The effect of pressure is negligible. It is customary to speak of substances as "insoluble" when their solubility is exceedingly small, but it is probable that few (if any) are really insoluble, and by special methods, based on electrical conductivity measurements, the concentrations of solutions of many of these "insoluble" substances have been measured; *e.g.* at 20° C., silver chloride ·00016 gm. per 100 c.cs. water, calomel ·00031 gm. per 100 c.cs. water.

* Mellor, *ibid.* I. 766.

The effect of grain size must not be confused with the increased rate at which finely powdered solids dissolve, for it is an actual difference in solubility. *E.g.* for gypsum particles ·0004 cm. in diameter the solubility at 25° C. is 2·085 gms. per litre, and this increases to 2·476 gms. per litre when the particles are only ·00006 cm. in diameter.*

We are at present unable to account for the differences in the solubilities of substances in various solvents, but evidence is accumulating which shows that there is probably a connection between solubility and the chemical constitutions of solute and solvent.

2. Practical Determination of Solubilities.—The procedure is similar to that adopted for very soluble gases: (1) Make a saturated solution at the required temperature. This may be done by stirring excess of finely powdered solid with the solvent in a vessel immersed in a thermostat. (2) Analyse a given weight of the saturated solution by chemical analysis, or determine the weight of solute by evaporation to dryness. If w_2 gms. of solution contain w_1 gms. of solute, then $w_2 - w_1$ gms. of solvent were used in making the solution.

An alternative method is sometimes made use of, particularly when a number of determinations are to be carried out rapidly at different temperatures. A known weight of solid is mixed with a known weight of solvent and well stirred while gently heating. The temperature is noted when the last crystal is just about to disappear, and then on cooling the temperature is noted at which this crystal again begins to grow. The mean of these two readings gives the temperature at which the given weight of solid saturates the given weight of solvent. This can be quickly repeated with successive portions of solid, and so the effect of temperature on solubility determined.

3. Temperature and Solubility.—If we knew the true heat of solution (*i.e.* the thermal effect of dissolving the solute in the nearly saturated solution), we could deduce from le Chatelier's rule the effect on solubility of raising or lowering the temperature.

Since this rule only applies to systems in equilibrium, we

* Mellor, *ibid.* I. 508.

must apply it in this case to **the saturated solution in equilibrium with the solute**, and the heat of solution will be the thermal effect of dissolving the solute in the nearly saturated solution. In practice this is seldom measured, but values for heat of solution are given under specified conditions in which heat of dilution (or the thermal effect of diluting the saturated solution) is usually included. It is impossible to tell from these values alone what the true heat of solution will be. *E.g.* it is not an exception to the rule to find that the solubility of caustic soda increases with the temperature even though much heat is developed when solid caustic soda dissolves in water.

Applying the rule, we find that substances like potassium nitrate, which absorb heat on dissolving (in a nearly saturated solution), become more soluble as the temperature rises ; and conversely substances like calcium citrate or hydroxide, which evolve heat under like circumstances, become less soluble on raising the temperature.

4. Supersaturation.—If the solubility of a substance decreases with falling temperature, then cooling a solution will eventually make it saturated ; and on further cooling, unless solute is deposited, it will become supersaturated. It is quite easy in some cases to obtain comparatively stable supersaturated solutions. If nuclei are not present to start precipitation, a considerable degree of supersaturation is possible before the system passes from the metastable condition to the labile unstable state in which spontaneous deposition of solid occurs (*cf.* p. 73). If, however, a minute particle of the solid is introduced into a supersaturated solution, the mixture is at once unstable and deposition of solid occurs on the particle acting as a nucleus. Particles of solids isomorphous with the solute will also start precipitation, and when nearing the limit of the metastable region, dust particles or mere shaking will be sufficient : facts which have to be remembered when preparing such solutions.*

* If a crystallisation is delayed by supersaturation, it is sometimes useful to " inoculate " or " seed " the solution by introducing a small crystal. Very often the dust in the air contains isomorphous particles which render this unnecessary.

5. Solubility Curves.—If the solubility of a substance is plotted against the temperature at which it is determined the resulting curve represents the concentrations of solutions which can exist in equilibrium with solute at various temperatures. Thus in Fig. 14, A represents a solution of 30 gms. of potassium chlorate in 100 gms. water, and the curve shows that this can only exist in equilibrium with solute at 66° C.

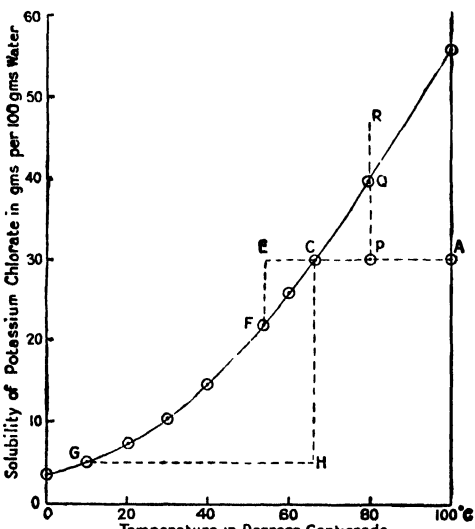


FIG. 14.—Solubility curve of potassium chlorate.

At 80° C. a solution of this concentration would be represented by P (**unsaturated**). On evaporation, if the temperature remains constant, the concentration will increase as represented by PQ until it is saturated (at Q). Further evaporation would tend to increase the concentration towards R (**supersaturated**), and so solid will be deposited and the concentration remains constant (at Q).

Moreover, inspection of the curve will show us the effect of cooling a solution, for suppose we start with an unsaturated solution P and cool it, the concentration will not vary until

the point C is reached when it will become temporarily supersaturated (E) and then deposit solid until its concentration sinks to F. These steps being in practice very small, the result is a continuous change in concentration (represented by CG) as the temperature falls from 66° C. to 10° C. During this process the weight of solid deposited will be 25 gms. (CH). Solubility curves, therefore, give us very precise information concerning the process of crystallisation.

6. Crystallisation.—If in a given solvent the solubilities of the constituents of a mixture are widely different, a separation can be effected by shaking the mixture with a little solvent and filtering. The purification of a substance, however, frequently involves the separation of an impurity having very similar properties to those of the substance itself. In such cases a partial separation can be effected **if the solubility curves for the two substances are sufficiently divergent.** We have therefore to find a solvent which at one temperature will dissolve the whole mixture, but at a lower temperature will dissolve one constituent nearly completely and the other very slightly. On cooling, the latter will then crystallise out nearly pure.

EXAMPLE.—If a mixture of potassium chlorate and potassium chloride be dissolved in water, concentrated by evaporation until saturated with the former, and then cooled, the concentrations of the chlorate and chloride will vary as shown by AA'G and BB'J (the original solution before concentrating contained AX and BX gms. of the two salts) (Fig. 15). The weight of the chlorate crystallising out is considerable, and none of the chloride should apparently have left the solution. In practice, separation in this way is always imperfect, for some of the more soluble ingredient is always " carried down " on the surface of the deposited crystals, but by repeating the process (see below) the degree of purity can be increased.

The problem of crystallisation is one which frequently confronts the manufacturing chemist and a reference to accounts of the manufacture of potassium nitrate, sodium carbonate (Solvay process), potassium chlorate, and potassium chloride (from carnallite), will show to what extent it has been solved.

Many solvents other than water are employed, particularly in organic chemistry, *e.g.* alcohol, ether, acetone, the choice depending on the effect of temperature on the solubilities of the substances forming the mixture. Solvent recovery is an

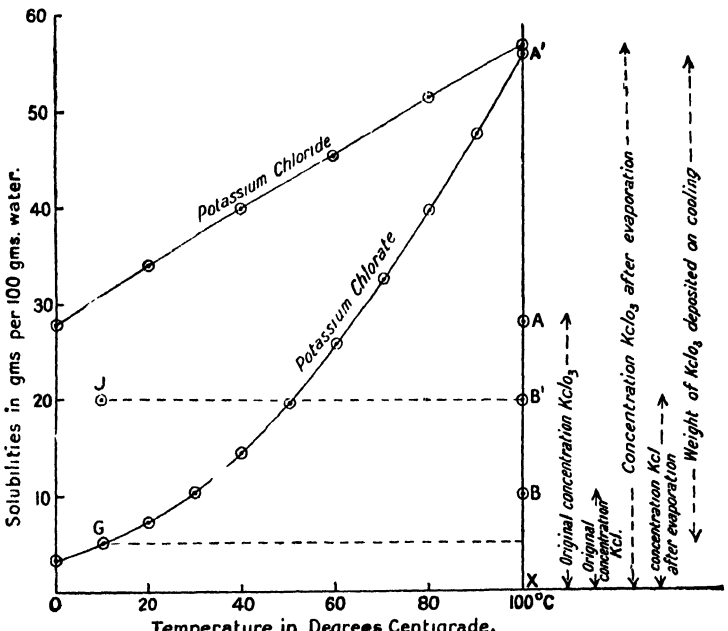


FIG. 15.—Separation of a mixture by crystallisation.

important item when using expensive solvents like acetone on a technical scale.

7. Recrystallisation. Fractionation.—The imperfect separation resulting from a single crystallisation divides the mixture into two halves or fractions. One, with a larger proportion of the less soluble ingredient than was present in the original mixture, has crystallised out and been filtered off; the other, with a larger proportion of the more soluble ingredient, forms the filtrate. If the crystals be dissolved and recrystallised, the result will be a crop of crystals still richer

in the less soluble ingredient, and this process can be repeated *ad lib.*

If the filtrate is not also attended to, however, there will be a considerable waste of material, and sometimes (as in Pattinson's process for desilvering lead) both ingredients are required in a state of purity. Hence, as a rule, both fractions have to be treated, and the treatment is often complicated by dividing the original mixture into several fractions instead of two; *e.g.* by taking away the crystals formed at the end of definite intervals: (1) richest in A; (2) less rich in A . . . and so on to (*n*) the final mother liquor richest in B.

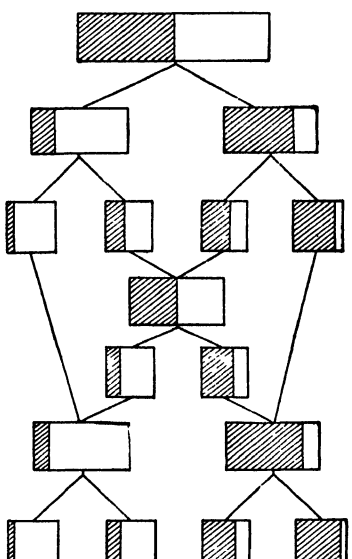


FIG. 16.— Fractionation of a mixture of two substances.

A precisely similar treatment is given to the fractions obtained by any of the physical methods of separation so that **fractionation** *is a general term embracing fractional crystallisation, distillation, diffusion, etc. It indicates that by continued repetition of a process on the fractions thereby obtained, two fractions approximating more and more to the two pure substances will result.*

It is necessary to carry out a fractionation in the laboratory to understand the details fully (fractional distillation being most suitable for this purpose), but the diagram (Fig. 16) may give some idea of what occurs in the simple case of two primary fractions.

8. One Solute and Two Solvents. Ether Extraction

If a solute A has the same molecular state in two solvents B and C, then on shaking it with a mixture of the two (assuming these to be immiscible) we find that

$$\frac{\text{concentration of solute in B}}{\text{concentration of solute in C}}$$

is a constant depending only on the temperature and not on the actual amounts of B and C present (the distribution law referred to on p. 77). This constant is called the **partition coefficient,** and if it is large then solvent B shaken with a solution of A in C will extract a large proportion of A from the other solvent.

EXAMPLE.—The partition coefficient of iodine between carbon disulphide and water at 15 C. is 410. Hence, if an aqueous solution of iodine is shaken with carbon disulphide nearly all the iodine is afterwards found to be dissolved in the latter.

A practical application of this principle is found in an often-used method of separating mixtures (or purifying substances), termed " ether extraction." In **ether extraction** an aqueous solution of a mixture is shaken with ether. One ingredient is to be extracted by the ether as completely as possible and as free as possible from the others, separation being completed by tapping off the aqueous layer in a separating funnel. It is easy to prove that, with a given weight of ether, the weight of solute extracted is far greater if successive small doses of ether are used instead of one extraction with the same total volume. An example may make this clear.

EXAMPLE.—$\frac{\text{Concentration of succinic acid in ether}}{\text{Concentration of succinic acid in water}} = \frac{5}{1}$.

Suppose 100 gms. of aqueous solution contain w gms. of succinic acid and we shake with 100 gms. of ether, the result will be an aqueous solution containing $\left(\frac{1}{1+5}\right)w$ gms., and an ethereal solution containing $\left(\frac{5}{1+5}\right)w$ gms. But if we divided the ether into two 50-gm. portions and extracted first with one of them, we should get an aqueous solution containing $\left(\frac{2}{2+5}\right)w$ gms., since $\frac{\text{wt. of acid in 50 gms. ether}}{\text{wt. of acid in 50 gms. water}} = \frac{5}{1}$, and therefore 2 : 5

would be the relative weights of acid in the 100 gms. of water and the 50 gms. of ether. A second extraction with the other 50 gms. of ether, from the aqueous solution containing $\frac{2w}{7}$ gms., would leave an aqueous solution containing $\frac{2}{7} \times \frac{2}{7}w$ or $\frac{4}{49}w$ gms., so the total weight of acid extracted would be $\frac{45}{49}w$ gms., instead of $\frac{5}{6}w$ gms. when only one extraction was employed.

9. Abnormal Solubility Curves.—The solubility varies with the temperature in a regular manner in most cases, as shown by the smooth solubility curves. Hence, when we obtain a curve such as Fig. 17 with a **discontinuity** * (indicating an abrupt change in solubility) occurring at 32·5° C., we may regard this as abnormal, and due to something exceptional taking place at this temperature. Now the properties of the solution do not alter abruptly at this temperature, but the change is in the solute which is dissolving. If sodium sulphate crystals be heated in contact with a saturated solution, they lose their water of crystallisation at 32·5° C.

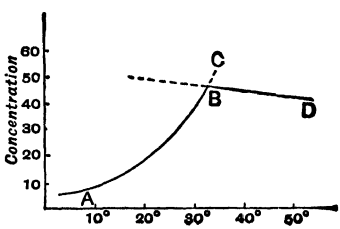


FIG. 17.—Solubility curve of sodium sulphate.

(From Findlay's *The Phase Rule*, modified.)

$$Na_2SO_4.10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$$

is a system in equilibrium at the transition point 32·5° C. Above and below this temperature anhydrous salt and decahydrate are the respective stable forms. Above and below this point we are examining the solubility curves for two different substances—anhydrous salt and decahydrate. These have the same solubility at the common point B, and the curve is in fact a composite of two curves.

Try to predict the effect of warming a solution of sodium sulphate saturated at 32·5° C.; *and also, the effect of adding a crystal of the decahydrate to a solution saturated at a temperature above* 32·5° C. *Then test your conclusions experimentally.*

* See p. 46.

10. Hydration. Water of Crystallisation.—If pure copper sulphate ($CuSO_4$), which is a white powder, be dissolved in water, the crystals formed on evaporation are blue and on analysis are found to have the formula $CuSO_4.5H_2O$. The simple ratio between the number of salt molecules and the number of water molecules is in favour of regarding this blue substance as a true compound, and other evidence (such as fixity of composition) supports this view. Hence it is called a **hydrate** * or compound with water, and the latter is frequently termed " water of crystallisation."

If a substance on analysis does not correspond to a simple empirical formula it is in all probability a mixture. *E.g.* the eutectic alloy of tin and lead containing 63 % tin would have the formula $Sn_{\frac{63}{119}}Pb_{\frac{37}{207}}$, or $Sn_{3\cdot44}Pb$, if it were a compound, and other evidence justifies our belief that such a substance is really a mixture. Sometimes by sheer coincidence the composition of a mixture will correspond to a simple formula, but such cases are rare. *E.g.* Levol's alloy (Ag 71·9 %, Cu 28·1 %), is a heterogeneous mixture, although its composition agrees with a formula Ag_3Cu_2.

It must not be concluded from the number of crystalline substances which are hydrated that water of crystallisation is present in all crystals, for many crystalline substances are only known in the anhydrous † condition ; *e.g.* NaCl, $AgNO_3$. We shall have to consider later the actual state of the molecules of a substance when dissolved in a solvent, but it should be noted that the existence or non-existence of **solid** hydrates is no answer to the broader question whether hydrates exist in solutions.

Another problem of interest concerns the forces which bind together the molecules of water and anhydrous compound. The latter (although " saturated " in the sense discussed on p. 20) must evidently possess **" latent "** or **" residual " valencies** of some kind, and it is therefore not surprising to find that **" molecular compounds "** exist in great variety ; *e.g.* double salts such as $K_2SO_4.Al_2(SO_4)_3.24H_2O$, or substances

* Compounds between solutes and solvents other than water have been called " solvates," and the act of combination, " solvation."

† A damp solid is simply a *mixture* of solid and saturated solution.

like $CaCl_2$ $8NH_3$. Whatever explanation is offered, these forces must be weaker than those binding the atoms of saturated compounds, for we find that molecular compounds can as a rule be easily decomposed into their constituents. *E.g.* crystalline hydrates readily lose their water when heated, and double salts when dissolved in water behave as though their constituent single salts were quite free from one another.

11. The Freezing of Dilute Solutions. Cryohydrates. —If a solution is cooled, precipitation of solid will commence when it becomes saturated, but if it is very dilute it may not be saturated when the temperature has fallen to its freezing point. This will be below the freezing point of the pure solvent, for in nearly all cases the freezing point of a solvent is lowered by dissolved substances,* but when it is reached pure solvent will separate out. The remaining solution must in consequence become more concentrated.

The separation of pure solvent on freezing a dilute solution is a most important fact. It can be tested experimentally by freezing a coloured solution, such as potassium permanganate, and examining the colourless ice formed round a central column of solution. Tasting the ice formed in rocky pools on the seashore affords another proof of the same fact, provided that the adhering layer of salt water is first washed off.

It was shown by *Blagden* in 1788 that the depression of the freezing point was proportional to the concentration of the dissolved substance (**Blagden's law**), and hence the freezing point of a solution must steadily fall, for it becomes more concentrated as solid solvent separates. Will this go on indefinitely? No! Because the solute has a definite solubility at all temperatures (even below 0° C.) and the solution must eventually become saturated. On further cooling it would become supersaturated if more solvent separated, and consequently salt will be deposited as well. Let us summarise.

On cooling a dilute solution:

(1) Temperature falls to freezing point.
(2) Pure solvent separates in solid form.

* *Cf.* p. 47.

(3) Solution remaining is more concentrated.
(4) Temperature has to fall further before freezing can continue.
(5) Solution eventually becomes saturated.
(6) Solid salt and solid solvent are deposited simultaneously.
(7) Concentration of solution is no longer altered, and
(8) Freezing point no longer changes.

Hence, from this point onwards the solution freezes at a constant temperature like a pure substance, and the solid formed is of constant composition also. It is proved to be a heterogeneous mixture and not a compound by (1) microscopic examination ; (2) having a composition not agreeing with any simple formula ; (3) having a composition and freezing point which can be varied by altering the pressure.

The solid mixture of ice and salt deposited at −22° C. in this way was thought to be a compound by *Guthrie*, who gave it a formula, $NaCl.10H_2O$ (23·6 % NaCl corresponds more nearly to $2NaCl.21H_2O$, and called it a **cryohydrate** or hydrate produced by cooling.* The temperature at which it formed he called the **cryohydric point.** These names are still used though it is established that the solid is not a hydrate, but a **eutectic mixture** formed at a **eutectic point** in precisely the same manner as a eutectic or lowest melting alloy (*cf.* p. 44).

The cryohydric or eutectic point is the lowest temperature which can be reached before all has solidified, and it may appear strange at first sight that the same result is obtained if a **concentrated** salt solution is cooled ;—a steady fall of temperature to the eutectic point and then solidification as a whole. The explanation is that in this case solid salt is being deposited from the moment that the solution becomes saturated, and ice only appears for the first time at the eutectic point. Reference to Fig. 18 will make the whole of this discussion clearer. AO is the freezing-point curve for dilute salt

* Guthrie published in the *Phil. Mag.* for 1875 a list of cryohydrates with their cryohydric points.

solution. This is plotted from experimental results and represents the equilibrium between solid ice and solution—any point on this curve represents the temperature at which a solution of definite concentration will freeze, *i.e.* can exist in equilibrium with ice. BO is the solubility curve representing the equilibrium between solid salt and solution, and it will be noted that these curves intersect at O, which is the cryohydric point. The discussion above should now be followed by tracing the change in an original solution (represented by X)

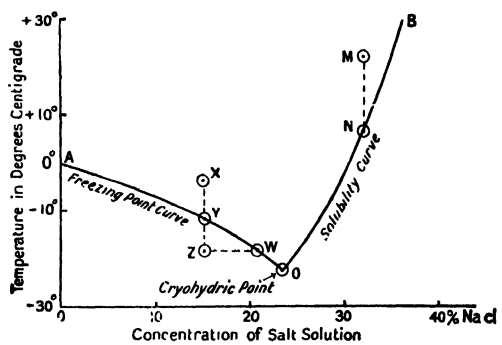


FIG. 18.—The freezing of a salt solution (diagrammatic).

when it is cooled. The dotted line XYZW represents in an exaggerated way what happens (YZ is a degree of supercooling not reached in practice, and the change from Y onwards is to all intents and purposes following the curve YO). If an original solution M is cooled, the change is MNO with salt separating from N to O. What happens at O? No change in either concentration or temperature can occur without entering an unstable region, so the remaining solution freezes unchanged.

O is evidently a **transition point** at which ice and solid salt can exist in equilibrium with solution and vapour. Above this, if solution and vapour remain, either salt or ice will have to disappear; below this both salt and ice can coexist if either solution or vapour disappears.

If instead of cooling a dilute solution we mix ice and solid

salt the temperature steadily falls until the cryohydric point is reached. This is the basis of a "freezing mixture," and the explanation given is as follows:

(1) In contact with the air a little ice will melt.

(2) Some salt dissolving will form a concentrated solution, the temperature of which will be much above its freezing point.

(3) More ice will melt to dilute this solution, as it is obviously an unstable system in contact with ice at 0° C.

(4) The latent heat required to melt this ice is taken from the surrounding mixture and so the temperature of this falls, and only when the cryohydric point is reached will the system be in stable equilibrium.*

12. Solutions of Liquids in Liquids.—Some pairs of liquids can be mixed in any proportions without two layers forming. The result is always a homogeneous mixture (solution), so that a saturated solution is an impossibility and the mutual solubility of such liquids is infinite; *e.g.* alcohol and water.

On the other hand some liquids appear to be quite immiscible (*e.g.* water with mercury, or with certain oils), but it is open to question whether the solubilities are really zero or only too small to detect with our present apparatus.

Between these two extremes we find liquids with finite solubilities, so that homogeneous mixtures are possible up to definite saturation concentrations. Between these limits two layers will form. *E.g.* 9 % ether in water and 1·1 % water in ether will be the compositions of the two layers always present if there is between 9 % and 98·9 % ether present (see p. 48).

Since the mutual solubilities vary with the temperature, it is evident that the limits of partial miscibility will also vary. It sometimes happens that at a certain temperature (called the **critical solution temperature**) the two layers have the same composition so that the whole mixture is homogeneous. In such cases the liquids will be completely miscible

* This is neglecting one or two minor factors (such as radiation from the air) which in practice make the final temperature reached by a freezing mixture slightly higher than the cryohydric point.

above (or below) this temperature, according to the manner in which the solubilities are affected by temperature.

EXAMPLES.—(1) Phenol and water (mutual solubility increases with rise in temperature) are completely miscible **above** 68·4° C.

(2) Nicotine and water (mutual solubility increases with fall in temperature *) are completely miscible **below** 61° C.

13. Evaporation and Boiling.—From the surface of a liquid molecules are continually passing into the vapour phase —a process known as **evaporation.** This is balanced (if the space above is closed) by the reverse process of **condensation** (*cf.* p. 114), for the concentration of molecules in this space rises until rate of evaporation is equal to rate of condensation. The molecules in the vapour phase will exert a pressure on the containing walls, and this **vapour pressure** will have a constant value as long as the concentration of these molecules is constant. Experiment shows that at a given temperature this is always the case—the vapour pressure of a liquid in equilibrium with its vapour being independent of the amount of liquid present. Hence if we remove vapour from the surface of a liquid (*e.g.* by blowing on it), further evaporation will occur and the liquid can in this way be completely converted into vapour at temperatures far below its **boiling point.** This " boiling point " is the temperature at which ebullition or boiling occurs, a process differing from evaporation in two respects: (1) it is not a surface phenomenon, and (2) it can take place at one temperature only. If heat is supplied to any point in a liquid at this temperature, change of state occurs (we are here neglecting superheating) and the liquid boils without change in temperature.†

There is a very important connection between vapour pressure and boiling point, for it has been shown experimentally that:

* When below 120° C. Above 120° C. the mutual solubility increases with rise in temperature, so that a second or upper critical solution temperature is reached at 210° C., above which they are again completely miscible.

† If heat is not supplied externally the temperature will fall. Boiling will then cease, but evaporation will continue.

(1) *The vapour pressure of a liquid increases with temperature.*
(2) *The vapour pressure becomes equal to the pressure due to the atmosphere above it when the boiling point is reached.*

EXAMPLES.—(1) In an open dish water boils at 100° C. when the atmospheric pressure is 760 mms. (Q) and at 102° C. when the atmospheric pressure is 816 mms. (S) (see Fig. 19).

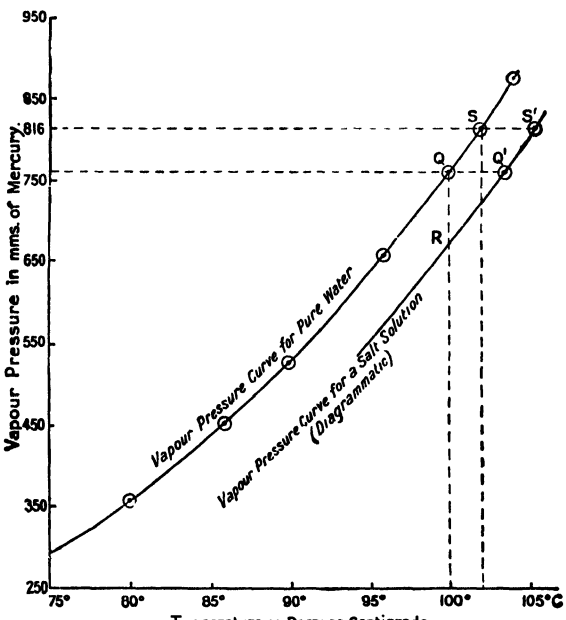


FIG. 19.—Vapour pressure and boiling point.

(2) If the pressure inside a vessel is reduced by means of a pump to 100 mms., water would boil in it at 52° C. The chemist takes advantage of this when distilling liquids which would decompose at their normal boiling points, for by distilling under reduced pressures the boiling points can be reduced to temperatures at which decomposition does not occur.

Vapour Pressure Measurement.—Direct measurements

can be made by introducing the liquid into the space above the mercury in a barometer tube, but the method is inaccurate and seldom used. Indirectly, the vapour pressure of a liquid can be determined by distillation and observation of the pressure under which it boils at a given temperature. A determination which is much more often made is the lowering of vapour pressure produced by the addition of solutes (see below), and special methods have been devised for this purpose (see p. 143).

NOTE.—A **volatile liquid** *is one which has a large vapour pressure at low temperatures, so that a small rise in temperature will bring its vapour pressure to atmospheric pressure: i e. it will have a low boiling point.*

14. The Vapour Pressure of Solutions.—(a) *Non-Volatile Solutes.*—Dissolved substances lower the freezing points of solvents and (if non-volatile) have a similar effect on their vapour pressures. This is not a coincidence; the two are related, as will be shown later. Hence solutions boil at higher temperatures than the pure solvents (see Fig. 19), and *Wüllner* proved experimentally in 1858 that the lowering of the vapour pressure was proportional to the concentration of dissolved substance (*cf.* Blagden's law, p. 91). For short distances around the boiling points the vapour pressure curves are almost straight lines, and hence, as can be seen from the figure, rise in boiling point QQ′ will be nearly proportional to lowering in vapour pressure QR. Also the curves are nearly parallel, and this agrees with the experimental observation that for dilute solutions **rise in boiling point is proportional to the concentration of dissolved substance.**

NOTE.—The vapour pressure lowering is proportional to the concentration of solute, but it also depends upon the temperature (*i.e.* on the original vapour pressure of the solvent). However, it was shown by *Von Babo* (1848) that the **relative lowering of vapour pressure** $\left(\frac{P-P'}{P} \text{ or } \frac{\text{lowering of v.p.}}{\text{original v.p.}}\right)$ **is independent of the temperature,** and therefore in comparing the effects of different solutes we must remember to compare relative lowerings of vapour pressure (see p. 121).

EXAMPLE.—At 71·5° C. the v.p. of water is 249·5 mms.

This is lowered by 14·9 mms. to 234·6 mms. by adding 13·82 gms. potassium chloride to each 100 gms. of water. But at 98·1° C. the v.p. of water is 708·7 mms. and a similar addition reduces it by 42·4 mms. to 666·3 mms. The " relative lowering " is the same in each case : $\frac{14{\cdot}9}{249{\cdot}5} = \frac{42{\cdot}4}{708{\cdot}7} = {\cdot}060$.

(b) *Volatile Solutes* (*e.g.* solutions of liquids in liquids).

Each solute lowers the vapour pressure of its corresponding solvent, so that the vapour pressure of the mixture must be less than the sum of the partial pressures of the two pure liquids at the same temperature.

But since both constituents of the mixture are volatile, the vapour pressure of the mixture **may or may not** be greater

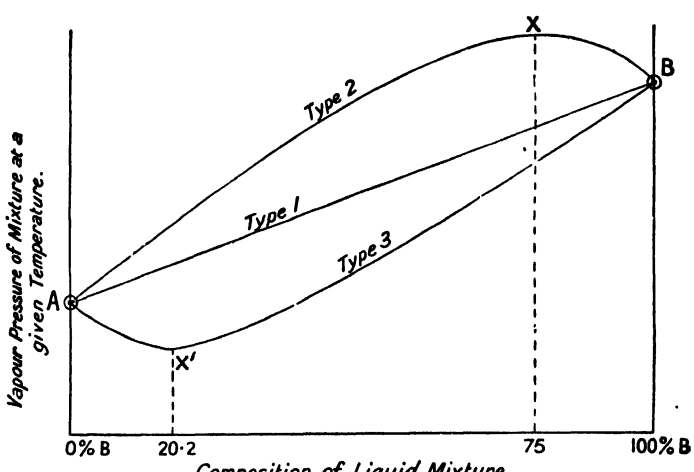


FIG. 20.—Mixed liquids. The variation of vapour pressure with composition.

than that which would be produced by these separately. The curves (Fig. 20) show the three different types of relation found between the vapour pressure and the composition of the mixture, and there is evidently **no simple relation** between these quantities. These curves are plotted from experimental

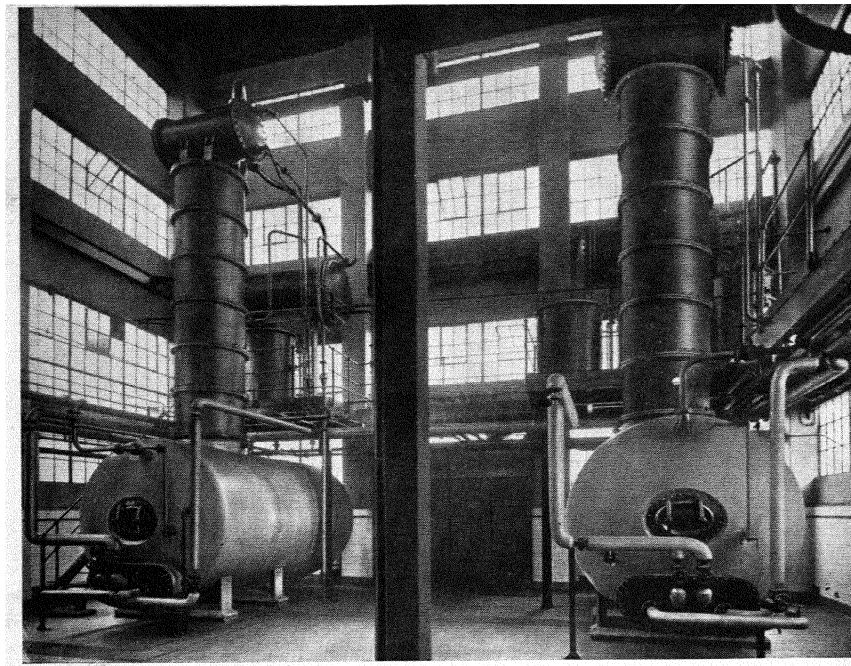


PLATE III. Benzole Stills used by the Lancashire Steel Corporation in the Production of Solvent Naphtha.

measurements, and an examination of them will enable us to deduce the effect of boiling solutions of each type.

It will be easier to understand what follows if the facts below are clearly grasped.

(1) The vapour pressure due to a mixture rises with the temperature.

(2) When the vapour pressure reaches external pressure the mixture boils ; *i.e.* high vapour pressure means low boiling point.

CASE 1.—**If the curve connecting vapour pressure and composition has no maximum or minimum** (*e.g.* methyl alcohol and water) (Fig. 20, Type 1), the vapour distilling over (and hence the distillate) is **not** of the same composition as the boiling mixture (forming the residue in the flask). In such cases the more volatile constituent tends to come over first, and therefore the vapour always contains a greater proportion of that constituent.

In consequence, the residue becomes steadily richer in the less volatile constituent, and the boiling point will steadily rise as the vapour pressure due to the mixture changes towards that indicated by point A (Fig. 20, Type 1). By redistilling the distillate and residue (*i.e.* by fractionation), a fairly complete separation can be brought about unless the two constituents have boiling points very close together.

To avoid numerous redistillations a device known as a fractionating column is often employed. A large air-cooled surface is exposed to the ascending vapour and this is thereby partially condensed, so that the vapour which passes over has had to pass through a column of liquid before it reaches the condenser (see Fig. 20A). The less volatile constituent is condensed in much larger proportions than the more volatile, so that the distillate is richer in the latter than would have been the case if no fractionating column had been employed.

CASES 2 AND 3.—**If the curve connecting vapour pressure and composition shows a maximum or minimum value** the effect of distillation is quite different for the following reasons :

(1) *When the mixture has the composition corresponding to*

the maximum or minimum vapour pressure, the composition of the vapour is the same as that of the liquid.

Hence, it distils unchanged at a constant temperature (provided that the external pressure is constant), just as though it were a pure substance.

It was at first thought that these mixtures were compounds,

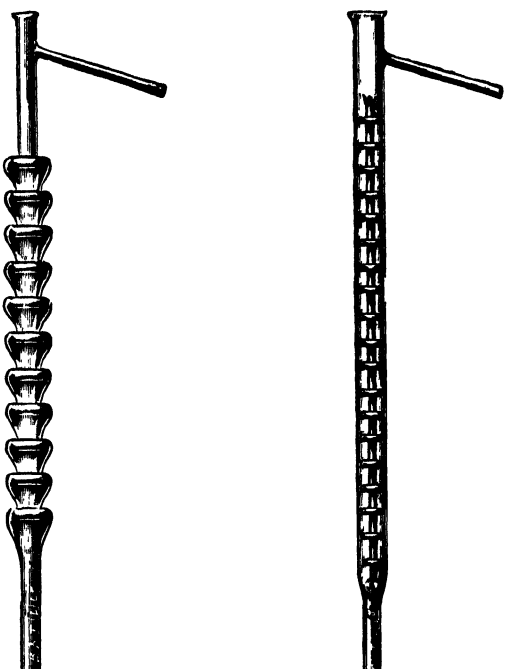


FIG. 20A.—Types of still heads or fractionating columns.

but since the composition can be varied by changing the external pressure, this idea has been abandoned, and they are now called **constant boiling mixtures.** *E.g.* hydrogen chloride and water form a constant boiling mixture boiling at 110° C. under a pressure of 760 mms. and containing 20·24 % HCl. If the pressure is decreased to 100 mms. it is found to contain 22·9 % of hydrogen chloride and boils at 61° C.

(2) When the mixture has any other composition, then, as usual, we find that the vapour coming over tends to be that having the maximum vapour pressure. If we consider first the case of Fig. 20, Type 2, where **the curve shows a maximum** (*e.g.* for propyl alcohol and water), *then throughout the distillation a nearly constant composition vapour comes over, forming a nearly constant composition distillate.* The residue will alter in composition either towards A or B, the boiling point rising as shown by the curves XA or XB. These are really two separate curves each similar to Fig. 20, Type 1, and the whole is a composite (*cf.* Fig. 18). If the original mixture lies on XA (*i.e.* the proportion of A is greater than in the constant boiling mixture X) then the residue alters as shown by XA. Similarly an original mixture lying on XB will tend towards B on distillation.

EXAMPLE.—75 % propyl alcohol and 25 % water form a constant boiling mixture. Distillation of a 90 % (alcohol) solution will cause a vapour to come over containing more water (25 %) than in the original solution (10 %), and hence the residue gets richer in alcohol. Distillation of a 50 % solution will, however, cause the residue to get richer in water.

Considering next Type 3, Fig. 20, where **the curve shows a minimum** (*e.g.* for hydrogen chloride and water) we shall have one liquid (A or B) coming over nearly pure when boiling commences, according to which side of X′ represents the composition of the original mixture. Thus a 50 % hydrogen chloride solution will start by losing acid, but a 10 % solution will start by losing water. As distillation proceeds the vapour composition steadily changes and the boiling point rises, as shown by curves AX′ or BX′, so that in any case the residue tends to the composition X′ and then boils unchanged.

NOTE.—If a pair of liquids form a constant boiling mixture, the composition of this will be the extreme limit of separation possible by fractionation. Thus a solution of ethyl alcohol in water cannot be concentrated beyond 98·4 % alcohol by fractionation at atmospheric pressure; and fractionation of aqueous solutions of hydrochloric acid will tend to a maximum concentration of 20·2 % acid.

FUMING LIQUIDS.—A liquid exposed to air will evaporate, and mixtures of vapour and water vapour will be formed if the air is moist. If these correspond to liquid mixtures of low vapour pressure, the amount present in the vapour phase may be too great and some condensation will occur. The fine drops of liquid give the appearance of fumes in the same way that steam from an engine forms a visible cloud on condensation.

(c) *Immiscible Liquids.*—Each liquid will in this case behave independently, so that the *vapour pressure due to the mixture is equal to the sum of the partial pressures. Boiling will occur*

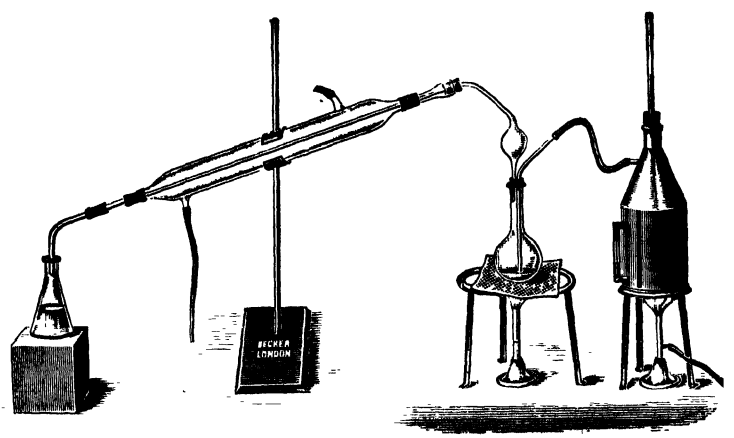


FIG. 21.—Steam distillation apparatus.

when this equalises the external pressure. It follows that the boiling point must be less than that of either of the pure liquids, and advantage is taken of this in **steam distillation.** For if steam is passed into a liquid, the resulting mixture will boil below 100° C. whatever may be the boiling point of the liquid itself (see Fig. 21).

EXAMPLES.—Nitrobenzene (b.pt. 209° C.) mixed with water boils at 99° C. The water supplies the greater part of the vapour pressure, but the nitrobenzene vapour pressure at 99° C. is sufficient, when added to the water vapour pressure

at 91° C., to make the total equal to atmospheric pressure. Similarly benzene (b. pt. 80° C.) will boil at 69° C. if steam is passed in; aniline (b. pt. 184° C.) at 98° C.; toluene (b. pt. 111° C.) at 84° C.; naphthalene (b. pt. 218° C.) at 98° C.

The volume of vapour distilling over will be proportional to its partial pressure, so that in steam distillation the volume of water found in the distillate is relatively large. This is to a certain extent compensated for by the greater vapour densities of the less volatile liquids; thus, with aniline,

$$\frac{\text{wt. of aniline vapour distilling}}{\text{wt. of water vapour distilling}} = \frac{\text{partial pressure}_{(\text{aniline vapour})} \times \text{vapour density}_{(\text{aniline})}}{\text{partial pressure}_{(\text{water vapour})} \times \text{vapour density}_{(\text{water})}}$$

(d) *Partially Miscible Liquids.*—As long as only one layer is present we have an unsaturated solution, which behaves like the homogeneous mixtures discussed above (b). **When two layers are present** we have two immiscible liquids as in (c), but since each is a solution, its vapour pressure will be lower than that of the pure solvent. Hence the *vapour pressure will be constant but less than the sum of the partial pressures of the two pure liquids.*

As an exercise, this should be represented graphically by a vapour pressure-composition curve, and the effect of distillation deduced.

15. Deliquescence and Efflorescence. — Crystalline hydrates are continually losing water molecules from their surfaces by evaporation, for the vapour pressures can be measured experimentally. Thus at 10° C. the following approximate values have been obtained:

$CaCl_2.6H_2O$	3 mms.,
$FeCl_3.6H_2O$	6 mms.,
$Na_2CO_3.10H_2O$	24 mms.,
$Na_2SO_4.10H_2O$	28 mms.

Now at this temperature the maximum aqueous vapour pressure is about 9 mms., so that substances like the last two mentioned will **always** exert a greater aqueous vapour

pressure than the air in contact with them. In course of time, such substances are bound to lose their water of crystallisation * if exposed to the air, and the process is termed **efflorescence** owing to the powdery coating of anhydrous salt which forms on the surface of the crystals.

On the other hand, substances like calcium chloride, $CaCl_2.6H_2O$ or ferric chloride, $FeCl_3.6H_2O$ will lose none of their water if exposed to ordinary moist air in which the aqueous vapour pressure is generally as much as 9 mms. On the contrary, atmospheric aqueous vapour will condense on the surface of such solids † and dissolve some of the substance to form a concentrated solution. If the vapour pressure of this solution is less than that due to the water vapour in the air, further condensation will occur until the whole solid is dissolved.

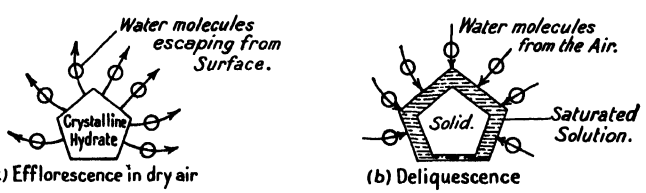


FIG. 22.—Diagrammatic representation of efflorescence and deliquescence.

This process is known as **deliquescence,** and it accounts for the state of ferric chloride which has been kept for any length of time in badly stoppered bottles.

NOTE.—A **hygroscopic** substance is one which absorbs water in any manner and is not necessarily dissolved thereby. *E.g.* blotting paper and calcium chloride are both hygroscopic, but the former is not deliquescent. **Dehydrating** or **desiccating agents** can be of either class. *E.g.* calcium chloride deliquesces, but strong sulphuric acid does not, being already liquid.

* We are neglecting here any cases in which intermediate hydrates are formed with vapour pressures greater than this.

† The formation of surface films of moisture is found to take place on *any* solid in contact with water vapour. The explanation cannot be given here.

16. Solutions of Solids in Solids.—It has been shown experimentally that some solids in contact can mix by diffusion,* and the result must evidently be a " solution." Mixed crystals (p. 28), and certain alloys (p. 44) are also solutions (*i.e.* homogeneous mixtures) of solids in solids. Examples of partially miscible solids are known,† and the partition law has been found to hold for solutions of iodine in solid benzene and liquid benzene, so that in every respect these " solutions " are comparable with liquid solutions. It is worth remembering here that the term " solid solution " is also used for solutions of gases in solids (p. 79), for the result is a homogeneous solid whatever may be the nature of the constituent absorbed.

DEMONSTRATIONS.—1. Illustrate supersaturation, and the effect of adding nuclei (sodium thiosulphate and sodium acetate are very suitable for this purpose).

2. Illustrate the partition law (iodine in water and carbon disulphide), and ether extraction.

3. Show the effect of warming sodium sulphate solution saturated at 32·5° C.

4. Freeze dilute solutions of potassium permanganate. Study freezing point depression of salt solutions and temperature of freezing mixtures.

5. Illustrate miscibility of liquids. Use ether and water, and phenol and water, to illustrate points of importance.

6. Demonstrate the relation between vapour pressure and boiling point. Distillation under reduced pressures.

7. Boiling points of salt solutions of different concentration.

8. Display fractionating columns of different types and discuss them.

9. Steam distillation apparatus should be displayed.

10. Show the effect on hydrochloric acid vapour of having a damp surface in contact.

11. Efflorescence and deliquescence. Salts should be left exposed for several days under various conditions.

* Roberts-Austen showed that gold could diffuse into lead (*Proc. Roy. Soc.*, 1900 (67), 101).

† $BeSO_4$ and $BeSeO_4$ will form mixed crystals in any proportions up to a limit when the relative weights present are 7·33 : 1.

PRACTICAL WORK.—1. Determinations of solubilities. If the members of a class find values at different temperatures, a solubility curve can be plotted. Excellent practice in volumetric analysis is given by finding solubilities of acids, alkalies, chlorides, iron salts, etc.

2. Separation of potassium chloride from potassium chlorate by crystallisation; preparation of potassium perchlorate or potassium nitrate. Solubility curves should be referred to before starting.

3. Ether extraction, fractional distillation, steam distillation can be illustrated by any suitable example, but the student must carry out the operations himself.

4. Blagden's law can be tested, or boiling point rise studied, using non-volatile solutes.

5. Distil an aqueous solution of hydrogen chloride of known strength. Note the temperatures at which various mixtures distil over by withdrawing portions from time to time and analysing them (titration). Also analyse the distillates at definite intervals.

QUESTIONS.—1. Describe in detail how you would determine the solubility of oxalic acid in water at 60° C.

2. Plot a solubility curve from the following data. (Cane sugar in water)

Temperature	0°	10°	20°	40°	60°	80° C.
Wt. solute per 100 gms. water	179	190	204	238	287	362 gms.

Hence deduce the solubility of cane sugar at 50° C.

3. Write short notes to explain the meaning of the following terms: supersaturation; deliquescence; efflorescence; cryohydrate; constant boiling mixture.

4. Summarise the methods available for separating mixtures, and explain what is meant by "fractionation."

5. Why is the solubility curve of sodium sulphate said to be abnormal?

6. Discuss the effect of (*a*) cooling a solution of salt by means of a freezing mixture, (*b*) heating a mixture of ethyl alcohol and water.

CHAPTER VII

THE PROPERTIES OF SOLUTIONS (*continued*)

1. Diffusion.—If two liquids are in contact, diffusion occurs until the mixture becomes homogeneous, if the liquids are completely miscible. This process is very slow in comparison with gaseous diffusion, as we should expect from the kinetic explanation of diffusion given on p. 70, for in liquids the molecules have much less " elbow room " and their movements are therefore impeded.

Considering solutions as liquids in which solute and solvent particles are moving, we may expect to find that diffusion occurs whenever a solution is placed in contact with a layer of solvent. Experiments are easily devised to show that this actually does happen, and if a coloured solution such as copper sulphate be used, the movement of the coloured boundary gives some idea of the slowness with which diffusion occurs in liquids.*

In such cases, the **rate of diffusion** is measured by the weight of solute passing in unit time from the solution into the solvent. Accurate measurements are not easy since any attempt to remove portions of the mixture for analysis is likely to disturb the remainder, but the difficulty has been got over in various ways, and in the Bakerian Lecture to the Royal Society for 1849, *Graham* published results from which he drew the following conclusions:

(1) The rate of diffusion depends on the nature of the solution.
(2) It increases rapidly with rise in temperature.
(3) It is directly proportional to the concentration of the solution.†

* A little agar-agar jelly dissolved in both solvent and solution will make it impossible to spoil a diffusion experiment by shaking, and also gives a much sharper boundary. It is found that the rate of diffusion is only very slightly altered by the presence of the jelly.

† In 1855 a more complete relation was established known as Fick's law:

$$\frac{Q}{t} = KA\frac{dc}{dx},$$

where Q is the weight of solute diffusing in time t across an area A, and

Graham continued his experiments for twelve years, and came to the conclusion that substances could be divided into two distinct classes: (1) **Colloids** which (in aqueous solution) diffuse extremely slowly, and (2) **Crystalloids** which diffuse comparatively quickly under similar conditions. Typical of the first class was glue—hence the name "colloid" from the Greek κόλλα; and of the second class the crystalline substance sugar. The approximate times taken for equal weights of various substances to diffuse from solutions under identical conditions, he found to be as follows:

Hydrochloric acid.	Sodium chloride.	Sugar.	Albumen.	Caramel.
1	2·3	7	49	98
Crystalloids.			Colloids.	

Graham thought that a "radical distinction in intimate molecular condition must exist between crystalloids and colloids," and he also speaks of the "peculiar form of aggregation known as 'the colloidal state of matter.'" We must be careful to note that his use of the term "colloidal" does not coincide with our present use of it. By "colloidal solutions" we now mean disperse systems (see p. 49) containing particles of ultra-microscopic size, and *any substance can (on this view) exist in the colloidal condition;* the term is therefore not restricted to "certain substances" as it was by Graham. Graham's "colloids" were substances which happened to produce colloidal solutions (in the modern sense) when they dissolved in water. They were classified under one head

dc is the difference in concentration at two points on either side of the imaginary boundary *dx* cms. apart. K is a constant termed the "diffusivity" which depends on the temperature, and the nature of the solution. This relation is very similar to that concerning the flow of heat in a bar of cross-section A between two points *dx* cms. apart, differing in temperature by $d\theta$: $\frac{Q}{t} = KA\frac{d\theta}{dx}$, where K is the thermal conductivity.

owing primarily to their slow rate of diffusion, and also owing to their having certain other properties in common which may now be summarised.

Graham's crystalloids.	Graham's colloids.
1. High rate of diffusion in solution.	1. Low rate of diffusion in solution.
2. Usually crystalline (like sugar and salt).	2. Usually amorphous, gummy, or resinous (like albumen, starch, and glue).
3. Low molecular weight (*e.g.* the inorganic acids, bases and salts).	3. High molecular weight (*e.g.* complex organic substances).
4. Easily soluble in water.	4. Comparatively insoluble in water.
5. Solutions have a large osmotic pressure (see later).	5. Solutions have a small osmotic pressure.
6. Diffuse readily through parchment or animal membranes.	6. Will not diffuse readily, if at all, through parchment or animal membranes.

The last property was made use of by Graham for separating colloids from crystalloids in a solution. He called the process of separation **dialysis,** a membrane forming the bottom of a vessel known as a dialyser (see Fig. 23). If a solution is placed in this and floated on water, the crystalloids will diffuse through and leave the colloids behind.



FIG. 23.—A dialyser.

For practical applications of dialysis, reference should be made to text-books of Inorganic Chemistry under " Preparation of Silicic Acid " and " Dialysed Iron " (the latter is a medical preparation of some importance). Proteins which are in the colloidal state are sometimes purified by dialysis. An interesting application is in the extraction of sugar from beet. Mashing up the beet makes it difficult to separate the sugar from the mixture obtained, so it is merely cut into slices and these are steeped in water until the sugar has diffused through the cell lining which acts as a membrane.

In the life processes of plants and animals, diffusion is of extreme importance. Materials which are to be stored up, such as starch in plants and glycogen in animals, are colloids which are in consequence easily retained where they are required. When transfer of material takes place, however, such as the products of carbon assimilation from a leaf to other parts of a plant, or products of digestion into the blood stream through the intestinal walls, we find that crystalloids are the moving substances. Anyone who has tried to make a meal of dry biscuits on a hot day will have realised that starch "goes down" with difficulty, and will have regretted his inability to convert it into sugar—a process normally carried out by a catalyst (ptyalin) in the saliva!

2. Osmosis.—If a solution could be separated from some of the solvent by a membrane which was impervious to solute molecules but would allow the solvent molecules to pass through freely, diffusion of the latter into the solution would occur until a state of equilibrium was set up. This would be reached when the rate of diffusion of solvent was the same on both sides of the membrane. **The observed result would have been a flow of solvent through the membrane into the solution.** Membranes of this kind can be obtained, and are called **semi-permeable** owing to their property of being impermeable to the solute. The first recorded observations of their behaviour are those of the *Abbé Nollet*, who in 1748 filled a bladder with alcohol and immersed it in water. Water entered faster than alcohol diffused out (the animal membrane not being absolutely impermeable to alcohol) and the bladder swelled until it nearly burst. On filling the bladder with water and immersing it in alcohol, he observed that the bladder shrank considerably.

An amusing parallel to the above is afforded by placing an egg in distilled water (after first dissolving off the shell in hydrochloric acid), for the outer skin of the egg acts as a semi-permeable membrane. If another egg is placed in strong brine, the rate of diffusion of water will in this case be more rapid from the contents of the egg to the brine, and this egg will behave in the contrary way to the first one. A flow of solvent

produced in this way is said to be an "osmotic flow"—the process being termed **osmosis.***

Perfectly semi-permeable membranes are an ideal, but in plant and animal tissues membranes are found which are selective in action; *i.e.* they will allow the passage of some substances and not of others. Many important physiological effects are due to osmosis. Thus, it is partly by osmosis that water enters the root hairs from the soil; interchange of materials from cell to cell is controlled by the selective permeability of the protoplasmic lining; certain movements such as the opening and closing of stomata, are caused by the changes in turgidity or "turgor" resulting from osmosis;

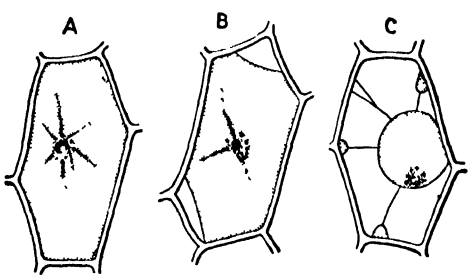


FIG. 24.—Plasmolysis of a plant cell.
(From Findlay's *Physical Chemistry for Students of Medicine.*)

and the wilting of a plant on a hot dry day is the direct result of loss of turgor in the cells supporting the plant. The contents of a plant cell shrink away from the rigid cellulose wall when it loses turgor, and the cell becomes flaccid or **plasmolysed.** The result of plasmolysis is well illustrated by the behaviour of the egg which was immersed in brine (see also Fig. 24).

It is stated that the sensation of thirst which follows after swallowing salt is due to the osmotic loss of water from tissues which become bathed in the concentrated salt solution.

3. Semi-Permeable Membranes.—For experimental purposes the most efficient semi-permeable membrane which has been found is a thin film of copper ferrocyanide. This is

* *ὠσμός* (a push).

extremely frail, but when supported on a framework it has then been found to give satisfactory results. Thus, if a porous pot is filled with a dilute potassium ferrocyanide solution and then placed in a vessel containing a dilute copper sulphate solution, the solutions diffuse into the pores. Where they meet these form a skin of copper ferrocyanide, firmly supported owing to the minuteness of the openings. *Pfeffer* used such membranes in all his experiments (to be described presently), and *Morse* (using cane sugar solutions) was thus able to maintain an osmotic pressure of over 12 atmospheres for 60 days without sign of a leak,* so that these membranes are evidently not far removed from being perfectly semi-permeable.

The way in which the membrane acts is not known. The simple explanation that it is an " atomic sieve " which allows solvent molecules to pass through its pores, but not larger particles such as molecules of solute or hydrated solute, is not found to account satisfactorily for all the facts, and alternative suggestions have been put forward. Perhaps the most likely hypothesis is that which is based on differences in solubility: that if a substance can dissolve in the membrane it will do so, and then diffuse through it until it reaches the other side; whereas the membrane would be impermeable to substances which are insoluble in it. We must remember that other explanations have also been put forward which are by no means disproved and (to quote Faraday):

" The philosopher should be a man willing to listen to every suggestion, but determined to judge for himself. He should not be biased by appearances; have no favourite hypothesis; be of no school; and in doctrine have no master."

4. The Result of Osmosis: Osmotic Pressure.—The swelling of the egg which was immersed in water is a clear indication of an increase of pressure inside the egg, and as this is the result of osmosis it is referred to as **osmotic pressure.** If some method of measuring the increase in pressure be adopted, using an imitation " egg," it will be found that this

* *J. Amer. Chem. Soc.*, 1911, 45, 558.

reaches a definite value * (*i.e.* the flow of water is eventually the same in both directions) after an interval of many hours.† Thus in the diagram (Fig. 25), a solution in a flask is shown separated from water by a piece of animal bladder, and **the osmotic pressure of the solution is measured by the excess hydrostatic pressure on the solution side of the membrane under these conditions.**



FIG. 25.—Illustration of osmotic pressure. (From Mellor's *Modern Inorganic Chemistry*.)

5. The Cause of Osmotic Pressure.—Do the particles of salt in a salt solution exert pressure on the walls of the bottle? If we adopt the kinetic explanation of solution (p. 72) we are bound to conclude that they do. Is this, then, the cause of the osmotic pressure *the existence of which can only be demonstrated by using a semi-permeable membrane in the manner just described?* The answer is: possibly, but not necessarily. Other hypotheses have been put forward which can account for the phenomenon, such as chemical attraction (or compound formation) between solute and solvent which would drag the latter through the membrane.‡ Also, purely physical explanations have to be seriously considered, such as the capillary forces which would come into play if a membrane behaved like a series of capillary tubes. We must refer again to Faraday's words and leave it to future workers to establish the correct explanation. Enormous forces have to be accounted for. *E.g.* a 6·5 molar solution of cane sugar produces an osmotic pressure of over 250 atmospheres when separated from water by a copper ferrocyanide membrane; and we must remember

* This is assuming the membrane to be perfectly semi-permeable If the experiment is carried out with parchment or animal membranes the solute diffuses through slowly, and so after the maximum pressure has been set up it slowly sinks to zero; *i.e.* the membrane "leaks."

† Reference to Fick's law of diffusion will show that the final stages of this process must be very slow.

‡ The very earliest ideas were of this nature. M. Traube in 1867 refers to "endosmotic force" as the attraction between solvent and solute. He considered that it could be measured in this way.

that **the actual fact observed is a flow of water through the membrane producing a hydrostatic pressure.** Can this pressure be due to the solute particles? Quite possibly, for van 't Hoff's suggestion that solute particles in a solution behave like molecules of a gas in a space of the same volume, leads at once to a "bombardment hypothesis." It would require a definite pressure to prevent an unsupported membrane from being moved by a bombardment of solute particles, so it is suggested that if the membrane is fixed this "bombardment pressure" will make itself felt in other directions, namely by balancing a column of mercury in a manometer. This view is a direct deduction from the kinetic hypothesis, for the process of **solution of a solid is analogous to evaporation of a liquid.** That is to say, it continues until a definite concentration is reached in the $\left\{\begin{matrix}\text{solution}\\\text{vapour phase}\end{matrix}\right\}$, this then being termed a $\left\{\begin{matrix}\text{saturated solution}\\\text{saturated vapour}\end{matrix}\right\}$. This is attained when

$$\text{rate of } \left\{\begin{matrix}\text{solution}\\\text{evaporation}\end{matrix}\right\} = \text{rate of } \left\{\begin{matrix}\text{precipitation}\\\text{condensation}\end{matrix}\right\}$$

and as the vapour pressure due to bombardment is then a maximum, it is reasonable to argue *by analogy* that the solute particles are in a similar manner exerting a maximum "solution pressure." This term represents the bombardment pressure *: what we measure and call the **osmotic pressure** is the hydrostatic pressure equal to this when a membrane is used in the manner described. An ingenious experiment devised by *Arrhenius*, and carried out by *Ramsay* in 1894, shows that osmotic pressure might be caused in this way if we assume completely analogous behaviour between dissolved solute particles and gaseous particles. Heated palladium (at 600° C.) is permeable to hydrogen but impermeable to nitrogen, so that it can be utilised as a semi-permeable membrane to separate a solution of nitrogen in hydrogen from some pure hydrogen. If the

* It has been used by Nernst as a measure of the tendency a substance has to dissolve, and in this sense has led to some important deductions.

actual bombardment pressure due to the nitrogen is P, then the diagram (Fig. 26) should make it clear that the excess

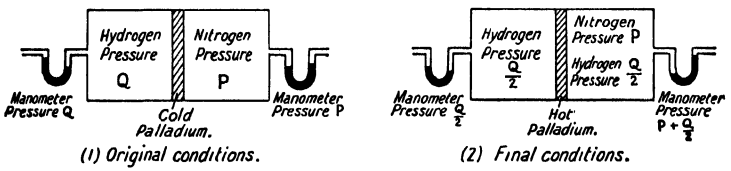


FIG 26.—The method of measuring osmotic pressure illustrated by Ramsay's experiment.

pressure on the right of the membrane is a measure of this when equilibrium has been established. This was realised experimentally.

6. The Results of Osmotic Pressure Measurements.—Using a copper ferrocyanide membrane of the type described above, and a manometer arranged as shown in the diagram (Fig. 27), *Pfeffer* investigated the effect of varying temperatures and concentrations on the osmotic pressures of solutions. His results were published in 1877, and ten years later they were used by *van 't Hoff* to confirm his theoretical deductions. These we will now consider.

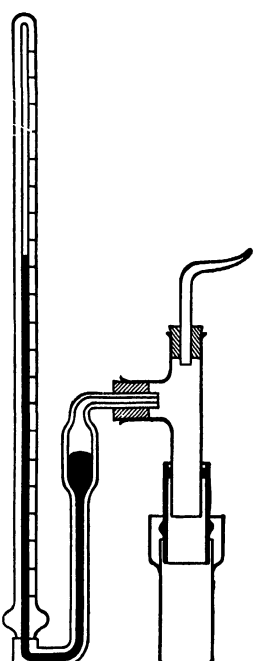


FIG. 27.—Pfeffer's osmotic pressure apparatus. (From McEwen's *The Properties of Matter.*)

Van 't Hoff was much impressed by the analogous behaviour of substances in the gaseous state and substances in solution (see previous paragraph). He therefore applied to the case of solutions, certain lines of reasoning (based on the laws of thermodynamics) which had already led him to some important conclusions in connection with gases. His deductions involved

one very important assumption :—that the solutions were infinitely dilute. This must be kept in mind, for it means that approximate agreement with experimental work is all that can be expected—an approximation which improves as the dilution increases. He concluded that :

(1) Osmotic pressure at constant temperature is directly proportional to concentration.

(2) Osmotic pressure is directly proportional to absolute temperature.

(3) Osmotic pressure is equal to the gas pressure which the solute would exert if it existed as a gas in the volume occupied by the solution.

The three " laws " of osmotic pressure thus stated may be summarised by saying that the relation PV=RT holds for **dilute** solutions as well as for gases. Thus (1) is analogous to **Boyle's law ;** (2) to **Charles' law ;** and (3) to **Avogadro's hypothesis,** for it signifies that 1 gm. mol. of any solute * dissolved in 22·4 litres of solution † at 0° C. will produce an osmotic pressure of 1 atmosphere (76 cms. of mercury). It follows that equal volumes of all (dilute) solutions at N.T.P. (P being an osmotic pressure of 1 atmosphere) contain equal numbers of solute molecules.

We can state this conclusion in several ways, all of which are of importance :

(1) Osmotic pressure $\propto$ number of solute particles (molecules) present in a given volume.

(2) Equimolecular solutions (*i.e.* solutions containing in equal volumes weights of solutes proportional to their molecular weights) will produce the same osmotic pressure. They are said to be **isosmotic.**

(3) The value of R in the relation PV=RT has the same

* Van 't Hoff's deductions do not involve the nature of the solution, but experiment has shown that many substances behave abnormally. These are the electrolytes (or substances whose solutions will conduct the electric current), and their abnormal behaviour will be referred to later.

† Recent investigations by Morse have shown that better agreement with experimental results is obtained if the volume of solvent be regarded here instead of the volume of solution.

numerical value whether applied to dilute solutions or to gases (see below).

Some of Pfeffer's results obtained with cane sugar solutions are given below for comparison with values calculated by van 't Hoff, and it will be seen that there is a reasonable agreement considering the large experimental errors involved.

TABLE II.

OSMOTIC PRESSURE AND CONCENTRATION.

(Cane sugar solutions between 13·2° C. and 16·1° C.)

Concentration in gms. per 100 gms. water.	Pressure in cms. of mercury.	Pressure. / Concentration.
1	53·8	53·8
2	101·6	50·8
4	208·2	52·1
6	307·5	51·3

TABLE III.

OSMOTIC PRESSURE AND TEMPERATURE.

(1% cane sugar solutions.)

Temperature in °C.	Absolute temperature.	Pressure.	Pressure. / Absolute temperature.
6·8	279·8	50·5	·180
14·2	287·2	51·0	·178
22·0	295·0	54·8	·185
32·0	305·0	54·4	·178
36·0	309·0	56·7	·184

(3) *Analogy between Osmotic Pressures and Gas Pressures.*—A 1 % solution of cane sugar (mol. wt. 342) at 0° C. exerts an osmotic pressure of 49·3 cms. of mercury. Substituting in the formula PV=RT we should get

$$R=\frac{49\cdot3\times13\cdot6\times34{,}200}{273}=83{,}960,$$

which is in very good agreement with the gas constant (84,760) considering the experimental difficulties and the fact that the

solution is not infinitely dilute. Hence, osmotic pressures for dilute solutions can be calculated from the relation PV=84,000T, but with concentrated solutions the calculated results are far from the observed values. *E.g.* for a 2·2 molar solution of cane sugar (*i.e.* 75 %), the value obtained by Lord Berkeley and Hartley was 135 atmospheres, but calculation gives only 52·8.

More accurate measurements have been made recently by *Morse* (1901–12), *Lord Berkeley* and *Hartley* (1906), and *Frazer* and *Myrick* (1916),* but their attempts to arrive at a general relation between osmotic pressure, temperature and concentration for **concentrated solutions** have been unsuccessful. Using dilute solutions the agreement between their results and calculations from the relation PV=RT is as close as can be expected for solutions which are not "infinitely dilute." It is interesting to note that the agreement becomes better as the temperature rises (*cf.* deviations from the gas laws, p. 64). The reason that Pfeffer's figures are given above (instead of these more accurate results) is that they were the values used by van 't Hoff in establishing his ideas on the nature of solutions.

7. Abnormal Osmotic Pressures.—Applying the relation PV=RT to solutions of many substances, the calculated values of the osmotic pressures are not found to agree with experimental results. Thus a solution of sodium chloride of concentration 11·7 gms. per litre (*i.e.* $\frac{11{\cdot}7}{58{\cdot}5}$ gm. mols. per litre) should exert an osmotic pressure at 0° C. of $\frac{11{\cdot}7}{58{\cdot}5} \times 22{\cdot}4$ atmospheres, but experiment shows that it exerts nearly 8·4 atmospheres, which is 1·87 times as much. There were so many cases like this, that van 't Hoff proposed PV=i(RT) as a more generally applicable relation, where i is a numerical factor depending on the nature of both solute and solvent and also on the concentration of the solution. We shall discuss the meaning of van 't Hoff's i factor (or coefficient) in Chapter IX., and at present may consider substances to be abnormal if i is not unity.

* Details of these researches are given in Findlay, *Osmotic Pressure* (Longmans, second edition, 1919).

8. Methods of Comparing Osmotic Pressures.—Direct measurements of osmotic pressure require special apparatus and much time and skill, but it is comparatively easy to compare the osmotic pressures of two solutions by a method due to the botanist *de Vries*. If plant cells * are placed in solutions of different concentrations, it is not difficult to see under the microscope at what particular concentration the solution just fails to plasmolyse the cells (see p. 111). The solutions inside the cell and outside are then said to be **isotonic.** We can in this way find the concentrations of isotonic solutions of different substances; *i.e.* the concentrations at which they produce the same osmotic pressure, if they are all equally affected by the semi-permeable membrane.† Hence if we determine the actual osmotic pressure in any one of these solutions we shall know it for all of them.

NOTE.—Since isotonic solutions (if they are also isosmotic) must be of equimolecular concentration, we have here a very simple method of comparing molecular weights. Thus, 3·15 and 1·3 are the concentrations (in gms. per 100 c.cs.) of isotonic glucose and glycocoll solutions. Therefore, since these equal volumes contain equal numbers of molecules, the molecular weights of these substances will be in the ratio 3·15 : 1·3.

9. Properties of Solutions related to Osmotic Pressure.—The osmotic pressure of a dilute solution is proportional to the number of solute molecules present in a given volume of solution, and thus to the concentration of the solution and to $\frac{1}{\text{molecular weight of solute}}$. Hence, determinations of osmotic pressure would serve to fix the molecular weights of substances if only the experimental work was easier.

* De Vries used the epidermal cells of the leaves of certain plants, *e.g.* tradescantia discolor, but the method has been extended to the determination of the osmotic pressures of the solutions in many plant cells, and (with slight modifications) in certain animal cells, such as red blood corpuscles. (See Findlay, *Physical Chemistry for Students of Medicine.*)

† It is because this is not always the case that the term isotonic is used here instead of isosmotic. Obviously, if the membrane allows part of a solution to leak through, we shall not measure its full osmotic pressure but something less.

EXAMPLE.—A 2 % solution of glucose exerts an osmotic pressure of 2·75 atmospheres at 30° C. But 1 gm. mol. in 22·4 litres at 0° C. would exert a pressure of 1 atmosphere. Hence

$$\frac{2}{M}\times\frac{22{,}400}{100}\times\frac{303}{273}=2{\cdot}75 \text{ or } M=180.$$

Now, there are three other properties of **dilute** solutions which are proportional to $\frac{\text{concentration of solution}}{\text{molecular weight of solute}}$ (*i.e.* to the osmotic pressure), and as these are comparatively easy to measure they are used in determinations of molecular weights (details in Chapter IX.). They are (1) the depression of the freezing point, (2) the relative lowering of the vapour pressure, and (3) the rise in the boiling point produced by solutes;—properties which have been briefly referred to in the previous chapter.

It follows that (*a*) weights of solutes proportional to their molecular weights will all produce the same effect on a given volume of a solvent; viz. the same osmotic pressure, freezing point depression, etc., and (*b*) molecular weights can be compared by taking equal weights of solutes and comparing the freezing point depressions, etc., which they produce in a given volume of a solvent. The magnitude of the effect will depend upon the solvent employed.

EXAMPLES.—(*a*) 3·42 gms. of cane sugar, ·32 gm. of methyl alcohol, or ·60 gm. of urea dissolved in 100 gms. of water depress the freezing point by ·185° C. (These weights are $\frac{1}{100}$ gm. mol. in each case.)

(*b*) ·60 gm., 1·20 gms. and 2·40 gms. of urea would depress the freezing point of 100 gms. of water by ·185° C., ·37° C. and ·74° C. respectively.

Molecular Weights from Freezing Point Depression, Measurements, etc.—Hence, if w gms. of a solute whose molecular weight is M be dissolved in s gms. of solvent, the depression Δ is given by $\Delta\propto\frac{w}{s}\times\frac{1}{M}$. If K is the depression produced by M gms. in 100 gms. of solvent (this is a constant

for the particular solvent), then $\Delta = \frac{100K}{M} \times \frac{w}{s}$;—a useful form of expression to use when molecular weights are to be calculated from freezing point depressions. A similar relation applies to molecular weights and boiling point rises. Calculations from vapour pressure lowering have to take into account the original vapour pressure of the solvent, and also the weight of it present. If $\frac{P-P'}{P}$ is the relative lowering of vapour pressure, it is found experimentally that $\frac{P-P'}{P} = \frac{n}{N+n}$, where n and N are the numbers of molecules of solute and solvent present. If w gms. of a substance of molecular weight M be employed, $\frac{w}{M}$ is the number of molecules of it present. In calculating N for the solvent, M must be taken as its molecular weight in the gaseous state; *i.e.* twice its vapour density.

NOTE.—Concentrations are usually given in gms. per 100 **grams** of solvent instead of in a given **volume** of solvent. This obviously does not affect the proportionality, but it is important to notice that it is the weight of **solvent** and **not solution** (*cf.* footnote on p. 116).

Substances which in solution produce abnormal osmotic pressures (see p. 118) also produce abnormal freezing point depressions, etc. The explanation offered is the same in all cases: that these "osmotic effects" are proportional to the number of solute **particles** present in a given volume of solvent, and the abnormal substances are those which we believe to associate or dissociate on solution, so that n molecules do not become n particles when dissolved (see Chapter IX.).

10. The Relation between these "Osmotic" Properties.—The one fact common to the three processes of osmosis, evaporation, and freezing, is that solvent is separated from solution by some definite boundary. Now, whenever solvent leaves a solution and makes it more concentrated, work has to be done, and vice versa. By applying the laws of thermodynamics

to these processes, van 't Hoff was able in 1887 to deduce the relations mentioned above and thus to confirm the empirical rules which had been put forward by *Raoult* a few years before.

(a) *Raoult* had made use of Blagden's law (p. 91), and some work of *de Coppet* (1871), and concluded in 1884 that for a given solvent

$$\text{freezing point depression} \propto \frac{\text{concentration}}{\text{molecular weight of the solute}}.*$$

The depression produced by 1 *gm. mol. of any solute in* 100 *gms. of solvent is a constant for that solvent and is termed the* **molecular depression or freezing point constant.**† This was confirmed by van 't Hoff (assuming very dilute solutions to be taken), who calculated the freezing point constant for water as 18·9 from a formula $K=\frac{\cdot 02T^2}{L}$, where L is the latent heat of fusion of ice. Raoult's value obtained experimentally was 18·5.

(b) Raoult had also arrived at a relation between vapour pressure lowering and the molecular concentration of the solution (1886): $\frac{P-P'}{P}=\frac{n}{N+n}$. This conclusion, which was an extension of earlier work by *Von Babo* (1848), *Wüllner* (1858), and *Tamman* (1883), reduces to $\frac{P-P'}{P}=\frac{n}{N}$ if the solution is very dilute (*i.e.* n small compared to N), and this was confirmed by van 't Hoff. It can also be arrived at by reasoning from the kinetic hypothesis, an ingenious proof having been devised by Arrhenius.

(c) We have seen that boiling point rise is approximately proportional to vapour pressure lowering (p. 95), and *Beckmann*

* It may be asked how Raoult can have done this without knowing any molecular weights, for few of his solutes were volatile and so the molecular weights could not have been obtained from their vapour densities. As a matter of fact "formula weights" were used by Raoult. *E.g.* for sugar—(empirical) formula $C_{12}H_{22}O_{11}$—the formula weight 342 was taken as the molecular weight.

† Actually such a solution would be too concentrated for Raoult's rule to be applied, but it is a value calculated from determinations made in more dilute solutions, and is convenient for reference purposes.

in 1889 arrived at a relation connecting boiling point rise and molecular concentration of solution, exactly parallel to Raoult's freezing point relation. The boiling point constant can be calculated from the formula $K=\frac{\cdot 02T^2}{L}$ where L is the latent heat of evaporation of the solvent. Thus, for water $K=5\cdot 18$ (value from experimental data $=5\cdot 2$).

DEMONSTRATIONS.—1. Diffusion of liquids should be illustrated using aqueous solutions with and without jelly. Copper sulphate solution in contact with water forms a good example.

2. Illustrate dialysis using a mixture of starch and sodium chloride in solution. Iodine and silver nitrate can be used to detect the passage of these through the membrane.

3. Simple demonstrations of osmotic pressure are most important; *e.g.* the thistle funnel experiment. The egg experiment (p. 110) is amusing, and " chemical gardens " always prove fruitful sources of discussion.

PRACTICAL WORK.—Molecular weight determinations follow Chapter IX., so there is little for the student to do at this particular point.

QUESTIONS.—1. Why did Graham divide substances into " colloids " and " crystalloids " ? Explain the importance of liquid diffusion to plants and animals.

2. What do you understand by the statement that the osmotic pressure of a salt solution is P cms. of mercury ? How would you demonstrate the existence of this pressure ?

3. Describe how the osmotic pressure of a solution can be (*a*) measured directly, (*b*) compared with that of another solution.

4. State the laws of osmotic pressure. What was van 't Hoff's theory of solution which was based on these laws ?

5. Why are osmotic pressure measurements seldom used for determining molecular weights ? Show how the difficulty has been overcome.

6. Calculate the osmotic pressure which would be produced by a solution of ·092 gm. of urea in 100 c.cs. water at 30° C. The molecular weight of urea is 62.

7. ·75 gm. of arsenious chloride lowers the freezing point of 50 gms. of acetic acid by ·322° C. Calculate the freezing point constant for acetic acid if the molecular weight of arsenious chloride is 181·5.

8. If a 1 % solution of cane sugar produces an osmotic pressure of 54·8 cms. at 22·0° C., what will be the osmotic pressure produced by 1·71 gms. in 150 gms. of water at 10° C. ?

9. The vapour pressure of water at 14° C. is 11·98 mms. What will be the vapour pressure of a 15 % solution of glucose at this temperature ? The molecular weight of glucose is 180.

CHAPTER VIII

COLLOIDAL SOLUTIONS

1. THE smallest particles which can be seen with the aid of a microscope are about ·0001 mm. across, whereas single molecules are about one-thousandth of this size. With the ultramicroscope (described below) the presence of particles can be detected when they lie between these two limits in point of size, and systems consisting of such ultramicroscopic particles dispersed in some solvent medium are known as **disperse systems** or **colloidal solutions.** We have already referred to the fact that these have peculiar properties quite apart from their chemical nature (see pp. 50 and 109), and some of these will now be considered.

2. In dealing with colloidal solutions we refer to the solvent as the **dispersion medium** and to the solute particles as the **disperse phase.** Mixtures consisting of particular phases have in some cases been given special names; *e.g.*:

Solid	particles	dispersed	in a	liquid	medium	: suspensions.
Liquid	,,	,,	,,	liquid	,,	: emulsions.
Solid	,,	,,	,,	gas	,,	: smokes.
Liquid	,,	,,	,,	gas	,,	: mists.
Gas	,,	,,	,,	liquid	,,	: foams.

NOTE.—The term "suspension" is used when the solid particles are large enough to be visible, though sometimes too small to settle out under the action of gravity. A "fine suspension" is a stage between a "coarse suspension" and a true "colloidal solution," but there is no difference between these three except the degree of dispersion. The term "emulsion" is similarly used for liquid particles of visible size dispersed in a liquid medium. For greater degrees of dispersion (*i.e.* true colloidal solutions) the terms **suspensoid** and **emulsoid** are used, but unfortunately these do not indicate that the

disperse phase is solid and liquid respectively, but are related to the properties of the solutions (see para. 6).

3. The Preparation of Sols.—We will confine our remarks to suspensoids and emulsoids in this chapter and will first of all consider how these systems can be obtained. The liquid and apparently homogeneous form of colloidal solution is known as a **sol** and this term will be used from this point onwards.

Two methods of preparation are available: (1) We can start with a large mass of solute and disperse or scatter it in a solvent, or (2) we can start with a true solution and aggregate the solute molecules until they are of ultramicroscopic size. Both these methods have been employed successfully, but practical details cannot be given here. Three of the more generally used types of preparation will be briefly referred to.

(*a*) By the simple action of the solvent certain substances form sols; *e.g.* gelatine. Graham's "colloids" were of this nature.

(*b*) Chemical reactions in solution frequently give rise to precipitates and in some cases the substance "precipitated" may remain in the colloidal state, if this "Irish" use of the term "precipitated" be allowed. This method can be illustrated by passing sulphuretted hydrogen through an aqueous solution of arsenious oxide (a substance which is very slightly soluble in water). The clear yellowish liquid which is formed, and can be filtered just like water, is a sol of arsenious sulphide. Many metal sols (*i.e.* sols in which a metal like gold or mercury is the disperse phase) can be obtained in this way by the action of reducing agents on solutions of their salts.

(*c*) *Bredig's method.*—An electric arc is formed between metal wires immersed in a liquid. Particles of the metal become detached and form a sol. *E.g.* with gold wires immersed in water, red or violet liquids are obtained which are quite transparent—these are gold sols. It has been found that the colour of a sol (seen by transmitted light) depends upon the size of the dispersed particles. As the size of the particles decreases the colour alters from red to blue; *i.e.* in the direction of decreasing wave length.

4. The Ultramicroscope.—

"As thick and numberless
As the gay motes that people the sunbeams."
MILTON—*Il Penseroso.*

When a beam of light passes through a darkened room, an observer *at one side of the beam* can see the path of it by means of the light scattered or reflected from the dust particles which it strikes. These particles are too small to be visible but their presence is revealed by the light which they scatter. The visible track of the beam is known as the **Tyndall phenomenon** after the great English scientist of last century, who investigated it, and it can sometimes be observed when a light beam passes through an apparently homogeneous liquid. In such cases the liquids must contain suspended particles to scatter the light, though these may be too small

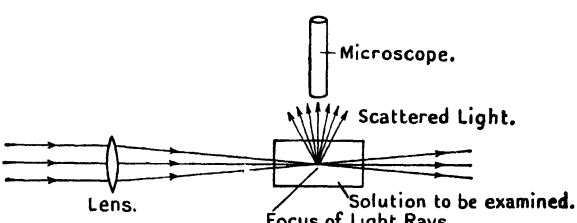


FIG. 28.—The ultramicroscope.

to be seen under the most powerful microscopes. Obviously the amount of light so scattered will be very small, and hence a search for it with a microscope will give the best chance of discovery. The combination of a microscope and a beam of light arranged as shown in the figure (Fig. 28) is known as the **ultramicroscope.** It is most important to remember that **no particles can be seen by it** in the ordinary sense, but a series of points or discs of light or even a diffuse light seen through the microscope indicates the presence of particles in the solution under examination.

5. The Brownian Movement.—One interesting fact disclosed by means of the ultramicroscope is that the dispersed particles in a colloidal solution are in rapid motion.

They dart about in an apparently haphazard manner like "a swarm of dancing gnats in a sunbeam" (Zsigmondy), and the phenomenon is known as the **Brownian movement** because *Robert Brown* had noticed in 1827 a similar effect with small but visible particles seen under an ordinary microscope.

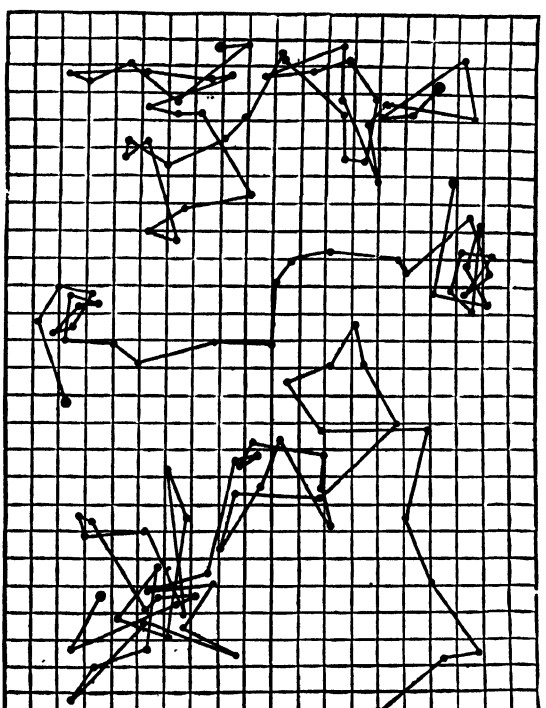


FIG. 29.—The Brownian movement.
(From *Philosophical Magazine.*)

Brown was a botanist, and he was examining a suspension of fine pollen grains in water when he made this discovery. He certainly did not realise its importance. It has now been established that the particles are being hustled about by a disorderly crowd of solvent molecules, and the real existence

of molecules is brought home to us when we look at the results of their Lilliputian bombardment. Of course with a large particle, the number of blows it receives at any moment is very big, and the net result will be nearly nil since these blows will be delivered in all directions. But if the particle is small enough the few blows received at any instant will have a resultant effect sufficient to move it,* and hence our kinetic theory of matter is confirmed in a most convincing manner.

6. The Properties of Colloidal Solutions.—(1) *Optical Properties.*—They are, as we have stated, apparently homogeneous liquids until examined by means of the ultramicroscope. Their colour depends upon the size of the dispersed particles.

(2) *Diffusibility.*—The rate of diffusion is very slow, as was the case with Graham's "colloids," and related to this we find that they exert very small osmotic pressures. Molecular weights have been calculated from these osmotic pressures and of course have very large values (*e.g.* for hæmoglobin about 16,000), but it is questionable whether the laws of osmotic pressure should be applied to systems which are not true solutions. After all, we shall not find in this way the "molecular weight" of the molecules, but only that of clusters of molecules!

(3) *Jellies and Gels.*—The solid form of a colloid is called a **gel**; familiar examples are cotton, silk, artificial silk (rayon), and rubber. Typical gels are formed by the coagulation of a sol, the colloidal particles aggregating to form coherent flocculent precipitates. There is one familiar kind of gel which is quite distinctive—the ordinary "jelly." A typical example of a jelly is to be seen when a solution of gelatine sets on cooling to an apparently homogeneous elastic solid or semi-solid. This process is called **gelatinisation** to distinguish it from ordinary coagulation or precipitation. In the latter case separation from the solvent usually takes place, or else the coagulum (like white of egg) does not again liquefy to a sol when the conditions are reversed.

Jellies are therefore an extreme instance where no marked

* A more detailed account should be read in Perrin, *Atoms*, when it will become clear that the study of the Brownian movement has given us definite proof of the existence of molecules.

change has taken place in the dispersed particles, but these have in some way become linked together to form a structure ramifying throughout the whole mass.

Gel Formation and the Classification of Colloids.—Colloidal solutions were formerly divided into two sharply defined groups known as reversible and irreversible colloids, or emulsoids and suspensoids respectively. The latter were distinguished by being much more unstable and liable to irreversible coagulation, but it has been found impossible to maintain this rigid form of classification. Two terms which are now in use are **lyophile colloids** (emulsoids, reversible colloids): those in which the disperse phase has such an affinity for the solvent that sols can be formed by simple mixing; and **lyophobe colloids** (suspensoids, irreversible colloids): those in which the affinity between the disperse phase and the solvent is not sufficient for this purpose. If water is the solvent, these terms become hydrophile (water loving) and hydrophobe (water hating) respectively.

Even this classification, however, is far from perfect as will be seen by the qualifications in the following table:

Emulsoids.	Suspensoids
1. Disperse phase formerly assumed to be liquid.	1. Disperse phase usually solid.
2. Form spontaneously from gels (lyophile); frequently can gelatinise.	2 Do not form readily from gels; rarely gelatinise.
3. Viscous liquids with small surface tension.	3. Viscosity and surface tension very nearly the same as for the pure solvent.
4. Exert an appreciable osmotic pressure.	4. Practically no osmotic pressure.
5. Usually show only a diffuse light under ultramicroscope.	5. Usually show the existence of definite particles under the ultramicroscope.
6. Usually coagulated by heat, but require considerable quantities of electrolytes to cause precipitation (see below).	6. Usually coagulated by heat, and also by traces of electrolytes (see below).
7. Have a " protective " action on suspensoid sols (see below).	7. Stability increased by the addition of emulsoids (see below).

(4) *Electrical Properties. Coagulation.*—If a difference of potential is maintained between two plates in a sol by means of a dynamo or electric battery, the dispersed particles migrate towards one or other of the plates. This phenomenon is known as **kataphoresis,** and shows that the particles must carry an electrical charge. These charges are found to be balanced by charges opposite in sign carried by ordinary ions.* However, since the conductivity is usually very low, the charges on any particular particle must be incomparably fewer than the number of atoms or molecules composing it. Kataphoresis is therefore a kind of electrolysis in which a few ordinary ions move in one direction, and corresponding charges of opposite sign are carried in the opposite direction by the particles moving as a whole.

Thus we distinguish :

Negative colloids. (−vely charged particles which move to the anode.)	Positive colloids. (+vely charged particles which move to the cathode.)
Sols of gold, silver, platinum.	Sols of metallic hydroxides such as the hydroxides of iron, aluminium and chromium.
„ sulphur, silicic acid.	
„ arsenious sulphide.	
„ soap.	
„ certain acid dyes such as congo red.	„ certain basic dyes such as methylene blue.

In a similar manner the particles of clay in a fine suspension are found to be negatively charged, which shows clearly that there is no hard-and-fast line between solutions, colloidal solutions, and suspensions.

Kataphoresis is identical in nature with " ionic migration " (see p. 222), or the movement of charged atoms (ions) in a true solution under the influence of an electric field. There is in fact no sharp boundary between :

(1) The charged particles in a true electrolyte like potassium chloride (charged atoms or radicals).

* An " ion " is an electrically charged atom or radical which conveys the current during the electrolysis of a solution (see Chapter X.).

(2) The charged particles in " colloidal electrolytes," like the soaps. These undergo electrolysis like electrolytes, but one of the ions is a complex consisting partly of aggregated molecules; *i.e.* a " colloidal ion " or, as it has been termed, " ionic micelle."

(3) The charged particles in a suspensoid (like a gold sol), in which charged aggregates of molecules carry the current.

Finally, to complete the parallel, we may note the existence of neutral or uncharged colloids like collodion, and of true solutions like sugar solutions, which are non-electrolytes for a similar reason.

We do not know for certain how the particles obtain their charge, but in some cases at any rate it appears to be at the expense of the dispersion medium. Thus, it is suggested that in hydrosols the hydrogen ions are sometimes adsorbed (*i.e.* attached to the surface of the particles) to a greater extent than the hydroxyl ions, so that the water is left negatively charged with respect to the particles. Evidence in favour of this view is accumulating, but it is not yet more than a working hypothesis.

The charges on the particles are often an important factor in keeping them from aggregating, for if they are neutralised precipitation immediately occurs. Thus, if a positive sol (*e.g.* ferric hydroxide) is added to a negative sol (*e.g.* arsenious sulphide) both are precipitated (mutual precipitation), but two positive sols or two negative sols can often be mixed without precipitation resulting. It will be pointed out in a later chapter that electrolytes (or solutions which will conduct the electric current) contain both positively and negatively charged atoms or radicals (known as ions), and that the number of unit charges carried by an ion is 1, 2, 3, . . . when the valency of the atom (or radical) is 1, 2, 3, . . . respectively. Hence, it is not surprising to find that sols are coagulated by the addition of electrolytes, positive sols being affected chiefly by the anion (or negative radical), and negative sols by the cation (or positive radical). Moreover, it was shown by *Hardy* that in general:

The precipitating effect of an ion depends on its valency. Hardy's rule is clearly in accordance with expectations. Thus, to coagulate a definite arsenious sulphide sol required quantities of sodium chloride, barium chloride, and aluminium chloride in the ratio 51 : ·67 : ·093 ; and to coagulate a given ferric hydroxide sol required quantities of hydrochloric, sulphuric, and citric acids in the ratio ·5 : ·002 : ·0007 ; the acid radical is clearly the important factor in the latter case (the positive sol being coagulated by the negatively charged ions) and the positive radical in the former case.

Many of the important applications of colloid chemistry are concerned with the precipitation brought about by neutralisation of the charged particles. Such diverse phenomena as the settling of the mud suspended in river water when it comes into contact with the salt water in the estuary, and the fixing of colloid dyes to fabrics by means of oppositely charged colloid mordants, being of this nature.

Moreover, the **stability of a colloid,** or its resistance to coagulation, is of vital importance, and this is found to be very much altered by the addition of emulsoids. Emulsoids have a protective effect on suspensoid sols (possibly by forming a protective coating on the individual particles), for much larger quantities of the precipitant are then required to bring about coagulation. In illustration it may be mentioned that the gelatin in photographic plates prevents the coagulation of the silver bromide sol formed when the potassium bromide and silver nitrate are mixed in the process of manufacture.

(5) *Surface Phenomena.*—The peculiar properties of colloidal solutions are largely due to the enormous surface exposed by the small mass of material forming the disperse phase. *E.g.* a cube whose side is 1 mm. has a surface of 6 sq. mm., but if this is broken up into cubes whose sides are 10^{-5} mms. the total surface exposed is 6×10^{10} sq. mms. Now at the boundary of any two media certain forces are brought into play which do not exist in the body of these media. We are familiar with these forces (under the name of surface tensions) at the boundaries where liquids are in contact with the air, or with glass vessels. They will evidently be

of particular importance in the case of colloidal solutions where the surface of contact between solute and solvent is of such enormous dimensions. The most important result from a practical point of view is that substances brought into contact with colloidal solutions tend to become condensed on the surface of the colloidal particles in the same way that moisture in the air becomes condensed on any glass surface which it touches. This condensation is known as **adsorption** and is a purely surface effect which must not be confused with absorption, a process involving penetration of the interior. To illustrate the adsorptive behaviour of surfaces, the decolorisation of coloured solutions by animal charcoal may be studied, and the adsorption of gases has already been mentioned (p. 78).

As a result of their great adsorptive power, colloids are particularly good catalytic agents (see p. 205), for the reacting substances are brought into intimate contact. *E.g.* **enzymes** (organic catalysts found in living creatures) are invariably colloidal material. Adsorption plays an important part in so many processes that only a few can be mentioned here:—(1) the adsorption of dyestuffs by colloidal mordants; (2) the retention in the soil of mineral salts by the colloidal humus, for otherwise the rain would soon wash away these salts; (3) the action of drugs and poisons on the animal system; (4) the purification of drinking water by filtration through colloidal material. Not without reason has the study of colloids been termed the investigation of "the world of neglected dimensions," when we consider the comparatively recent time during which these important ultramicroscopic systems have claimed the attention of scientists.

DEMONSTRATIONS.—1. If possible exhibit metal sols of different colours.* The formation of emulsoid sols is easily demonstrated with gelatine, and with an arsenious sulphide sol coagulation can be investigated.

2. Show the Tyndall effect by passing a beam of light through ordinary water. It will probably not be necessary to add anything to the water, but a drop of silver nitrate with most

* Some useful hints are given in the *School Science Review*, *VI.* 27.

tap waters will produce a cloudiness very suitable for demonstrating this effect.

3. The decolorising action of animal charcoal should be illustrated.

QUESTIONS.—1. Describe the methods by which colloidal sols are usually obtained.

2. Why do colloidal solutions exhibit so many characters which are absent in true solutions? Give a general account of the properties of colloidal solutions.

3. Describe and explain the ultramicroscope.

4. Explain the difference between "coagulation" and "gelatinisation." What are the main differences between "suspensoids" and "emulsoids"?

5. Write an essay on the "practical importance of a study of colloids."

PART III.—THE SCAFFOLDING

CHAPTER IX

MOLECULAR WEIGHT DETERMINATION. DISSOCIATION

SECTION (1).—MOLECULAR WEIGHT DETERMINATION

1. The Importance of Molecular Weight Determinations.—(a) *Fixing Formulæ.*—The empirical formula for a substance can be written down as soon as it has been quantitatively analysed; *e.g.* H_2O for water, HO for hydrogen peroxide, NaCl for salt. This does not indicate the actual number of atoms in the molecule, and the true formula is that simple multiple of it which corresponds to the molecular weight. Thus the molecular weight of water is 18 and $H_2+O=18$ so the molecular formula is $(H_2O)_1$ or H_2O. The molecular weight of hydrogen peroxide is 34 and $H+O=17$ so the molecular formula is $(HO)_2$ or H_2O_2. There is no method of determining the molecular weights of solids, but the molecular weights of substances can be found in solutions, or in the state of vapour, and (except in cases where there is reason to believe otherwise) the molecules are supposed to be the same under these conditions as in the solid state. If the molecular weight cannot be determined (directly or indirectly) it is usual to write the simplest formula; *e.g.* C for carbon instead of C_n. The "structure" of the molecule of a substance (*i.e.* the arrangement of the different atoms in it) can often be arrived at by examining either the reactions of the substance or the methods of synthesising it. In this way its relationship to other substances, whose formulæ are known, can be determined and so its formula can be written down. *E.g.* acetic acid appears

to be CH_3COOH and not CH_2O from this type of chemical reasoning.

The unsatisfactory nature of such conclusions will be apparent when the molecular weight of acetic acid is discussed (p. 157), for this indicates the existence of $C_4H_8O_4$ molecules ($(CH_3COOH)_2$) except at high temperatures. Indeed, our only safe guide as to the nature of the molecules of a substance is to determine its empirical formula and then its molecular weight. When we write NaCl for the formula for **solid** salt we must remember that this only indicates that equal numbers of sodium and chlorine atoms are present (see p. 34).

NOTE.—A very approximate value for the molecular weight is sufficient to decide what multiple of the empirical formula is to be taken for the molecular formula.

(b) *Indications of "Dissociation" and "Association."*—We shall see in this chapter that "things aren't always what they seem." Also that molecular weight determinations provide the clues which unmask mixtures masquerading as simple substances, and show the existence of secret decompositions and combinations which cannot be detected by the most skilful analyst.

NOTE.—For deciding the extent to which molecules are "dissociated" (decomposed) or "associated" (combined) in the manner described in this chapter, the molecular weights of substances must be determined as accurately as possible.

2. The Methods available for Determining Molecular Weights.—(1) Analysis of a substance followed by a study of its reactions, leading by "chemical reasoning" to its probable formula. *E.g.* if acetic acid is CH_3COOH its molecular weight is $2\times12+2\times16+4=60$.

(2) Determination of the vapour density of a substance leads directly to its molecular weight **in the state of vapour** (molecular weight $=2\times$ vapour density).

(3) For dissolved substances several methods are available based on the principles discussed in Chapter VII. Thus, we can calculate the molecular weight of a substance **in a dilute solution** from measurements of (*a*) the osmotic pressure, (*b*) the freezing point, (*c*) the vapour pressure, or (*d*) the

boiling point of the solution. Alternatively, the molecular weights of substances can be **compared** in this way by comparing the effects which they produce on the same solvent. Any solvent can be employed (even mercury), so the scope of this method is wide, the freezing point measurements being most easily carried out.

(4) For liquids (*i.e.* pure liquids—not solutions), a method is available based on surface tension measurements. The importance of this lies not in the details of the method, but in the fact that it is the only method available for pure liquids. All other molecular weight determinations have to be carried out with solutions or vapours.

(5) Special methods are available for organic acids of known basicity and for organic bases. The silver salts of the acids are decomposed by heating and the molecular weight of the acid (H_nX) calculated from the quantitative results of the reaction $\underset{(108n+X)}{Ag_nX} \rightarrow \underset{(108n)}{n}Ag$. The chloroplatinates of the bases are decomposed by heating and metallic platinum is left. If Y is a monacidic base, the reaction is $Y_2.H_2PtCl_6 \rightarrow Pt$ and from the quantitative results of this Y can be determined.

4. Details of the Methods mentioned above.* — (a) *Vapour Density Determinations.*—Four different methods of determining vapour densities are employed: (1) For substances which are gaseous at ordinary temperatures—**Regnault's method,** already described on p. 69. (2) and (3) The methods of *Hofmann* and *Victor Meyer*, in which the volume occupied by a given weight of substance is measured when this has been vaporised. (4) The method of *Dumas*, in which the weight of vapour which fills a flask of known volume is determined. The last method requires comparatively large quantities of material and is somewhat difficult to carry out, but it is capable of more accurate results than the two preceding it. The principle on which it is based can be seen by considering an example.

* As explained in the preface, experimental details are not to be sought for in this book. The student is expected to carry out molecular weight determinations for himself in the laboratory, but the object of the present chapter is to explain the principles underlying the determinations, and the importance of the results.

A Vapour Density Determination by Dumas' Method.—A large globe with drawn-out neck (see Fig. 30) weighed 23·45 gms. when full of air at 15° C. and 72·6 cms. pressure. A little of the liquid to be examined was introduced and vaporised by placing the globe in a constant temperature bath. When all had been vaporised, vapour ceased to issue from the orifice so this was sealed off, and the globe when cool was weighed again. Weight of globe+vapour =23·72 gms. Temperature of bath=100° C. The neck of the globe was then broken under water and some water entered. Weight of globe+water (+residual air if any) =201·5 gms. Hence, volume of water which has entered=201·5−23·5 =178 c.cs. (The weight of air which occupied this space when the globe was weighed originally was only about ·2 gm., which can be neglected in comparison with 201 gms.) But weight of globe (+residual air)=23·45 gms.−(weight of 178 c.cs. of air at 15° C. and 72·6 cms. pressure), and if this is subtracted from 23·72 gms. we get the weight of vapour. Assuming that the vapour was at atmospheric pressure, and that we can neglect the expansion of the globe, this weight of vapour occupied 178 c.cs. at 100° C. and 72·6 cms. pressure, so the density at N.T.P. can be calculated by applying the gas laws.*

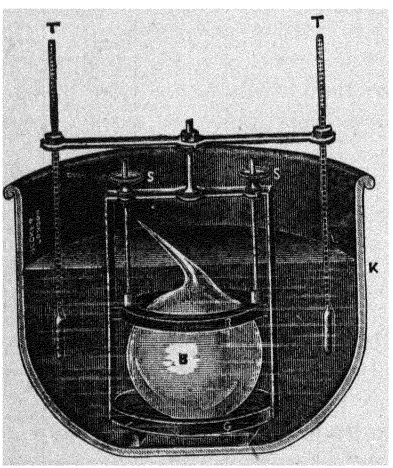


FIG. 30.—Apparatus for determining vapour densities by Dumas' method.

Hofmann's method is seldom used, but is necessary for substances which decompose when vaporised under ordinary

* The vapour is far from being an ideal gas, but it must be remembered that the density at N.T.P. is a convenient fiction. In practice the vapour would condense under these conditions.

conditions. In this method they vaporise under reduced pressure and therefore at much lower temperatures. A known weight of the substance in a little bottle (known as a Hofmann bottle) is introduced into the vacuum in a barometer tube (see Fig. 31). The vaporising liquid blows out the stopper and the volume of the vapour formed can be read off on the graduated tube. A jacket surrounding the tube allows

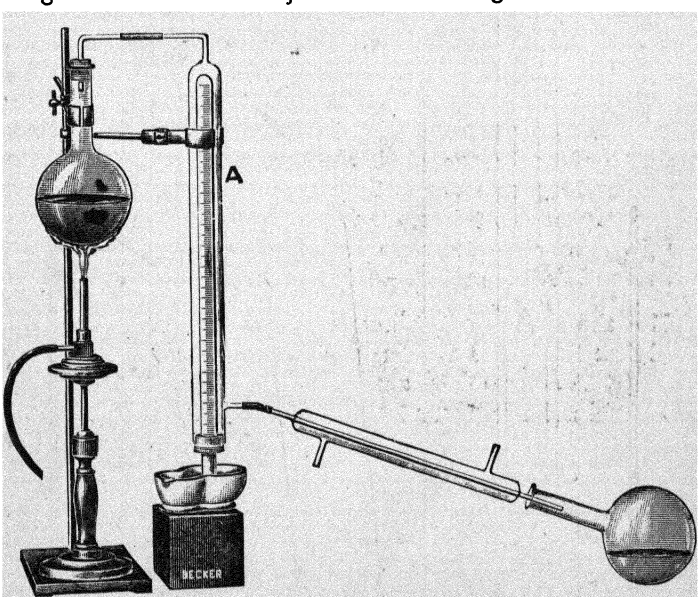


FIG. 31.—Apparatus for determining vapour densities by Hofmann's method.

a constant temperature to be maintained high enough to vaporise the liquid.

Victor Meyer's method is undoubtedly the most important and the one which is most often employed. The apparatus is shown in Fig. 32. A known weight of substance in a Hofmann bottle is dropped into the large bulb A and is rapidly vaporised. A constant temperature is maintained by the outer jacket—the vapour of a boiling liquid is usually employed, but electrical

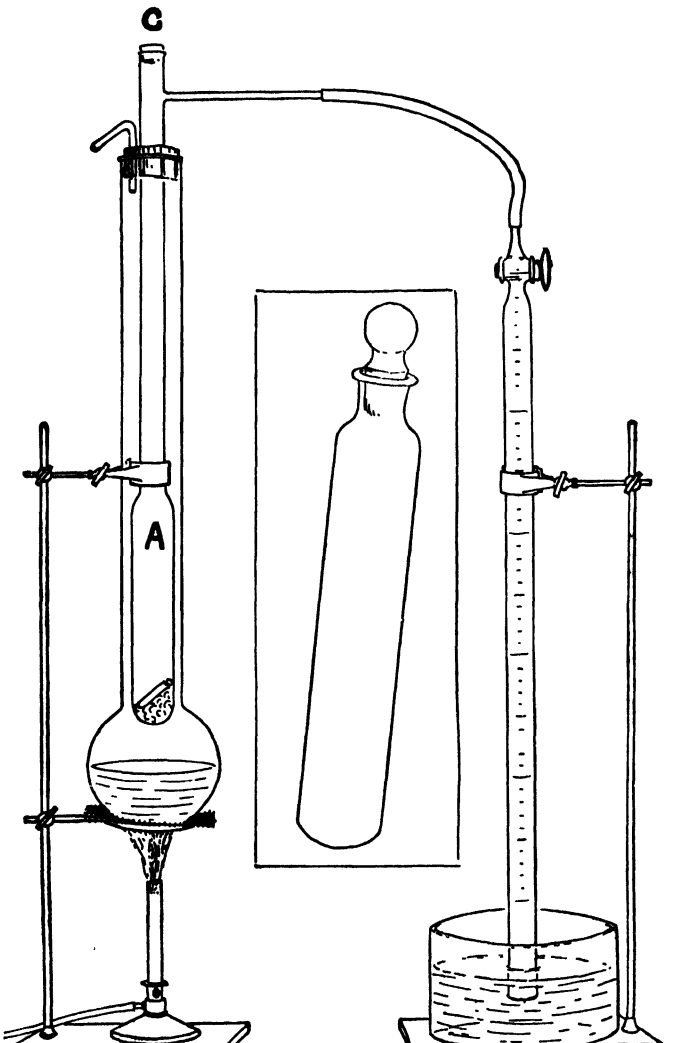


FIG. 32.—Apparatus for determining vapour densities by Victor Meyer's method.

(From Macbeth's *Organic Chemistry*.)

heating has proved successful for high temperatures. Before dropping the bottle, the air in the apparatus must have reached the temperature of the jacket and ceased to expand, so that the vapour formed in A drives over an equal volume of air into the measuring apparatus shown. The jacket temperature must be about 50° C. above the boiling point of the substance, as the vaporisation must be rapid. Otherwise diffusion of the vapour will occur, and some of it may leave the hot region and condense before the volume of air has been measured.

The air driven over contracts as it cools, but its volume is measured **at the temperature and pressure of the laboratory**, and so its volume at N.T.P. can be calculated without knowing the jacket temperature. Assuming that the vapour obeys the gas laws to the same extent as air, this will be the volume which the weighed quantity of vapour would occupy at N.T.P. (see footnote to previous page), and therefore the density is determined.

Advantages of Victor Meyer's Method.—(1) Small quantities of material (about ·1 gm.) are sufficient. (2) The jacket temperature need not be known accurately as long as it remains constant. (3) The determination is comparatively simple to carry out. The apparatus need not be of glass. *E.g.* using porcelain, iridium and other heat-resisting materials the vapour densities of substances have been determined up to 2,000° C.

(b) *Molecular Weights of Dissolved Substances.**—(1) *Osmotic Pressure Measurements.*—These have already been referred to, and the molecular weight of a solute is that weight which when dissolved in 22·4 litres of a solvent at 0° C. exerts a pressure of 1 atmosphere (p. 116).

(2) *Cryoscopic Method.*—It has been shown (p. 120) that 1 gm. mol. of a substance dissolved in 100 gms. of solvent produces a depression of the freezing point K (which is a constant for the particular solvent); and that if *w* gms.

* These methods are applicable to *dilute solutions* only, for the reasons given in Chapter VII. The relations between molecular weight and osmotic pressure, etc., do not hold except in very dilute solutions.

of solute in s gms. of solvent produce a depression Δ, the molecular weight of the solute is $w \times \frac{100}{s} \times \frac{K}{\Delta}$ (see also p. 122).

VALUES OF K (MOLECULAR DEPRESSION OF FREEZING POINT).

Water	18·5	(normal freezing point	0° C.)
Benzene	50	(,, ,,	5·5° C.)
Acetic acid	39	(,, ,,	17° C.)
Phenol	74	(,, ,,	40° C.)

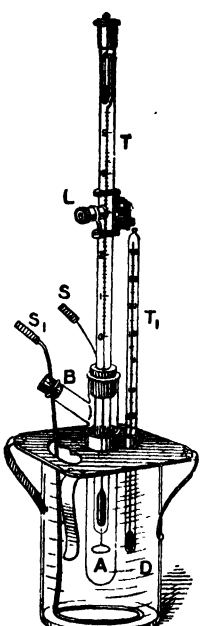


FIG. 33. — Beckmann's apparatus for freezing point determinations.

(From Mellor's *Modern Inorganic Chemistry*.)

The experimental determination of the depression of the freezing point involves the accurate measurement of a small temperature change, and a special type of thermometer was designed by Beckmann, which is illustrated in the figure (Fig. 33).

The freezing point of the pure solvent is first found, and then a known weight of solute is introduced and the new freezing point found. (The weight of solvent used must of course be known.) Precautions have to be taken on account of supercooling, for the freezing point must be determined before an appreciable quantity of solid has separated. In *Richard's* method the freezing point of a solution of unknown strength is first found, and then a portion of it is withdrawn and analysed.

(3) *Lowering of Vapour Pressure.*—A relation between the molecular weight of a solute and the relative lowering of vapour pressure it produces when dissolved in a solvent has already been given (p. 121), viz.:

$$\frac{P-P'}{P} = \frac{\frac{w_1}{M_1}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$$

By measuring the vapour pressure P of the pure solvent, and the vapour pressure P−P′ of the solution, the value of M can

be calculated if we use a solvent of known molecular weight (M_2) and know the weights w_1 and w_2 of solute and solvent respectively. In practice the direct measurement of these vapour pressures is difficult, and since the lowering is very small accurate results are not possible. Several ingenious methods have been devised by which these quantities can be determined.

The apparatus shown in Fig. 34 may be used to demonstrate the principle of the method, but it is not suitable for molecular weight determinations. Pure solvent and solution are contained in the left- and right-hand flasks respectively.

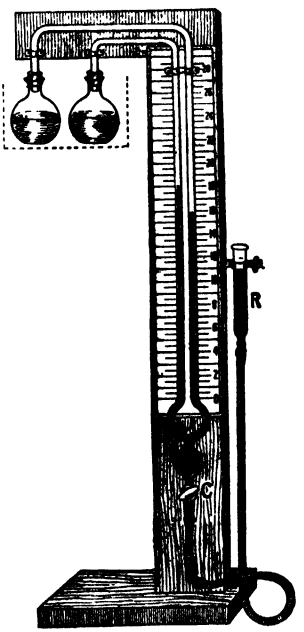


FIG. 34.—Apparatus for illustrating lowering of vapour pressure.

(From Mellor's *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*.)

(4) *Ebullioscopic Method, based on rise in the boiling point.*—The relation between boiling point rise, concentration of solution, and molecular weight of solute has already been given (p. 121), being an exact parallel with that used in the cryoscopic method. The molecular rise in the boiling point K is the rise produced by dissolving 1 gm. mol. of a solute in 100 gms. of solvent.

VALUES OF K (MOLECULAR RISE IN BOILING POINT).

Water	5·2	(normal boiling point	100° C.)
Alcohol	11·5	(,, ,,	78·8° C.)
Ether	21·0	(,, ,,	35° C.)
Acetone	16·7	(,, ,,	56·3° C.)

If w gms. of solute dissolved in s gms. of solvent produce a rise $t°$ C., then the molecular weight of the solute is $w \times \frac{100}{s} \times \frac{K}{t}$

The method, as originally carried out by Beckmann, consisted

in finding the boiling points of solvent and solution in succession (using a Beckmann thermometer) by a straightforward distillation method. Reflux condensers were used to keep

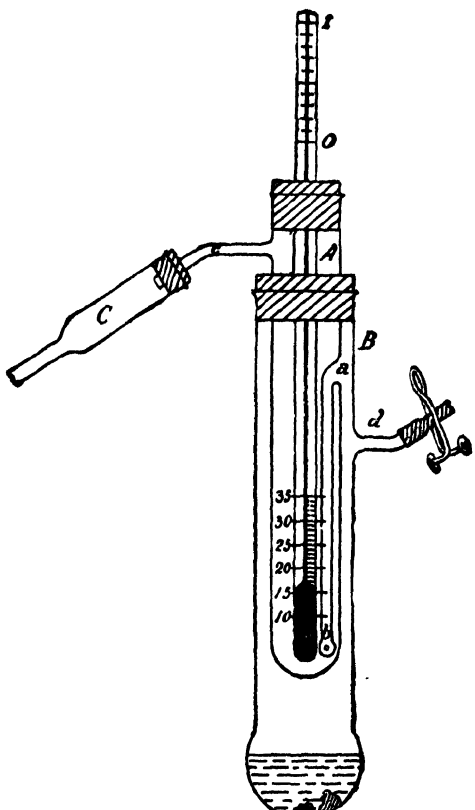


FIG. 35.—McCoy's apparatus for determining boiling point rise. (From Findlay's *Practical Physical Chemistry*.)

the concentration constant, and precautions were taken to avoid superheating.

Improved types of apparatus have been devised by *Landsberger, Walker, Lumsden, McCoy* and others, the main differences

being in the methods by which the liquid is vaporised. By reading volumes of solvent and solution instead of using weighed quantities, the determinations can be made much more rapidly and with sufficient accuracy for the purpose of fixing molecular formulæ.* Thus in the McCoy apparatus, vapour from the boiling solvent enters the solution from an outer jacket (see Fig. 35). The solution is *thereby* brought to its boiling point without fear of superheating, and by graduating the vessel, the volume of solution can be read off when required. If a known weight of solute is used, a series of determinations can be rapidly made by allowing solvent vapour to enter and dilute the solution between successive readings.

Section (2).—Abnormal Vapour Densities. Thermal Dissociation

5. Abnormal Results of Molecular Weight Determinations.—When the formula for a substance is clearly indicated by its reactions and the value of the molecular weight obtained by one of the above methods does not agree with it, we are entitled to regard this as an "abnormal" state of affairs (*cf.* p. 76).

Examples.—(1) The empirical formula for ammonium chloride is NH_4Cl ($14+4+35{\cdot}5=53{\cdot}5$), but the vapour density ($14{\cdot}4$ at 940° C.) indicates a molecular weight of about half this value—which is obviously impossible.

(2) With many substances (*e.g.* nitrogen peroxide) the vapour density varies with the temperature, and hence the molecular weight is apparently variable!

(3) The molecular weights of substances in solution are in many cases found to be greater or less than the values which would normally be expected. Thus the molecular weight of sodium chloride by the cryoscopic method corresponds to a formula $\frac{1}{2}(NaCl)$.

What conclusions are we to draw in such cases? Either

* The value of K is of course not the same if 100 c.cs. of solvent is used instead of 100 gms. The values for water, alcohol, ether and acetone in this case are 5·4, 15·6, 22·2, 30·3.

(1) the molecular weight is abnormal, *i.e.* the formulæ for these substances are for some reason not what we expected them to be, or (2) the method used in determining the molecular weight is faulty; *i.e.* the vapour density, or freezing point depression, etc., is abnormal so that we cannot calculate the molecular weight by the usual methods.

Search for the cause of abnormalities has always proved a profitable line of research. In this particular case we shall not only learn the limitations of our methods of determining molecular weights—a sharp warning to us not to apply our rules and "laws" indiscriminately in the future—but we shall learn a great deal about the complexity of molecules and the existence of mixtures which are in a state of "dynamic equilibrium."

6. Abnormal Vapour Densities.—If the vapour density of a substance indicates a molecular weight less than the empirical formula weight (*e.g.* ammonium chloride), or varying with the temperature (*e g.* nitrogen peroxide) we consider it to be abnormal. Search for the cause must follow the lines of scientific method; *i.e.* must start with hypotheses.

A Reasonable Hypothesis.—The substance may decompose on heating, so that the vapour whose density we determine is actually an entirely different substance, possibly a mixture.

This would certainly account for the abnormal density, for suppose that NH_4Cl became NH_3+HCl on heating, the density would be

$$\frac{(14+3)+(1+35{\cdot}5)}{2+2}=\frac{53{\cdot}5}{4}=13{\cdot}4$$

The experimental values (14·5 at 350° C., 14·4 at 940° C.) are bigger than this, so we will assume further that the NH_4Cl molecules are not all decomposed. The vapour will in this case be a mixture of NH_4Cl, NH_3 and HCl molecules in such proportions that the mixture has the observed density.

The latter assumption would account for the vapour density varying with the temperature, for this would indicate a change in the composition of the mixture. Thus, N_2O_4 molecules would have a vapour density of 46, and if these decomposed

completely into NO_2+NO_2 the vapour density would be 23; intermediate values therefore indicate varying mixtures of these molecules (see Table IV.).

Verification of this Hypothesis.—We must get positive evidence for the existence of these mixtures before we can accept this idea, however plausibly it may account for the abnormal densities of the vapours. Ordinary chemical analysis unfortunately proves to be useless (for reasons which will be clear later), and *we must therefore examine the physical properties of the vapours and make no attempt to separate the mixtures into their constituents.*

EXAMPLE.—Some nitrogen peroxide is taken in a sealed flask and gently heated. The **density** of the vapour varies as shown in the table, and the **colour** varies from pale yellow to a dark brown which reaches its maximum intensity when the temperature is 140° C. It will be seen that this point corresponds (according to the vapour density) to complete decomposition of the N_2O_4, so that if N_2O_4 is colourless and NO_2 dark brown we have visible evidence for our hypothesis.

TABLE IV.

Temperature in degrees C.	Vapour density	% wt. of NO_2 in the vapour.†	% wt. of N_2O_4 in the vapour.*
26·7	38·29	20	80
39·8	35·54	29	71
49·6	32·80	40	60
60·2	30·05	53	47
80·6	26·01	77	23
100·1	24·27	90	10
135·0	23·40	97	3
140·0	(23·0)	(100)	(0)
154·0	22·79	See footnote	
183·2	22·72		

* Above 140° C. the colour again diminishes. This has been shown to be due to decomposition of some of the NO_2 molecules into nitric oxide and oxygen. The vapour density falls gradually from 23 at 140° C. to 15·3 at 620° C. when all the NO_2 molecules are decomposed.

† The method of calculating the composition of the mixture from the vapour density is given on p. 155.

In carrying out the experiment it should be noted that on cooling the changes in colour, and in density, proceed in the reverse direction. These facts are in agreement with the existence of two reactions:

$$N_2O_4 \rightarrow NO_2 + NO_2 \text{ on heating,}$$
$$N_2O_4 \leftarrow NO_2 + NO_2 \text{ on cooling,}$$

or simply $N_2O_4 \rightleftarrows NO_2 + NO_2$.

the arrows representing the **reversibility** of either reaction.

Colour change also occurs when phosphorus pentachloride vapour is heated, and the greenish colour developed indicates the proportion of free chlorine in the mixture. This confirms the evidence of the vapour density that we are dealing with a reversible reaction:

$$\underset{\text{colourless}}{PCl_5} \rightleftarrows \underset{\text{colourless}}{PCl_3} + \underset{\text{green}}{Cl_2}$$

the vapour density varying from 52 at 300° C. to 73 at 182° C. (PCl_5 should have a vapour density=104).

Many other ingenious experiments have been devised, notably in connection with ammonium chloride (see the porous plug experiment mentioned on p. 162), phosphorus pentachloride, and calomel. Wurtz's experiment will be referred to later, but it will be sufficient to state here that all the evidence is in favour of the hypothesis we have given. The most remarkable results were those obtained by *Baker*, who found that after prolonged drying, some of these substances, *e.g.* ammonium chloride and calomel, gave normal vapour densities.*

NOTE.—If, on reversing the conditions, the products of a reaction themselves react so as to reform the original substances we call the reaction a "reversible reaction." These are not only met with in connection with abnormal molecular weights, and the following are worth examination before

* An excellent account of the historical attempts to establish the existence of mixtures in these abnormal vapours is to be found in Fenton, *Outlines of Chemistry*, Chapter III. Text-books of inorganic chemistry should also be consulted for details of the following substances whose vapour densities are abnormal: ammonium chloride, nitrogen peroxide, phosphorus pentachloride, calomel, hydrogen fluoride, the chlorides of aluminium and iron, arsenious oxide, and the elements sulphur, phosphorus, arsenic, bromine, and iodine.

proceeding to the discussion of balanced actions and chemical equilibrium.

(1) $2HCl+CdS \rightleftarrows H_2S+CdCl_2$. A precipitate of cadmium sulphide occurs when hydrogen sulphide is passed into cadmium chloride solution, but this redissolves if concentrated hydrochloric acid is added.

(2) $BiCl_3+H_2O \rightleftarrows BiOCl+2HCl$. Addition of water will cause precipitation of the oxychloride, but this will redissolve if concentrated hydrochloric acid is added.

(3) $3NH_4CNS + FeCl_3 \rightleftarrows 3NH_4Cl + Fe(CNS)_3$. A striking example due to *Gladstone* of physical properties being used in studying equilibrium mixtures. The intensity of the red colour indicates clearly the proportion of ferric thiocyanate present.

7. Balanced Actions. Chemical Equilibrium.—We must now consider why we could not employ chemical analysis in determining the composition of these vapours.

In all these cases we are dealing with reversible reactions; *e.g.* $NH_4Cl \rightarrow NH_3+HCl$ on heating, $NH_4Cl \leftarrow NH_3+HCl$ on cooling. A reversible decomposition is termed a **dissociation,** and if it is caused by heat, thermal dissociation. Thus, NH_4Cl dissociates into NH_3 and HCl (these are called the products of dissociation); N_2O_4 into NO_2+NO_2, etc.

Now we have found that dissociation is as a rule only partial and that the proportion of dissociated molecules (or **degree of dissociation**) varies with the temperature. Why is this? What stops the reaction $PCl_5 \rightarrow PCl_3+Cl_2$ from proceeding until all the PCl_5 molecules have been decomposed? Experiment shows that if the products of dissociation be removed the dissociation will continue until complete. If they are allowed to accumulate, however (as they would in a sealed flask), they will begin to recombine; *i.e.* the reverse reaction will proceed before the forward reaction is complete. We shall, in fact, have **two reactions proceeding simultaneously** as shown by the equation $PCl_5 \rightleftarrows PCl_3+Cl_2$. We cannot **prove** the coexistence of these two reactions by direct experiment, but the behaviour of the system is quite in accord with this assumption Now if the two reactions were proceeding with equal speed, the amount of PCl_5 decomposed per

second would be exactly reformed, so the **apparent result** would be nil. In other words, we should have a state of dynamic equilibrium (see p. 72) in which two equal and opposite changes produce the effect of equilibrium. The composition of the mixture (called the " equilibrium mixture ") will clearly remain constant under these conditions, and the two reactions are said to be balanced. Chemical analysis would interfere (or disturb the equilibrium) by removing one or other of the constituents of the mixture. *E.g.* if the chlorine was estimated by volumetric analysis, the reaction $PCl_5 \rightarrow PCl_3 + Cl_2$ would proceed to completion (see para. 8).

Note on Dynamic Equilibrium.—An analogy may prove useful in making clear the conception of two equal and opposite motions.

When moving staircases were a novelty, there was a charge of one penny made for travelling up one of these at the Crystal Palace. The enjoyment was soon over, but the author found that he could considerably prolong his pennyworth by walking in the opposite direction to that in which the staircase was moving. By walking with a velocity equal to that of the staircase, he actually remained in the same place —a state of equilibrium which the officials actively resented!

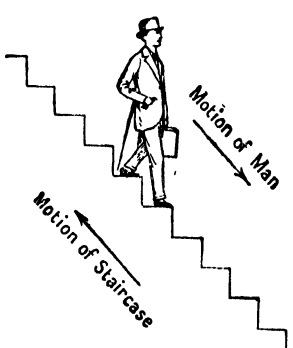


FIG. 36.—Equilibrium resulting from two equal and opposite motions.

Of course whenever he decreased his speed the position he occupied shifted (upwards), but if the staircase had in consequence decreased its speed a new position of equilibrium would have been reached. In chemical systems this kind of automatic compensation actually occurs, as we shall see in the next paragraph.

8. Reaction Velocity. The Law of Mass Action.—Chemical reactions proceed with definite velocity. This is not always easy to demonstrate as in many cases the velocity

is nearly infinite, but it is quite well illustrated by the time taken for a metal to dissolve in an acid. The finite velocity of reactions is such an important point that an experiment should be carried out to illustrate the fact (see the "time reaction" described on p. 162). Note also that the rate is dependent on conditions. *E.g.* increase in temperature **always** increases the rate of a chemical reaction. That is why the Bunsen burner is so much used in a chemical laboratory.

Concentration of the reagents also affects the velocity of a reaction, and in 1864 *Guldberg* and *Waage* formulated an important law known as **the law of mass action** which states that **the rate of a reaction is directly proportional to the molecular concentrations ("active masses") of the reacting substances.** Suppose then that we start with some phosphorus pentachloride in a sealed flask and heat it to 200° C. The reaction $PCl_5 \rightarrow PCl_3 + Cl_2$ is accelerated, but as the concentration of PCl_5 decreases, the rate of this reaction gets less. Simultaneously the concentrations of PCl_3 and Cl_2 are increasing, so that $PCl_5 \leftarrow PCl_3 + Cl_2$ starts to accelerate and its speed is eventually bound to become equal to that of $PCl_5 \rightarrow PCl_3 + Cl_2$. There will then be a state of equilibrium. Any interference with this system (such as removing the chlorine for analysis) which alters the concentrations on one side or the other of this equation will alter one of the opposing velocities and a change will result until once more the velocities become equal. The equilibrium can also be shifted by temperature or pressure changes owing to the fact that although both velocities are altered they are not altered to the same extent.* Wurtz's experiment in confirmation of the dissociation hypothesis was to heat phosphorus pentachloride in an atmosphere of one of the products of dissociation, viz.: phosphorus trichloride. In this case dissociation is prevented owing to the high velocity of $PCl_5 \leftarrow PCl_3 + Cl_2$ when such a large concentration of PCl_3 is present, and *Wurtz* found that the vapour density under these conditions was quite normal (104—corresponding

* See further remarks in Chapter XI.

to PCl_5). No more striking proof could be given of the correctness of these views.

It has been stated that chemical analysis is inadmissible, but by means of an ingenious device it may sometimes be used. Low temperature means slow reaction velocity, so that if we work at low temperatures, the change in equilibrium which would result from our interference would take place at a negligible pace. Thus, if hydrogen iodide vapour is heated and we wish to analyse the vapour ($2HI \rightleftarrows H_2+I_2$), we need only cool the vapour suddenly to room temperature and we can then estimate the iodine by volumetric analysis, for the change $2HI \rightarrow H_2+I_2$ due to removal of iodine is at room temperature too slow to interfere with the accuracy of the results.

Section (3).—Abnormal Molecular Weights in Solutions. Ionic Dissociation. Association

9. Abnormal Molecular Weights in Solutions.—With water as the solvent the molecular depression of the freezing point is found to be 18·5 when organic solutes like sugar or urea are used, and this agrees with the value calculated by van 't Hoff from the latent heat of fusion of ice (see p. 122). But if we use this value to determine the molecular weight of most inorganic substances cryoscopically we obtain abnormal results.

Thus the formula for sodium chloride would come to $\left(\frac{18{\cdot}5}{35{\cdot}3}\ NaCl\right)$ and for calcium chloride $\left(\frac{18{\cdot}5}{49{\cdot}9}\ CaCl_2\right)$!! In other words, if we accept NaCl and $CaCl_2$ as correct formulæ for these substances, then the freezing point depressions are abnormally large (nearly two and three times the values expected from Raoult's law).

The freezing point depression produced by a solute is directly related to the osmotic pressure of the solution (and also to the vapour pressure lowering, and boiling point rise), so it is not surprising to learn that solutes which in solution produce abnormal freezing point depressions give rise to similar abnormalities in osmotic pressure, etc. In fact so many of

these cases were found that van 't Hoff was obliged to write $PV=i(RT)$ instead of $PV=RT$ as the general relation between osmotic pressure, concentration and temperature. i is a factor, equal to 1 for substances which behave normally (1 gm. mol. per 22·4 litres at 0° C. producing an osmotic pressure of 76 cms.), but greater than 1 for substances like sodium chloride and calcium chloride. *E.g.* for sodium chloride it is between 1 and 2, the actual value depending on the concentration of the solution; and for calcium chloride it reaches a value of nearly 3 when the solution is very dilute.

Note on the Diluteness of Solutions.—The abnormalities mentioned here are far too large to account for as deviations due to the solutions not being infinitely dilute. The errors due to this are almost negligible when working with solutions containing less than $\frac{1}{10}$ gm. mol. per litre.

10. Van 't Hoff's "i" Factor.—The value of i is clearly a measure of the abnormality of these solutions, and experiment shows that it depends upon (1) the solute, (2) the solvent, and (3) the concentration of the solution.* Using water as a solvent the following results have been obtained.†

TABLE V.

Solute.	Concentration in gram equivalents per 1000 gms of water.	Value of i from freezing point measurements.
NaCl	·005	1·953
,,	·50	1·824
HCl	·005	1·991
,,	·10	1·917
H_2SO_4	·005	2·719
,,	·50	2·022
$BaCl_2$	·005	2·797
NaOH	·01	1·967
$CuSO_4$	·005	1·616
$Ba(NO_3)_2$	·005	2·833

* The value of i for a given solution is not quite independent of the temperature (see "Temperature and Ionisation" on p. 230), but the variation is very small.

† Noyes and Falk, *J.A.C.S.*, **32**, 1011, 1910, and **34**, 1436, 1912. Many of Raoult's original data were very inaccurate.

11. Ionic Dissociation.—We can give an adequate explanation of all these abnormal molecular weights by assuming, as we did in accounting for abnormal vapour densities, that we are not dealing in such cases with unchanged molecules, but that some of these at least are dissociated into two or more smaller particles; for if the osmotic pressure of a solution depends upon the number of solute particles present, then such a solution will exert a larger osmotic pressure than it would if none of the solute molecules had dissociated. The other osmotic effects will of course vary in proportion to the change in the osmotic pressure.

Now what can be the products of dissociation of a salt like sodium chloride? Surely $NaCl \rightleftarrows Na+Cl$ is not possible, with sodium and chlorine atoms coexisting in water! This difficulty is overcome by referring to the electrical properties of these solutions. All the solutes which behave abnormally * are **electrolytes** (*i.e.* their solutions will conduct the electric current), but non-electrolytes behave normally. The cause of electrical conductivity appears then to be the same as the cause of this abnormal behaviour. We shall see in the next chapter that the current is thought to be carried by electrically charged atoms or radicals called IONS, and in Chapters XIII and XIV further evidence will be found for the correctness of this view which strongly supports the hypothesis put forward above that abnormal molecular weights in solution are due to ionic dissociation.

12. Ionic Equilibria.—The value of i varies with the dilution (see Table VI) which suggests that the decomposition of the solute molecules into ions is reversible (a true case of dissociation). Unless this is complete there will be in the solution an equilibrium mixture of ions and undissociated

* They behave abnormally only in the sense that they do not obey Raoult's law or the $PV=RT$ relation. Actually we now recognise two distinct classes of substances—those which ionise and those which do not; and ionisation is regarded as a perfectly normal process where the former are concerned. Indeed, as stated on p. 34 (footnote), it is thought that in many cases the ions are already present before the substance dissolves, the solvent merely serving to separate them or give them more freedom.

particles.* Thus, for an aqueous solution of acetic acid we can write $CH_3COOH \rightleftarrows H^{\cdot} + CH_3COO'$ to represent the state of affairs. If this solution is diluted, the value of i increases from 1 to a maximum of 2 as the proportion of ionised molecules increases, and from any intermediate value we can calculate the "degree of ionisation," *i.e.* the composition of the equilibrium mixture.

TABLE VI.

THE EFFECT OF DILUTING A SOLUTION OF SODIUM CHLORIDE.

Concentration in gram equivalents per 1000 gms. water.	"i" from freezing point measurements.	Degree of ionisation calculated from "i."
·50	1·824	82·4%
·10	1·875	87·5%
·05	1·892	89·2%
·01	1·938	93·8%
·005	1·953	95·3%

13. Calculation of the Degree of Dissociation in Vapours or Solutions.—If 100 molecules of a substance are taken and α of these dissociate, there will be $100-\alpha$ left. If each dissociated molecule forms n particles (atoms, molecules or ions; it doesn't matter what they are), the total number of these will be $n\alpha$. Hence, instead of 100 molecules we shall have $100-\alpha+n\alpha$ particles, and any effect dependent on the number of particles present will be increased in the ratio $\frac{100-\alpha+n\alpha}{100}$, where α is % dissociation.

* This hypothesis is now thought to apply only to solutions which are feeble conductors of electricity—the so-called "weak electrolytes" (see p. 174). Strong electrolytes whose solutions are good conductors of electricity are believed to be completely ionised at all dilutions, so that the change in i value on dilution in such cases must indicate a change in the freedom of the ions or in their "activity" (see p. 239), and not in the actual number of them. The term "degree of ionisation," therefore, which is quite correctly employed when referring to weak electrolytes, is a complete misnomer when applied to strong electrolytes. It would be an improvement to refer in the latter cases to the "apparent degree of ionisation," and this should be understood in the pages which follow.

Abnormal behaviour due to dissociation can clearly be measured in this way, so that we have

(1) $i=\frac{100-a+na}{100}$, for substances in solution, where i is van 't Hoff's factor and is $\frac{\text{observed value}}{\text{normal value}}$ for osmotic pressure, freezing point depression, etc. Hence it follows that $i=\frac{\text{normal mol. wt.}}{\text{observed mol. wt.}}$

(2) $\frac{100-a+na}{100}=\frac{\text{normal vapour density}}{\text{observed vapour density}}$ for vapours, $\left(\text{since vapour density} \propto \frac{1}{\text{no. of mols. per unit mass}}\right)$.

EXAMPLES. — (1) Nitrogen peroxide, N_2O_4. Normal vapour density=46. At 60° C. the vapour density=30. What is the composition of the equilibrium mixture? $\frac{100-a+na}{100}=\frac{46}{30}$, and n in this case is 2 ($N_2O_4 \rightleftarrows 2NO_2$), so that $\frac{100-a+2a}{100}=\frac{46}{30}$, or $a=53$. The N_2O_4 is therefore dissociated to the extent of 53%; *i.e.* the vapour contains 47 molecules of N_2O_4 and 106 molecules of NO_2; the composition by weight will be 47% N_2O_4 and 53% NO_2.

(2) For ·14 molar potassium chloride the value of $i=1{\cdot}81$. What is the degree of ionisation? $\frac{100-a+na}{100}=1{\cdot}81$ and $n=2$, from which $a=81$. The solution therefore contains 81% of the potassium chloride in the form of ions and 19% as KCl "molecules." *

(3) For ·18 molar calcium chloride the value of $i=2{\cdot}48$. What fraction of the salt appears to be present in the ionised

* We are here assuming $KCl \rightleftarrows K^{\cdot}+Cl'$. According to modern views, however, no unionised molecules exist, yet the solution certainly behaves as though there was a state of equilibrium between the ions and some other particles. Perhaps these are clumps or aggregates of ions. It is still customary to write equations representing the equilibrium in solutions of strong electrolytes as above, however, though $K^{\cdot}Cl' \rightleftarrows K^{\cdot}+Cl'$ is suggested as an improvement.

condition ? $\frac{100-\alpha+n\alpha}{100}=2{\cdot}48$ and $n=3$,* from which $\alpha=74\%$.

The degree of ionisation of an electrolyte can also be determined from electrical conductivity measurements, and the agreement between the values obtained by these widely different methods is strong evidence for the correctness of our views (see the table on p. 177).

14. Association.—If the molecular weight of a substance indicates a formula **greater than** that expected from chemical considerations, it follows that some of the molecules have aggregated to form more complex molecules. The molecules are said to have **associated** or **polymerised.** Thus, acetic acid has the formula CH_3COOH corresponding to a molecular weight of 60, and above 350° C. the vapour density (30) is normal; but **as the temperature falls the vapour density gradually increases,** until it is over 50 before the vapour condenses at 118° C. The change is reversible, so we are evidently dealing with equilibrium mixtures

$$2CH_3COOH \rightleftarrows (CH_3COOH)_2$$

and if the doubled formula had been the normal one we should have said that acetic acid dissociated on heating.

Again, hydrogen fluoride (b.pt. 19·5° C.) according to its vapour density is HF above 70° C., but about 50° C. the vapour density corresponds to H_2F_2, and at 27° C. to H_3F_3. Recent work on this subject has indicated association to even more complex molecules H_6F_6 and suggests that the intermediate values may be merely equilibrium mixtures of these and the simple HF molecules. The cryoscopic method gives a molecular weight corresponding to H_2F_2 for the acid dissolved in water, and this agrees with the fact that it is found to be dibasic in solution by Ostwald's empirical method.†

15. The effect of the Solvent on the Nature of Dissolved Molecules.—This is clearly indicated by molecular weight determinations. The solute molecules may dissolve

* The equilibrium here is $CaCl_2 \rightleftarrows Ca^{\cdot\cdot} + 2Cl'$, so that each "molecule" produces 3 ions. For proof that valency decides the number of charges on the ion, see p. 167.

† Based on electrical conductivity measurements.

unchanged (*e.g.* sugar in water), dissociate into ions (*e.g.* sodium chloride in water); or associate (*e.g.* acetic acid in benzene).

EXAMPLE.—The molecular weight of acetic acid in benzene (cryoscopic determination) is nearly 120, which indicates the existence of a large proportion of doubled molecules. That is, the freezing point depression is about half the value expected from the formula CH_3COOH and Raoult's law. The molecular weight of this same substance in water (cryoscopic determination) is quite normal.*

Benzene is termed an **associating (or non-ionising) solvent,** as it tends to make molecules associate (or prevents them from ionising). Water is termed a **dissociating (or ionising) solvent,** as it tends to make molecules dissociate (or prevents them from associating).

Associating and Ionising Solvents.—The power which solvents have in this respect appears to be related to their electrical properties, their chemical nature, and the complexity of their own molecules (1) As a rule, liquids with high dielectric capacity are good ionising solvents, and it should be noted that in such media the electrostatic attraction between the oppositely charged ions would be small. (2) It has been found that as a rule liquids which are themselves associated (*e.g.* water, alcohols, fatty acids, acetone, nitriles, and paraffins) are ionising solvents; and liquids which are not themselves associated (*e.g.* hydrocarbons such as benzene and toluene, chlorbenzene, aniline, ether, carbon disulphide, carbon tetrachloride and chloroform) are associating, non-ionising, solvents. Solutions in the latter, it will be noted, will not conduct the electric current. There are some notable exceptions. *E.g.* liquid ammonia (which is not associated), is an ionising solvent, and acetic acid dissolves in ether as single molecules. Hence, the generalisations given above are not by any means clearly established. See also footnote on p. 174.

Note on the Complexity of Water Molecules.—The molecular weight of pure water (surface tension method) indicates that its molecules are associated, and this has been confirmed by

* It is actually a little below 60 owing to ionisation.

many independent lines of investigation * (notably, by a study of its peculiar physical properties). There appear to be two polymers of H_2O (or hydrol) : $(H_2O)_2$ (dihydrol), and $(H_2O)_3$ (trihydrol). Ice, water, and steam appear to be mixtures of these in which $(H_2O)_3$, $(H_2O)_2$, and H_2O respectively preponderate.

16. Further Evidence for the Existence of Associated Molecules.—The views just given are confirmed in a striking manner by a different line of investigation. If a solute be shaken with two immiscible solvents, the partition law $\left(\frac{\text{concentration in A}}{\text{concentration in B}} = \text{a constant}\right)$ holds if the solute molecules are identical in the two solvents. If, however, it dissolves as single molecules in A but as associated molecules in B (n single molecules in each complex molecule), the kinetic theory leads to a general law that $\frac{(\text{concentration in A})^n}{\text{concentration in B}} = \text{a constant}$, since $k_1 \times$ concentration in B $= k_2 \times$ (concentration in A)^n.

Experimental determinations of the partition (*i.e.* of the concentrations in A and B) are in agreement with this general law, and the simpler one is merely the special case when $n=1$. Hence we can determine n by such measurements, and the results agree with those obtained from molecular weight determinations.

EXAMPLE.—When benzoic acid was shaken with water and benzene the following results were obtained when different quantities of benzoic acid were used :

$$\frac{\text{concentration in water}}{\text{concentration in benzene}} = \cdot062,\ \cdot048,\ \cdot030.$$

This is clearly not constant, so that the molecular state of the benzoic acid cannot be the same in these two solvents. But from the experimental results

$$\frac{(\text{concentration in water})^2}{(\text{concentration in benzene})} = \cdot093,\ \cdot092,\ \cdot086.$$

* See Turner, *Molecular Association*, for a detailed account of the phenomena discussed in these paragraphs.

This is nearly constant, indicating that a large proportion of the benzoic acid molecules are doubled molecules in the benzene, if we assume that they are single molecules in the water. This is confirmed by the fact that molecular weight determinations (cryoscopic) in benzene vary from 160 to 210 ($C_6H_5COOH=122$) according to the concentration of the solution.

17. Equilibrium Mixtures.—"Things aren't always what they seem." We should now be able to realise that mixtures frequently masquerade as simple substances, defying the chemical analyst to distinguish them. The cases of dynamic isomerism mentioned on p. 57 (aceto-acetic ester and liquid sulphur) are good examples, and it is possible that many of our so-called "elements and compounds" are really mixtures of allotropic (or isomeric) forms in dynamic equilibrium. This is the point of view taken up by *Smits*, and it is difficult to disprove. It is, however, a generalisation built up on somewhat scanty evidence, and it is very doubtful how some of this should be interpreted.

Smits has extended some earlier work by *Baker* on the changes in boiling point and vapour pressure which occur when certain liquids (*e.g.* benzene) are drastically dried. The molecular weights of these liquids are found to undergo a corresponding change, which points to association and the existence of equilibrium mixtures. He has found that the vapour pressures of certain solids (*e.g.* sulphur trioxide and violet phosphorus) are altered in a similar manner, and has drawn the conclusion that many apparently simple substances may be equilibrium mixtures of this type.*

18. Summary of the Chapter.—This is perhaps the most important chapter in the book, for most of the succeeding work makes use of the principles here introduced. It is essential to notice the extent to which these are hypothetical, and to distinguish the basis of facts on which they rest. Should further discoveries seem impossible to explain in terms of these assumptions, we shall either have to revise our ideas or look further for the cause of the discrepancies.

* For further details, see Baker's *Presidential Address to the Chemical Society*, T., March, 1927; also Smits, *The Theory of Allotropy*; or Smith, *The Effects of Moisture on Chemical and Physical Changes.*

The main points in the chapter were as follows:

(1) Molecular weight determination enables us to fix molecular formulæ. Note the assumptions involved in these determinations: Avogadro's hypothesis, van 't Hoff's osmotic pressure laws, Raoult's empirical rules, the diluteness of solutions, etc.

(2) Abnormal molecular weights indicate that the molecules have become altered during their passage into vapour, or into solution. These alterations must be reversible if they take place at all.

(3) Chemical reactions proceed at a definite speed.

(4) Reaction velocity depends upon conditions such as temperature, pressure, and concentration of reacting molecules.

(5) Reaction velocity is proportional to the molecular concentrations of the reacting substances (law of mass action); and it follows that with a reversible reaction, a state of balance or equilibrium will be reached when the forward and back reactions are proceeding with equal velocity.

(6) The composition of an equilibrium mixture formed by the "balancing" of two opposite reactions is constant under given conditions. By altering the conditions, the point of equilibrium can be shifted; *i.e.* a change will take place which proceeds until a new state of equilibrium is reached with a mixture of different composition from the original.

(7) Chemical analysis is useless when we are dealing with mixtures in a state of equilibrium, but physical properties such as vapour density, apparent molecular weight, colour, electrical conductivity (of solutions), enable us to investigate the nature of such mixtures.

(8) Abnormal vapour densities indicate that the molecules of some substances dissociate (*i.e.* decompose reversibly) on heating, into atoms or simpler molecules (thermal dissociation).

(9) Abnormal molecular weights for dissolved substances indicate either (1) dissociation (called ionic dissociation because the products are thought to be electrically charged particles or ions), or (2) association, when two or more molecules appear to be aggregated.

DEMONSTRATIONS.—1. Display the various types of apparatus used in determining molecular weights. A full discussion of these is of more value than pages of written description.

2. *Evidence for Dissociation.*—(*a*) Heat nitrogen peroxide in a sealed flask and recool, noting the colour changes. Introduce the idea of reversibility. (*b*) Repeat with phosphorus pentachloride in a sealed flask. (*c*) Heat some ammonium chloride in a piece of combustion tubing and allow the vapour to diffuse through a porous plug (or the walls of a clay pipe). A piece of red litmus paper will indicate that ammonia is diffusing through more rapidly than hydrogen chloride. Point out that this only shows that *some* dissociation has occurred, the separation of the mixture disturbing the equilibrium and thus making the deductions somewhat inconclusive.

3. *Reversible Reactions.*—Demonstrate as many of these as possible, especially those mentioned on p. 149. Discussion of these paves the way for a clear understanding of mass action, the effect of concentration on equilibrium, removal of reacting substances from the sphere of action, etc.

4. *A Time Reaction.*—This should be as spectacular as possible, as its object is to press home the notion of reactions proceeding with a definite speed. Harcourt and Esson's experiment serves the purpose, and it need only be carried out in a qualitative manner. Thus, take a freshly made solution of potassium iodide, acidify it and add starch paste. Prepare ten equal volumes (about half a test tube each) of a dilute sodium thiosulphate solution. Add to the prepared solution of hydrogen iodide about 20 c.cs. of dilute hydrogen peroxide and remove the blue colour (due to liberated iodine) by adding one portion of sodium thiosulphate ($2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6$). After a definite time interval, the blue colour again appears (the solutions should be tried beforehand and diluted until the first time interval is about 4 minutes, in order to get suitable results for demonstration purposes). This is due to $H_2O_2 \rightarrow H_2O+O$, and the consequent oxidation of the hydrogen iodide. A second portion of sodium thiosulphate is now added, the time interval noted when the blue colour reappears; and the

process repeated. A rough graph can be plotted showing the decreasing speed of the reaction. This is a consequence of the law of mass action, for the concentration of hydrogen peroxide is steadily decreasing. (The concentration of hydrogen iodide remains constant, since sodium iodide is formed with each addition of sodium thiosulphate and the free acid present reconverts this into hydrogen iodide.) If the solutions used are too concentrated, the heat developed by the reaction causes the temperature to rise considerably, and this seriously affects the reaction velocity. The author has used $\frac{N}{10}$ sodium thiosulphate and a solution of hydrogen peroxide prepared by diluting 5 c.cs. of 20 volume strength to 100 c.cs., with satisfactory results.

PRACTICAL WORK.—(1) Molecular weight determinations should be carried out by as many methods as possible.

(2) Determine the degree of ionisation of a salt by a cryoscopic determination of the value of *i*.

(3) Qualitative experiments on reversible reactions should be carried out. Those which are usually involved in qualitative analysis are most useful.

(4) A more carefully carried out study of the Harcourt and Esson experiment, or of the rate of evolution of hydrogen from zinc and a dilute acid, will form a useful illustration of reaction velocity. Constancy of temperature is essential if any serious quantitative work is contemplated, and this needs a thermostat. If a uniform piece of metal can be obtained and divided into equal portions, the surfaces being similarly cleaned by a preliminary immersion in acid, a series of measurements can be carried out showing the effects of concentration of acid and temperature on the rate of reaction. With suitable attention to detail it is possible to use this experiment to determine the order of the reaction (see p. 194).

QUESTIONS.—1. Summarise the methods by which molecular weights can be determined. Why are these determinations so important?

2. Give your reasons for supposing that nitrogen peroxide vapour is a mixture Explain the terms "reversible change," "balanced action," and "equilibrium mixture."

3. Why are ammonium chloride and phosphorus pentachloride said to have abnormal vapour densities? Write notes on the formulæ to be assigned to calomel, hydrogen fluoride, and sulphur.

4. State the law of mass action. How would you show experimentally that a reaction proceeds at a definite speed?

5. Acetic acid sometimes exists in the associated condition forming doubled molecules. Explain the meaning of this statement and state on what evidence it is based.

6. Why cannot chemical analysis always show that a mixture *is* a mixture? What do you believe really exists in a solution of common salt?

7. Calculate the molecular weight of a monobasic organic acid if ·3652 gm. of its silver salt left ·1720 gm. of silver on heating.

8. Discuss the advantages of Victor Meyer's method of determining vapour densities, in comparison with other methods. Point out the sources of error in using this method. If ·158 gm. of a substance displaces 21 c cs. of air at 15° C. and 728 mms. pressure, what is the molecular weight of the substance? (Density of hydrogen at N.T.P. = ·09 gm. per litre.)

9. Calculate the molecular weight of a substance from the following data (Dumas' method):

Weight of globe + air at 0° C. and 760 mms. pressure = 51·125 gms.
" " + vapour at 150° C. and 760 mms pressure . . . . . = 52·710 gms.
" " + water (in place of the vapour) . = 301 gms.

(Density of air at N.T.P. = ·0013 gm. per c.c.)

10. ·275 gm. of sodium chloride dissolved in 75 gms. of water formed a solution freezing at −·221° C. Determine (*a*) the apparent molecular weight of the salt, (*b*) its degree of dissociation (K = 18·6), (*c*) the boiling point of this solution (K = 5·2).

11. The vapour density of arsenious oxide at 1265° C is 178. Calculate the composition of the equilibrium mixture, $As_4O_6 \rightleftarrows 2As_2O_3$ (As = 75).

12. Calculate the molecular weight of dextrose if 5·93 gms, when dissolved in 100 gms. of water at 0° C., lower the vapour pressure from 4·579 mms. to 4·554 mms.

CHAPTER X

THE THEORY OF IONIC DISSOCIATION

1. The Nature of Solutions.—The development of the theory of Ionic Dissociation, hinted at in the previous chapter and now to be discussed in detail, provides one of the best-known examples of the various stages of scientific progress. It is in this respect equalled only by a study of the rise and fall of the Phlogiston theory of Combustion, or of the rivalry between the Corpuscular and Wave theories of Light.

First we find the slow and laborious collection of facts. Then follow generalisations (or laws—see Chap. I.). Then come hypotheses to try and explain them and acute controversy, with the scientific world split into two camps, the believers and the unbelievers. Next we meet with a period of unreasonable confidence in the correctness of one of the hypotheses (which becomes known as a theory in consequence) when nearly all scientists are agreed as to its validity. Then more facts come to light; the theory fails to account for them satisfactorily, and has to be patched with additional assumptions or further hypotheses. A feeling arises that all is not well with the accepted explanations, and a period of intense research is ushered in, culminating either in a revised version of the original theory or perhaps in an entirely different idea.

A few years ago the theory of ionic equilibria which had been developed by *Arrhenius* and *Ostwald* was almost universally accepted. It had passed through a strenuous testing time, but had survived criticism, and it was thought that only time was needed to clear up the few awkward points with which it could not deal satisfactorily. But, on the contrary, increased knowledge of the electrical structure of matter (see Chap. XIV.) has opened our eyes to entirely new possibilities. The solvent, it appears, may not in all cases be causing ionisation, for the ions may be already in existence before the substance dissolves; there may then be no "molecule" to dissociate! Arrhenius' theory we now find can apply only to a limited group of substances, the weak electrolytes. Yet it was in its application to reactions between inorganic acids, bases, and salts (the strong electrolytes) that it originally proved most useful! This should be a warning to those who treat theories with too much confidence. In the words of Francis Bacon, "Read not to contradict or confute, nor to believe and take for granted, nor to find talk and discourse, but to weigh and consider."

2. The Development of the Theory.—To enable us to study the growth of this very important idea, the treatment in this chapter will be largely historical. It is in any case im-

possible to start with the facts which at the present day would lead us most directly to a belief in the existence of "ions," for they require an advanced knowledge of Physics for their understanding. Hence, we shall find here: (1) the generalised facts (or laws) dealing with electrolysis; (2) hypotheses to explain these; (3) the facts dealing with the electrical conductivity of solutions and particularly with the influence of varying dilutions; (4) Arrhenius' hypothesis of ionic equilibrium and a varying "degree of dissociation"; (5) a summary of the evidence in favour of this hypothesis, showing its enormous scope and value; and lastly (6) the great change which has had to be made in more recent times in view of our increased knowledge. The subject is continued in Chapter XIII., but the intervening sections dealing with the Law of Mass Action will need to be read first.

3. Electrolysis. The term "Ion."—*Faraday* in 1834 first introduced the term "ion." An ion was any substance which went to either anode or cathode on electrolysis. By 1838 he had become convinced that a "convection" process was the nature of electrolytic action, and he seems to have realised that the electric current was a transfer of electric charges carried by the particles of the electrolyte; *i.e.* by the ions.* He did not in any way suggest that ions could exist in a solution except during electrolysis. It was *Clausius* about twenty-five years after who first assumed that they might be formed by the dissociation of some of the solute molecules during the process of solution. This hypothesis due to Clausius we shall discuss in a moment.

4. Faraday's Laws.—Faraday arrived at two very important generalisations from his experimental results.

(1) The weight of a compound decomposed during electrolysis is proportional to the quantity of electricity which has passed through the solution. (N.B.—Quantity of electricity=current×time. *E.g.* 1 coulomb=1 amp. sec.)

(2) Equal quantities of electricity decompose weights of different compounds which are chemically equivalent. In other words, if a current be passed through a number of

* Faraday, *Experimental Researches in Electricity*, vol. i, 1839.

solutions in series, equivalent weights of elements will be simultaneously liberated at the various electrodes.

Thus, 96,500 coulombs (or 1 faraday) will liberate 1 gm. of hydrogen, 108 gms. of silver, $\frac{63{\cdot}6}{2}$ gms. of copper, etc. The weights of elements liberated by 1 coulomb will clearly be proportional to their chemical equivalents and are known as their "electrochemical equivalents;" *e.g.* $\frac{1}{96,500}$ or ·00001045 for hydrogen, $\frac{108}{96,500}$ or ·001118 for silver.

Faraday concluded that every univalent atom (or radical) while being liberated at an electrode must be associated with the same definite quantity of electricity.* Let us call this e units of electricity (it will be $+e$ on each cation and $-e$ on each anion since the solution as a whole is electrically neutral). Then a bivalent atom (or radical) must carry a charge $2e$, and an n-valent one a charge of ne. Hence, *the number of unit charges on the ion is a measure of the valency of the atom (or radical) forming the ion.*

EXAMPLE.—63·6 gms. of copper (1 gm. atom) are liberated by 2 faradays, whereas 35·5 gms. of chlorine (1 gm. atom) are liberated by 1 faraday. This is because each copper atom has two unit charges attached to it, whereas the chlorine atom only carries one unit charge. Hence, **equivalent weights** and not atomic weights are liberated by equal quantities of electricity.

5. The Mechanism of Electrolysis.—Any explanation of the phenomena of electrolysis has to account for the following facts.

(1) The facts summarised in Faraday's laws.

(2) The appearance of decomposition products at the electrodes only.

(3) The simultaneous appearance of products at the two electrodes, however far apart these may be.

* This "ionic charge" has been shown to have the value $4{\cdot}7 \times 10^{-10}$ electrostatic units which is identical with the charge on an electron—the fundamental unit of negative electricity (see p. 262).

(4) The relation between the current flowing and the potental difference (which will presently be discussed).

The notion of ions carrying one or more unit charges according to the valency of the atom (or radical) will account for (1). The charge is neutralised on touching the electrode, and the ion then becomes an ordinary atom (or uncharged radical)—a primary product of electrolysis. Consideration of (2) and (3) leads to the conclusion that the ions discharged at anode and cathode respectively probably come from different molecules near these electrodes. The fourth point is important since it leads to the deduction that the earliest known hypothesis of electrolytic action (Grotthus' hypothesis, 1805) is incorrect.

Grotthus supposed that a chain of molecules handed on electrically charged atoms (rather like a chain of people at a fire handing on a bucket of water) until one reached the electrode at the end of the chain and was discharged. If this were true, molecules would have to be broken up by the electrical energy supplied, and a certain minimum P.D. would be necessary for this purpose before electrolysis could commence. Now when an E.M.F. is applied to an electrolyte, the products of electrolysis accumulating at the electrodes tend to produce an E.M.F. in the opposite direction (" back E.M.F.," as it is called, due to " polarisation "), and this stops the current flowing unless the potential difference exceeds a definite value (the " decomposition voltage "). Provided that this value is exceeded, however, or that polarisation is prevented * a steady current will flow. Experiment shows that **this current is directly proportional to the potential difference between any two points in the electrolyte** † (*cf.* Ohm's law for solid conductors). Therefore no work is done by the electrical energy in splitting up the molecules. On these grounds it is argued that Grotthus' idea must be incorrect, and that some of the molecules at least must be split up before the E.M.F. is applied.

* If copper sulphate is electrolysed with copper electrodes, the electrodes remain unaltered during electrolysis, and hence the polarisation effect is nil.

† If E is the applied E.M.F. and e the back E.M.F., $C=\frac{E-e}{R}$.

Clausius in 1859 was led by a quite different line of investigation to the conclusion that in a solution there must be a constant interchange of atoms (or radicals) going on between the solute molecules. Hence at any instant he considered there would be a few of these atoms (or radicals) uncombined; *i.e.* in the act of changing partners. He suggested that these might form the ions or current carriers when an E.M.F. was applied, and that as they were discharged other molecules would dissociate to take their places. The idea of a dynamic equilibrium between molecules and ions is therefore due in the first place to Clausius. Thirty years later this hypothesis was modified by *Arrhenius*, who assumed that instead of a very few ions being present at any instant, a definite proportion of the solute molecules must always be dissociated: *i.e.* he introduced the notion of a definite "degree of dissociation" and of an equilibrium system comparable with those discussed in the last chapter. Arrhenius based his ideas on the results of electrical conductivity measurements to which therefore we must now refer.

6. Electrical Conductivity.—A good conductor of electricity has a high "conductivity;" *i.e.* a low resistance. If R is the resistance in ohms, then $\frac{1}{R}$ is the conductivity in reciprocal ohms (or mhos).

The *specific resistance* (σ) *of a conductor is the resistance of unit length of it when of unit cross-section.*

If the cross-section of a conductor is A, and its length is l, then $R=\sigma\times\frac{l}{A}$ since the resistance varies directly as the length and inversely as the cross-section.

The **specific conductivity** (κ) **is** $\frac{1}{\text{specific resistance}}$. It can be calculated from measurements of resistance, as shown by the following example.

EXAMPLE.—A copper wire 1 metre long has a resistance of ·005 ohm. The area of cross-section of the wire is ·03 sq. cm. What is the specific conductivity of copper? $R=\frac{\sigma l}{A}$, so that

$\sigma = \frac{\cdot 005 \times \cdot 03}{100}$ ohm $= 1{\cdot}5 \times 10^{-6}$ ohm. The specific conductivity is therefore $\frac{1}{1{\cdot}5} \times 10^6$ mhos or $6{\cdot}7 \times 10^5$ mhos.

When referring to the conductivity of solutions, it is the conductivity conferred by the dissolved solute which is of importance, rather than the length and cross-section of the liquid conductor. In other words, we wish to consider the conductivity of that volume of solution which contains a definite weight of solute. In order to make comparisons possible, we imagine it placed in a cell with parallel electrodes 1 cm. apart.

The molecular conductivity (μ) *and the equivalent conductivity* (λ) *are defined as the conductivities of solutions containing* 1 *gm. molecule and* 1 *gm. equivalent of the solute respectively, when contained in such a cell.*

We will now prove the following important relation:

Molecular conductivity = specific conductivity multiplied by the volume in c.cs. which contains 1 *gm. molecule of solute.*

In other words $\mu = \kappa V$, where V is termed the "dilution." Similarly, if V is the volume in c.cs. containing 1 gm. equivalent of solute, $\lambda = \kappa V$.

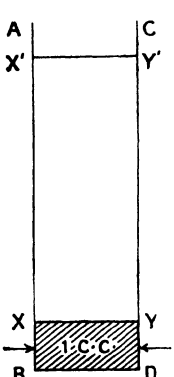


FIG. 37.

EXAMPLE.—For a $\frac{N}{10}$ solution of sodium carbonate, V = 10,000 c.cs. per gm. equivt. If $\kappa = \cdot 00925$, then the equivalent conductivity is 92·5 mhos.

Let us consider a rectangular vessel with one pair of sides 1 cm. apart. If we pour 1 c.c. of a solution into this, the area of each of these sides covered by it must be 1 sq. cm. Hence, the resistance of the solution measured between these sides (*i.e.* between the arrows in Fig. 37) will be its specific resistance σ.

Suppose the solution contains 1 gm. molecule of solute in V litres. With V litres in the vessel the level of the solution will rise to X'Y' and the area of each of the sides AB and CD covered by it will now be 1000 V sq. cms. Therefore the resistance

measured between these sides will now be $\frac{\sigma}{1000V}$. The conductivity will in consequence be $\frac{1000V}{\sigma}$ or $1000\ V \times \kappa$. But this is the conductivity of that quantity of solution which contains 1 gm. molecule of solute.

$$\therefore\ \mu = 1000V \times \kappa.*$$

7. Experimental Determination of the Molecular Conductivity of a Solution.—The method is briefly as follows:

(1) Measure the resistance of a solution of known molar concentration. The reciprocal of this gives the actual conductivity.

(2) Calculate the specific conductivity from the actual conductivity by means of a previously determined constant depending upon the dimensions of the apparatus (see below).

(3) Multiply the specific conductivity by 1000V, where V is the dilution in litres.

Using vessels of known dimensions *Kohlrausch* determined accurately the specific conductivities of many solutions (using the formula $R = \frac{\sigma l}{A}$ to obtain the specific resistance from the observed resistance). For example, he found that at 18° C., $\kappa = \cdot 01119$ for $\frac{N}{10}$ KCl. We can in our own determinations utilise these results of Kohlrausch and thus avoid the necessity of using vessels of known dimensions, as shown by the following example. If 50 c.cs. of $\frac{N}{10}$ KCl are placed in our apparatus and the conductivity at 18° C. is found to be ·00521, we know that $\frac{\cdot 01119}{\cdot 00521} \times$measured conductivity=specific conductivity. This will clearly be the case when 50 c.cs. of any liquid are placed in the apparatus, for the factor $\frac{\cdot 01119}{\cdot 00521}$ depends only on

* Since the dilution V is generally expressed in litres, the expression $\mu = 1000\ V\kappa$ is more common than $\mu = V\kappa$ in which V is in c.cs.

the dimensions of the cell. Hence, this factor $\frac{\cdot 01119}{\cdot 00521}$, is called the "**cell constant,**" and once this is determined we can always calculate specific conductivities from the measured conductivities obtained with this volume of liquid.

The resistance is measured by an ordinary Wheatstone's bridge method, as for a solid conductor, with one important difference. To prevent polarisation, which would behave like a continually varying resistance, an alternating current must be used instead of a direct current. This can be obtained from an induction coil or valve oscillator. A galvanometer will in consequence be useless for finding the "point of balance," and Kohlrausch in 1869 solved the difficulty by using a telephone

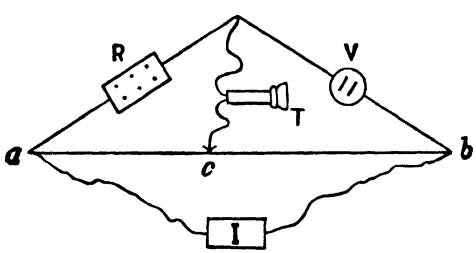


FIG. 38.—Apparatus for measuring electrical conductivity of a solution. (From Findlay's *Physical Chemistry for Students of Medicine*.)

instead. Minimum sound in the telephone shows that the minimum current is passing through it; *i.e.* the correct "point of balance."

NOTE.—(1) Exceptionally pure water must be used in making up and diluting all solutions whose conductivities are to be measured. This is often referred to as "conductivity water."

(2) A rise in temperature causes a marked change in conductivity (in most cases it is increased). The temperature coefficient is in many cases nearly 2% per 1° C., so that constant temperature is essential during a conductivity determination.

8. The Effect of Dilution on Conductivities.—If the current were carried by the whole of the solute, then an increase in the concentration of the solution would increase the

specific conductivity in the same proportion. And, of course, the molecular conductivity would be independent of the dilution under these circumstances. *Arrhenius* found that these conclusions were not supported by his experimental results. He argued from this that only a fraction of the solute was acting as a current carrier at any moment, and that the value

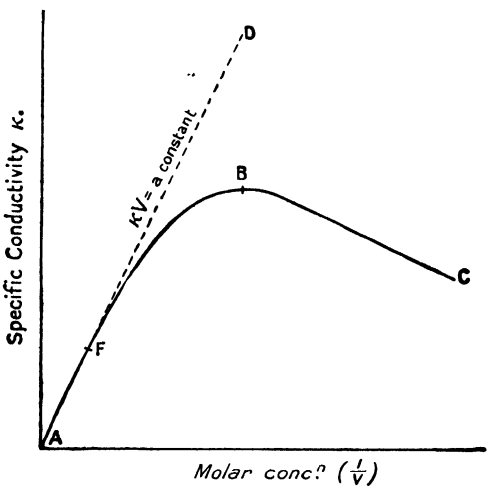


FIG. 39.—Specific conductivity and dilution.

of this fraction varied with the concentration of the solution. The two diagrams which follow show the general types of curve which he obtained from his results. Fig. 39 shows that κ is not directly proportional to the concentration except in very dilute solutions. (The dotted line AD would be followed if κV was constant.) It is clear that a large concentration of solute molecules does not mean a large specific conductivity, and that μ (which we have shown to be equal to κV) gradually increases as the solution becomes more dilute, reaching a maximum and constant value when the curve CBA touches the line AD (as at F). This fact is also illustrated in Fig. 40 which shows the increase in molecular conductivity with increasing dilution, and the attainment of a constant and maximum value at the point X.

Arrhenius accounted for these facts by modifying the hypothesis of Clausius. He assumed that at a certain dilution V there would be a definite fraction of the solute dissociated into ions (the " degree of ionisation "), and called the molecular

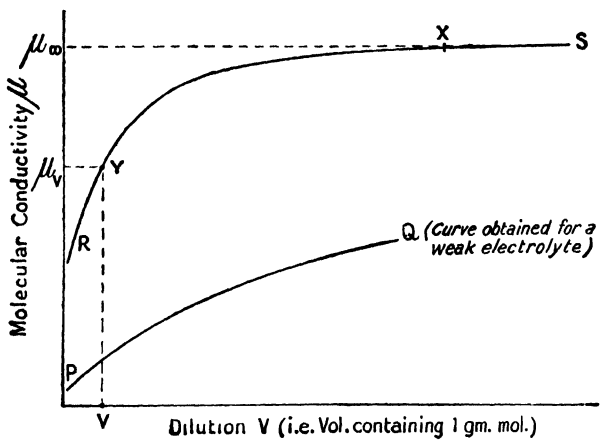


FIG. 40.—Molecular conductivity and dilution.

conductivity of such a solution μ_V (as shown by point Y in Fig. 40). On increasing the dilution he assumed that the degree of ionisation would increase until it was 100 % at what might be termed " infinite dilution ; " *i.e.* a dilution beyond which further decrease in concentration could not affect the molecular conductivity (μ_∞). From this point onwards all the solute molecules would be ionised—hence the constant value for μ_∞.

Arrhenius distinguished between " strong electrolytes," which have high conductivities, and " weak electrolytes," which have low conductivities, assuming the differences to be due to large and small degrees of ionisation respectively. Table VII. shows some actual values. In general, using water as solvent, the **inorganic acids, bases, and salts** form **strong electrolytes,*** and **organic compounds** give feebly conducting solu-

* Experiments with many non-aqueous solvents has shown that the nature of the solvent makes a great deal of difference. Thus. LiCNS is a

tions; *i.e.* form **weak electrolytes.** The distinction between strong and weak electrolytes is probably more fundamental than

TABLE VII.—APPARENT DEGREES OF IONISATION (N/10 AQUEOUS SOLUTIONS).

Type of electrolyte.		Approximate per cent. of solute ionised (from conductivity measurements).
Strong acids	nitric acid	92
	hydrochloric acid	91
Strong bases	potassium hydroxide	89
	sodium hydroxide	84
	barium hydroxide	80
Salts	potassium chloride	86
	sodium nitrate	83
	silver nitrate	81
	sodium acetate	79
Weak acids	acetic acid	1·3
	carbonic acid	0·2
	hydrocyanic acid	0·01
Weak base	ammonium hydroxide	1·4
Organic compounds	sugar, alcohol, organic esters.	nearly zero.

Arrhenius imagined, and his explanation of the differences is certainly incorrect (see footnote, p. 155). This became evident when attempts were made to obtain a definite mathematical relation between molecular (or equivalent) conductivities and concentrations.* The first was an equation due to *Ostwald* (known as the Dilution Law—see p. 237), which gave $\frac{\lambda_c^2 . C}{\lambda_0(\lambda_0-\lambda_c)}$ =a constant, and, excepting concentrated solutions in which other complications occur, this was in good agreement with the facts when dealing with weak electrolytes. But with strong electrolytes it failed utterly (see Table XIII., p. 238), and all attempts to patch it by means of corrections, *e.g.* for altering viscosity of the solvent, have now been abandoned. A relation discovered by *Kohlrausch*, $\lambda_0-\lambda_c=K\sqrt{c}$, where K is a con-

strong electrolyte in water or ethyl alcohol, but a weak electrolyte in acetone or nitromethane.

* Do not be confused by the modern use of " concentration " in place of " dilution." Since C is $\frac{1}{V}$, this only means writing λ_0 for λ_∞ (zero concentration is the same as infinite dilution), and λ_c for λ_v. Hence $\frac{\lambda_c}{\lambda_0}$ is the same as $\frac{\lambda_v}{\lambda_\infty}$. The tendency also is to refer to *equivalent* rather than *molecular* conductivities.

stant, is, however, found to fit the facts in such cases (again restricting ourselves to dilute solutions), and it should be noted that the two equations are totally different in character. Thus, if $\frac{\lambda_c}{\lambda_0}$ is plotted against $\sqrt{c}$, straight lines are obtained only when dealing with strong electrolytes.

Note on the Determination of μ_∞ (or λ_∞). In practice, when the dilution gets very great, conductivities become too small to measure with accuracy. Thus with a substance like acetic acid we cannot get much beyond a point such as Q on the curve PQ (Fig. 40), and it would be hopeless to guess at the probable value of μ_∞ from this. It is possible, however, to calculate the value of μ_∞ for any electrolyte from a knowledge of the mobilities of its ions (see p. 229). When we are dealing with strong electrolytes the straight-line relation of Kohlrausch referred to above is generally used, for then by a process known to mathematicians as "extrapolation" we can calculate the limiting value we require from a series of measured values of μ_c and C.

9. Degree of Ionisation.—Arrhenius knew that the conductivity of a solution depended upon three factors: (1) the number of ions; (2) their speed; and (3) the charge they carried; and he knew that Faraday's laws had proved that the ionic charge was constant. He then made the assumption that ionic speeds (mobilities) would be practically unaffected by dilution, basing his ideas on some very early work by Hittorf (see p. 222). In consequence he overlooked the enormous effect of the solvent, and of the inter-ionic forces, on the conducting power of the ions; fixing all his attention on changes in their number.

Assuming, therefore, that maximum conductivity meant maximum number of ions, and that a smaller conductivity at some different dilution meant a fraction α of the solute ionised, and the rest of it present as unionised molecules, it was clear to him that $\frac{\mu_v}{\mu_\infty} = \alpha$. *E.g.* if the molecular conductivity of an electrolyte is half its maximum value, then only half the solute molecules are ionised, and α (the degree of ionisation) is $\frac{1}{2}$ or 50%.

Arrhenius' theory of partial ionisation and of a state of

equilibrium in solution between ions and molecules was first published in 1883. It was seen to account for many different phenomena, such as the analytical tests for radicals, the colours of certain solutions, the differences in the strengths (or avidities) of acids, the nearly constant heat of neutralisation of all strong acids by strong bases, and the additive nature of the electrical conductivities of solutions. These points are discussed in the next paragraph, but even more important confirmation of his views was soon forthcoming. In 1886 van 't Hoff produced his theory of dilute solutions (p. 115), and the "degrees of dissociation" calculated from the i values of electrolytes (see pp. 153–6) were found to agree in most cases almost exactly with Arrhenius' degrees of ionisation. Here, then, was a comprehensive theory which would account for the abnormal "osmotic" properties of a solution, its electrical, and its chemical properties on a common basis! In the following year (1887) Arrhenius published a more detailed account of his theory, embodying all these points (see his "Faraday Lecture," *J.C.S.*, 1914).

Table VIII. shows the remarkable agreement referred to above. It is a small selection from some data compiled by Noyes and Falk (1910–12) which are much more accurate than any available in 1887. A correction has been applied for the viscosity of the solution in calculating α from the conductivity measurements. With solutions of concentration not exceeding N/10, these data show agreement within 2% with very few exceptions. Yet most of them were strong electrolytes! Arrhenius was surely justified in including them in his theory.

TABLE VIII.

Solute.	Concentration in gm. equivalents per 1000 gms. of water.	"i" from freezing point depression.	α from the "i" value.	α from electrical conductivity measurements.
			%	%
KCl	·01	1·943	94·3	94·1
,,	·05	1·885	88·5	88·9
,,	·10	1·861	86·1	86·0
,,	·50	1·800	80·0	77·9
NaCl	·005	1·953	95·3	95·3
HCl	·005	1·991	99·1	98·1
,,	·05	1·933	93·3	94·4
$Ba(NO_3)_2$	·005	2 833	91·7	89·8
$BaCl_2$	·01	2·756	87·8	88·3
Na_2SO_4	·10	2·472	73·6	70·4
$CuSO_4$	·005	1·616	61·6	70·9

10. Evidence in favour of the Ionic Hypothesis.—It is stated that when Ostwald received details of this hypothesis in a letter from Arrhenius he was filled with delight. Ostwald was at that time the leading authority on physical chemistry, and he replied to Arrhenius that the news had reached him on a very eventful day. It had begun with a severe attack of toothache, continued by presenting him with a daughter, and ended with the arrival of the letter.

The receipt of the hypothesis he seems to have considered the most important event of the three!

(1) *Analytical tests for "Radicals."*—The addition of silver nitrate to a solution causes precipitation of silver chloride if a chloride is present, but not if chlorine is present in any other form. Thus, chlorates, chloroform, etc., give no precipitate with silver nitrate. Silver nitrate is therefore a test for the "chloride radical" and not for chlorine. Again, a solution of potassium ferrocyanide does not give precipitates with reagents (such as ammonia) which precipitate iron from solutions of iron salts. The "ferrocyanide radical" is present in this solution, and not the "iron radical." The hypothesis accounts for this by stating that our tests are for the ions which are present, and that the ferrocyanide, chloride, sulphate ions (for example) are quite different from the iron, chlorate, and sulphide ions. The fact that mercuric cyanide solution does not give the reactions characteristic of mercury salts (such as a precipitate with hydrogen sulphide) is explained by supposing that the solution contains very few mercury ions, and its low conductivity supports this idea. We may express this in a general way by saying that **the behaviour of a solution is the additive effect of the ions which it contains.**

(2) *If the colours of solutions* of electrolytes are due to the colours of the ions present we can understand why all dichromate solutions are orange, chromate solutions yellow, permanganate solutions purple, etc. Solutions of chromium salts and manganese salts on the other hand contain no dichromate, chromate, or permanganate ions and therefore are not of these colours.

(3) Another additive effect due to the ions present is the electrical conductivity. *Kohlrausch* in 1876 proved experimentally that the **molecular conductivity** of a solution was **the sum of two quantities**, one due to the anion and the other to the cation (see p. 226).

(4) *The Relative Strengths of Acids.*—All acids contain replaceable hydrogen, yet some show their acid character much more markedly than others. Thus, by their action on metals and on indicators we can distinguish that nitric acid is a strong acid and that carbonic acid is a feeble or weak acid. The term "strength of an acid" therefore refers to its relative degree of "acidity" and not to its concentration. *E.g.* a dilute solution of nitric acid is a much stronger acid than a concentrated solution of acetic acid. There are several methods of comparing the strengths of acids and these will be discussed in Chapter XIII., but the results must be referred to here. In the first place, *one method is based on thermal measurements, and is absolutely free from any assumption of the existence of ions, but the results agree satisfactorily with those obtained by other methods based on the ionic hypothesis* (see Table XIV., p. 244). Moreover, it appears that the strengths of all acids do not decrease to the same extent when diluted. *All acids, in fact, tend to become equal in strength in infinitely dilute solution.* This astonishing fact was predicted by Arrhenius in 1883, assuming the correctness of his hypothesis.

His reasoning was as follows. Acids in solution dissociate into hydrogen ions and various anions. Thus, $HX \rightleftharpoons H^{\cdot} + X'$.* The common properties of acids must be due to the fact that their solutions all contain **hydrion** (hydrogen ions). Differences in acid character, or strength, are therefore assumed to be due to different concentrations of hydrion in their solutions. A weak acid like acetic acid is therefore a weak electrolyte and is little ionised in solution; *i.e.* its solution contains few hydrogen ions. A strong acid like nitric acid, on the other hand, is a strong electrolyte and its solution contains many hydrogen

* It is now believed that the hydrogen ions (called "protons"—see p. 266) are hydrated. Thus $H^{\cdot} + H_2O = H_3O^{\cdot}$, and in future pages whenever $H^{\cdot}$ is mentioned, $H_3O^{\cdot}$ should be substituted. An acid according to modern views is a "proton-donor," and a base is a "proton-acceptor."

ions. The "degrees of dissociation" for a few acids are shown in Table VII. and it is seen that this point of view is justified. But the degree of dissociation of an acid increases with the dilution (as shown by conductivity measurements) until it is completely ionised. This state is reached for a strong acid at moderate concentrations, but with a weak acid the degree of dissociation continues to increase until very great dilutions are reached. Hence, on dilution the weak acid decreases in strength less rapidly than the strong acid. They will not actually become equal until so dilute as to be indistinguishable from water.

EXAMPLE.—

	N	$\frac{N}{10}$	$\frac{N}{100}$	$\frac{N}{1000}$	$\frac{N}{10,000}$
Hydrochloric acid (concentration of hydrogen ions in gm. equivalents per litre)* . .	·81	·091	·0097	·00099	·0001
Acetic acid (concentration of hydrogen ions in gm. equivalents per litre)	·004	·0013	·0004	·00013	·00004

Thus, in normal solutions hydrochloric acid is 200 times as strong as acetic acid, but in $\frac{1}{10,000}$ normal solutions it is only $2\frac{1}{2}$ times as strong.

(5) *Relative Strengths of Bases.*—We recognise that a solution of caustic soda is a strong base, and that a solution of ammonia is a feeble or weak base and the ionic hypothesis explains these differences as due to the different concentrations of **hydroxidion** (hydroxyl ions) contained in their solutions. In other words, a base dissociates thus: $ROH \rightleftarrows R^{\cdot} + OH'$, and the remarks in the previous paragraph apply in a similar manner to the relative strengths of bases.

(6) *The Constant Heat of Neutralisation of Strong Acids and*

* Whenever we are dealing with strong electrolytes we must now regard "ionic concentrations" as "apparent concentrations," for they are calculated from "apparent degrees of ionisation" (cf. footnote, p. 155).

Bases.—Experiment shows that if 1 gm. equivalent of a strong acid be neutralised by 1 gm. equivalent of a strong base in dilute solution, the heat evolved is nearly always approximately 13,650 calories. According to the ionic hypothesis the process of neutralisation may be written thus

$$H^{\bullet}+X'+R^{\bullet}+OH'=H_2O+R^{\bullet}+X',$$

for strong acids, strong bases, and all salts are completely ionised. Water, on the other hand, is very little ionised.* The heat produced would therefore be due to $H^{\bullet}+OH'\rightarrow H_2O$ (the heat of formation of water from its ions). This is clearly independent of the nature of the acid and base used. But if we employed an acid or a base which was not 100% ionised (*e.g.* a weak acid or base) there would be heat effects due to their ionisation, which would have to occur prior to neutralisation. Hence, deviations from the constant value (13,650 cals. approx.) may indicate that either the acid or base is not 100% ionised. It is possible, however, that even our so-called strong acids and bases are not ideal in the above sense, and that heat effects (other than the 13,650 cals. due to neutralisation) may be due to work done in separating the ions, *i.e.* work done against inter-ionic forces.

EXAMPLE.—*Richards and Rowe* in 1922 neutralised HCl, HBr, HI and HNO_3 with KOH, NaOH and LiOH and obtained values (at 20° C.) varying only from 13,620 to 13,690 calories when working with very dilute solutions.†

(7) *Movement of Ions during Electrolysis.*—Using solutions with coloured ions in contact with colourless solutions, *Lodge* and others have measured the rate at which the coloured boundary moves, and thus arrived at the **absolute velocities of some ions.** The results agree satisfactorily with values deduced in a quite different manner (see p. 228).

(8) *Rapidity of Ionic Reactions.*—Reactions between solutions of inorganic salts generally take place practically

* The purest water is found to have an electrical conductivity which indicates the existence of 10^{-7} gm. equivalent of $H^{\bullet}$ and of OH', so that nearly all of it is unionised. Several independent lines of investigation have led to the same degree of ionisation for pure water, which is in itself strong evidence for the correctness of the hypothesis.

† Taylor, *A Treatise on Physical Chemistry*, I. 510.

instantaneously, but the time required for organic preparations will remind you that reactions between non-electrolytes are as a rule very slow. This suggests that reactions take place readily between ions, and may partly explain the enormous effect which water has on chemical changes (see p. 211).

(9) *The Dilution Law.*—Following Arrhenius' lead, *Ostwald* assumed that in solution there was an equilibrium mixture of ions and unionised molecules, and applying the Law of Mass Action deduced that $\frac{\lambda_c^2 . C}{\lambda_v(\lambda_0-\lambda_c)}$ should be a constant (see p. 237). This is known as the *Dilution Law.* Deductions from it were tested by measurements of the conductivity at different dilutions, and it was found to be quite satisfactory when dilute solutions of weak electrolytes were employed. It was argued that such excellent mathematical agreement could not result from a false hypothesis. This was quite reasonable, but the mistake made by Ostwald and his followers was that they tried to make it applicable to all electrolytes. Although the relation between conductivity and dilution in the case of strong electrolytes (as found by experiment) would not agree with Ostwald's law, it was thought for many years that this was due to a misinterpretation of the facts, and nobody dared to suggest that the law was not the correct one. Attempts were made to modify it (just as a modified Gas Law, " Van der Waals Equation," had been found to give a closer approximation to the truth than the simple PV=RT), but in vain. Corrections were applied to allow for the viscosity of the solvent, for solvation of the ions, and for other possible causes of the discrepancy between facts and theory. Chemists made up their minds that the theory was correct, and strove to make the facts fit in somehow ! This was unscientific, and in recent years it has been realised that they were making a big mistake. Strong electrolytes are *not* governed by the Dilution Law. The relation between their conductivities and dilutions is the *Kohlrausch* relation (p. 176). Evidently strong electrolytes do not fall within the scope of the simple Arrhenius hypothesis of partial ionisation and an equilibrium mixture of ions and unionised molecules. The theory of complete ionisation, which has already received a brief mention, has been

developed to deal with the strong electrolytes, and it is still not worked out in detail. A good many difficulties confront it, but considering the comparatively short time during which it has been realised that molecules are non-existent in solutions of strong electrolytes, the progress made is encouraging.

To return to the Dilution Law. The breakdown of this when applied to strong electrolytes has strangely enough been its salvation, for its failure had given hostile critics of Arrhenius' hypothesis their main point of attack. Now that we know that it should only be applied to weak electrolytes their murmuring is no longer heard. The agreement in such cases is too remarkable. The Dilution Law becomes one of the most convincing arguments in favour of the hypothesis.

There is still difficulty in interpreting results obtained in concentrated solutions. No doubt the ions here have less freedom, and inter-ionic forces will have more to say in the matter. However, this remains one of the problems for the future, and it will be well to preserve an open mind, remembering always that, at present, theory and fact only agree when dilute solutions are employed.

(10) *Practical Applications.*—A great many developments in applied chemistry have been based on the assumptions involved in the ionic hypothesis. The daily routine in vast industries such as leather tanning and brewing; in medical research; and in bacteriology, includes the measurement of hydrion concentrations, and the use of indicators whose behaviour is based entirely on ionic considerations. The fruitful results of the hypothesis do not prove its accuracy, but they certainly justify its existence.

11. Opposition to the Hypothesis.—For many years critics bitterly attacked the idea that a solution could consist of dissociated molecules when not under the influence of an E.M.F. Some of the points which they raised have already been mentioned, but a few of the others may be briefly summarised, though they are now only of historical interest.

(1) They would not admit that ions could have properties different from those of the uncharged atoms from which they were derived, and hence could not believe that in a solution of salt Na and Cl atoms could exist in contact with water.

(2) They pointed to the green colour of cupric chloride solutions when concentrated; for according to the hypothesis all cupric salts should give the same (blue) coloured solutions. The explanation of this anomaly, and of many like it, is to be found in the tendency for ions to combine or react with each other, or with the solvent, so as to form "Complex ions" (see p. 233). Thus in this present case the green colour is thought to be due to a $CuCl_3'$ anion.

(3) They suggested that since the ions differed in weight, they should, if independently present in a solution, be separable by diffusion. They were here completely disregarding the electrostatic attractions which oppositely charged ions must exert on one another.

(4) They were puzzled as to the source of energy by means of which the solvent apparently disrupted the molecules of the electrolyte. They did not guess that the electrolyte might consist of ions before it dissolved, and that all the solvent had to do was to give them freedom of movement by weakening the forces between them.

(5) They suggested that the abnormal osmotic effects produced by electrolytes might be due to association of the solvent molecules, or solvation of the solute molecules, for in either case there would result a reduction in the number of free solvent molecules, *i.e.* an apparent increase in concentration. These ideas, however, proved to be far less satisfactory than the ionic hypothesis, and they have now been abandoned.

12. Recent Developments, Influence of the Solvent.—Attention having been drawn to the true rôle of the solvent, research is now being actively carried out to investigate the extent of ionisation, the sizes and mobilities of the ions, and the effect of dilution, when working with non-aqueous solutions. The data so obtained, which at one time were such a puzzle to the believers in the Arrhenius hypothesis, are becoming of increasing importance, and it is now clear that we have no right (and no need) to restrict ourselves to the use of water as a solvent when tackling the problem of the nature of solutions. For further details the student is recommended to read a pamphlet published by the Science Masters' Association, *The*

Ionic Theory of Electrolytic Solutions, by Harold Hartley (price 1s. 1*d.*, post free).

13. Summary.—The value of the ionic hypothesis (or theory of ionic dissociation) is largely due to its scope, for we find the most diverse phenomena explained on a common basis. Although we may sometimes be dealing with partial dissociation and at other times with complete dissociation, yet the idea that in a solution of an electrolyte we have ions present instead of molecules is a most important step towards an understanding of the nature of solutions in general. It will be well to summarise at this stage the evidence in favour of this hypothesis, although many of the points mentioned are not discussed in detail until Chapter XIII. is reached. A final word of warning may not be amiss. Remember, the last word has not been said yet! We laugh now at Priestley's bigoted refusal to give up the idea of Phlogiston, but we must not be found guilty of a similar failing by chemists of the future. Let the breakdown of Arrhenius' theory when applied to a substance like common salt be ever present in our memories to prevent us from being over confident and using our theories as though they were facts.

The hypothesis explains :—

1. Faraday's laws and the phenomena of electrolysis.
2. The fact that Ohm's law holds for electrolytes.
3. The "additive" character of a solution. This behaves as though each ion produced its own effect; *e.g.* we find the reactions are those of the "radicals" (p. 178); the conductivity is the sum of two factors (p. 179); and the colour seems to be due to the ions present (p. 178).
4. The changes in electrical conductivity which occur on dilution.
5. The constant heat of neutralisation of strong acids and bases.
6. The agreement between the values for the degree of ionisation calculated from osmotic effects ("i" value) and conductivity data.
7. The validity of Ostwald's Dilution Law when applied to dilute solutions of weak electrolytes.
8. The agreement between the values for the relative strengths of acids (and of bases) obtained by different methods (p. 244), and the fact that all acids tend to equal strength as the dilution increases (p. 189).
9. The agreement between the values obtained for the degree of ionisation of water itself by many different methods.
10. The movements of coloured boundaries on electrolysis (p. 228); and the agreement between values for the absolute mobilities of the ions obtained by different methods.

11. The fact that traces of moisture have such a great influence on chemical changes (p. 211).

12. The reactions used in qualitative analysis; precipitation by the addition of a common ion; and the solubility of "insoluble" salts in acids (p. 230).

13. The behaviour of indicators, and the changes in "acidity" which occur during many chemical changes. The nature of hydrolysis.

DEMONSTRATIONS.—1. Illustrate the common phenomena of electrolysis, including primary and secondary products, effect of electrodes on secondary products, and polarisation.

2. Illustrate the hypothesis of Grotthus by means of a model.

3. Movement of a coloured boundary is useful to illustrate ionic migration. For details see *School Science Review*, III., 52, 1921.

4. Qualitative experiments to illustrate the applications of the ionic hypothesis; *e.g.* qualitative analysis reactions, common ion effect, etc. These are more fully discussed in Chapter XIII. Coloured solutions should also be shown and discussed; *e.g.* chromates and chromium salts.

5. Experiments on lack of reaction between solutes in non-aqueous solutions. *E.g.* pass dry hydrochloric acid gas into dry toluene and add a dry metal. Show the effect of adding water.

PRACTICAL WORK.—1. Determination of an electrochemical equivalent.

2. Determination of electrical conductivities (specific and molecular). If possible, solutions at different dilutions should be used and the change in α determined.

QUESTIONS.—1. State Faraday's laws of electrolysis. If 2·596 amps. flowing for 22 mins. liberated 1·130 gms. of copper during the electrolysis of a solution of copper sulphate, what is the electrochemical equivalent of this element?

2. What points in connection with electrolysis have to be explained by the ionic hypothesis? Why was Grotthus' hypothesis rejected?

3. Define the terms "specific conductivity" and "molecular conductivity" as applied to a solution. Prove that the latter is obtained by multiplying the former by the dilution in c.cs.

4. Describe how you would determine the specific conductivity of a solution experimentally. By means of curves show how the specific conductivity and molecular conductivity of a strong electrolyte vary with the dilution.

5. How can electrical conductivity measurements lead to a knowledge of the state of dissolved solute particles? Calculate the degree of ionisation of potassium chloride in $\frac{N}{50}$ solution at 18°C. from the following data: specific conductivity of this solution $=\cdot0024$; $\mu_\infty = 130$.

6. How is it that a dilute acid may be stronger than a more concentrated acid? What is the effect of dilution on the strength of an acid?

7. Explain the nearly constant value for the heat of neutralisation of strong acids by strong bases. The value of this constant is about 13,650 cals., but the heat of neutralisation of hydrocyanic acid by strong bases is about 2,800 cals. Explain this.

8. What is your opinion of the ionic hypothesis? Discuss the evidence for and against it.

CHAPTER XI

CONDITIONS UNDER WHICH CHEMICAL CHANGES OCCUR

1. "THIS race will take place weather and circumstances permitting" is a phrase sometimes seen in a sports programme. The chemist ought to attach a similar phrase to his equations: "This reaction only occurs under specified conditions"; for temperature, pressure and other factors play an important part in deciding whether substances will react, and what the products will be if they do. To continue the analogy, we may note that the times recorded at a sports meeting depend on the wind, heaviness of the ground, etc., and the speed of a chemical reaction is also dependent on the conditions under which it takes place. In the present chapter we shall study the effect of varying conditions on chemical changes in general. Let us assume the dynamic nature of chemical changes * as a working hypothesis for all of them, and see whether deductions from it are in accordance with the facts. That is, let us assume that all reactions proceed at a definite speed, and, if we are dealing with a system in equilibrium, let us assume that the composition of this system can only be changed by altering the rates of the two opposing reactions to different extents.

NOTE.—In order to treat all chemical changes as though they were governed by the same laws, some chemists make two important assumptions: (1) that all chemical changes are reversible; (2) that when no change can be demonstrated experimentally, it is sometimes permissible to consider that a change is proceeding exceedingly slowly. The first assumption is essential unless we are to distinguish "reversible" and "irreversible" changes as distinct types; the second if we wish to consider that temperature changes and catalysts can only alter the speed of reactions and not start them. Those who hold these views explain the apparent irreversibility of a reaction such as $2KClO_3 \rightarrow 2KCl + 3O_2$ when occurring in a

* This is outlined in pp. 149-152, which should be revised before proceeding with this chapter.

closed space, by assuming either that the reverse change is excessively slow or that the proportion of potassium chlorate in the equilibrium mixture is too small to detect experimentally. Again, they are forced to believe that hydrogen and oxygen are slowly combining at room temperatures if mixed together ($2H_2+O_2 \rightleftarrows 2H_2O$), but at a rate too slow to be verified experimentally. The equilibrium mixture, they would say, is nearly all water, and a catalyst or rise in temperature increases the rate at which equilibrium is attained.

Such views are difficult, if not impossible, to disprove, but they are by no means universally accepted. They enable us to treat all chemical changes on a common basis, and hence it is argued that they should be retained as a working hypothesis until evidence is produced against them.

2. The Mechanism of Chemical Changes.—An equation shows us only the initial reagents and the final products of a chemical change. It tells us nothing of the process itself; of what starts the reaction; or of what happens to the individual molecules. Sometimes "intermediate stages" are hinted at (see p. 59); but this is not often the case. The result of varying the temperature or other conditions on the reaction velocity or on the nature of the final products is the most valuable source of information as to the mechanism of a reaction.

If a reaction takes place at a measurable speed, each molecule before it can decompose or react with another molecule must be got into some special condition, for otherwise all the molecules would tend to "go off at once." Each molecule we may say has to be "activated" or given a supply of energy sufficiently greater than that possessed by an "inactive" molecule to enable it to take part in the chemical change. Collisions between the molecules are probably responsible for most of the "energy of activation" which they require,* but the absorption of radiation (heat, visible light, or ultra-violet light) may supply some of it. Possibly some catalysts are

* Most of our knowledge of this part of the subject is based on reactions between gases, where the molecules can move with comparative freedom, but it must not be supposed that every collision between molecules will be effective. No doubt only those moving with sufficient speed will impart enough energy to bring about "activation."

merely convenient energy transformers, inasmuch as they convert energy supplied in the form of heat or light into a form in which the reacting molecules can make use of it. *E.g.* chlorophyll in a green leaf absorbs sunlight, and the surrounding carbonic acid molecules are able to utilise the energy which it passes on to them, and thus combine to form sugar.

3. The Factors which affect Chemical Changes.—NOTE.—*Changes in reaction velocity must be clearly distinguished from changes in reaction products. Both should be mentioned when discussing the effect of conditions on a chemical change.*

(1) *Temperature :* (a) *Rise in Temperature always Increases Reaction Velocity.*—This is an experimental fact, the reaction velocity as a rule being doubled or trebled for a rise of 10° C. Thus, for the system $2HI \rightleftarrows H_2+I_2$ to reach a state of equilibrium at 440° C. is a matter of hours ; at 350° C. it takes days ; at 265° C. it takes months ; and at room temperatures the time required is indefinitely long.

(b) Many reactions apparently do not start until a certain temperature is attained. *E.g.* potassium chlorate does not appear to decompose below 372° C., but it is not certain that the reaction actually starts when it is first observed (see note in para. 1).

(c) The final products of a reaction may depend on the temperature. *E.g.* potassium chlorate is converted into either potassium perchlorate or chloride according to the temperature of decomposition ; and nitrogen peroxide and water, chlorine and water, concentrated sulphuric acid and sodium chloride or nitrate are other pairs of reagents which give different products at low and high temperatures. As a rule, the products at high temperatures are due to a secondary reaction between the products formed at lower temperatures (see law of successive reactions), so that we are not dealing with the same reaction at both temperatures.

(d) The composition of a system in equilibrium is altered by temperature changes in accordance with le Chatelier's rule,* since all reactions are either exothermic, *i.e.* cause

* See p. 54.

evolution of heat, or endothermic, *i.e.* proceed by absorbing heat.

Thus, $N_2+3H_2 \rightleftarrows 2NH_3+23{,}000$ calories,* so that, since rise of temperature must cause the reaction to proceed in such a way that heat is absorbed, the change will be in the direction $N_2+3H_2 \leftarrow 2NH_3+23{,}000$ cals. Remember, however, that **both forward and back reactions are accelerated by the temperature rise, but one is affected more than the other.** Le Chatelier's rule only enables us to predict **qualitatively** the effect of temperature changes. An equation has been deduced by *Nernst* (from thermodynamic considerations) which allows us to calculate, from a knowledge of the heat absorbed or evolved during a reaction, the actual change in composition which will result from a given temperature change.

(2) *Concentration of Reagents.*—(*a*) Reaction velocity is increased by increasing the concentration (the mass per unit volume) of any of the reagents. This is fully discussed in para. 4 (The law of mass action).

EXAMPLE.—The rate of decomposition of hydrogen peroxide decreases as its concentration decreases (see p. 193).

(*b*) The composition of a system in equilibrium will vary if the concentration of any of the substances present is altered, since one of the two opposing reactions will be altered in velocity (see para. 5).

EXAMPLE.—The system $BiCl_3+H_2O \rightleftarrows BiOCl+2HCl$ is shifted to the right or left respectively if water or hydrochloric acid is added.

(3) *Pressure* has practically no effect on solid and liquid systems, but since it alters the volume of gaseous systems, the concentration of the reagents is affected and hence reaction velocities will be affected. In an equilibrium mixture the effect of pressure variation depends upon whether the two opposing reactions are equally or unequally affected.

EXAMPLES.—(*a*) $PCl_5 \rightleftarrows PCl_3+Cl_2$. Reaction here causes a change in volume (Avogadro's hypothesis), so in this instance

* This indicates that 23,000 calories are evolved during the reaction $N_2+3H_2 \rightarrow 2NH_3$ involving the formation of 34 gms. of ammonia.

pressure changes will affect the two rates unequally and the equilibrium will be displaced. (*b*) $N_2+O_2 \rightleftarrows 2NO$. This reaction involves no change in volume (Avogadro's hypothesis) and pressure changes will affect both rates equally. This equilibrium is therefore not displaced by pressure changes. We can also deduce from le Chatelier's rule the direction in which change, if any, will occur; for increase of pressure causes reaction to occur in such a way that the volume decreases; *e.g.* $PCl_5 \leftarrow PCl_3+Cl_2$ when the pressure is increased (*cf.* p. 54).

(4) *Light.*—Some chemical changes are definitely affected by the incidence of light energy.* *E.g.* hydrogen and chlorine combine in sunlight at room temperatures; silver salts are discoloured by light and are in some way changed so that they can then be reduced to metallic silver by developers; and green plants are able to convert carbonic acid into sugar under the influence of sunlight. The wave-length of the incident light is an important factor, and it is the violet (and ultra-violet) rays (*i.e.* the high frequency or short waves) which are most chemically active. That is why sunlight and the light from burning magnesium are so efficient for photographic purposes.

In many cases the amount of chemical change is proportional to the total quantity of light energy absorbed, *i.e.* light energy is being converted into chemical energy.† Thus, when 1 gm. mol. of sugar is synthesised from carbonic acid in a green leaf, about 700,000 calories of energy are absorbed from the sun's rays. In other cases the light seems to act like a catalyst, accelerating (or possibly starting) a reaction which would normally proceed in the dark if suitably catalysed. Hence a very little light energy absorbed causes a large amount of chemical change. *E.g.* $H_2+Cl_2 \rightarrow 2HCl$ occurs with explosive violence in sunlight, so evidently energy is given out in this process, not absorbed. It seems probable that the "primary

* According to the **Grotthus-Draper** law (1841), it is only the energy actually absorbed that is effective. The term "light" used here is intended to include invisible radiation as well as visible light.

† A more exact statement of this relation is known as Einstein's Law of Photochemical Equivalence (1912), but since this involves the Quantum Theory it cannot be given here.

light process" is always the "activation" of some of the molecules present (*cf.* p. 188), but that this may, as in the cases just considered, be followed by a "chain" of secondary actions, or by the catalysing of the main reaction by a product of the primary process. If this happened, the primary process naturally need not occur to any appreciable extent.

Photochemistry is a comparatively new subject, but the value of "light baths" in curing certain diseases and in stimulating the growth of crops has already been proved. Great developments are confidently expected in the future.

(5) *Catalysts.*—Any substance added to a reacting system, which simply by its presence alters the speed of the reaction, although it is itself chemically unchanged at the end of the reaction, is termed a catalyst. Catalysis is discussed in para. 10, and the influence of moisture on p. 211.

(6) *Electrical Energy* has a marked effect on chemical systems. Just as chemical energy is convertible into electrical energy (voltaic cells), so electrical energy is convertible into chemical energy; *e.g.* decompositions brought about by electrolysis, and combinations brought about by the silent discharge (as in the ozonisation of oxygen). Be careful not to include the electric arc or furnace under this heading, for it is the heat energy in these cases which causes the chemical changes. Thus, sparking a mixture of hydrogen and oxygen is merely heating it strongly at one point.

(7) *Certain other factors* such as area of contact between reagents, nature of their surface, grinding and mixing must be included, for they alter the chance of collisions between molecules. The effect of these factors is, however, too indefinite to be treated more fully at present.

4. The Law of Mass Action.*—

The velocity with which a chemical reaction proceeds is directly proportional to the active masses of the reacting substances.

* As stated here the law applies to homogeneous (or single phase) systems only; *e.g.* to reactions between gases, or between substances in solution. For the treatment of heterogeneous systems, *e.g.* reactions involving gases and solids, or precipitates in contact with solutions, see p. 202 *seq.* Strictly speaking, nearly all reactions between gases are

Guldberg and *Waage* arrived at this law from theoretical considerations based on the laws of thermodynamics. It can also be deduced from the kinetic theory of matter on the assumption that reaction velocity is proportional to the number of collisions occurring in unit time between the reacting molecules. Moreover, it can be verified experimentally in two distinct ways (see next paragraph), so that there can be little doubt as to its validity.

Notes on the Law.—(1) *Reaction velocity*=amount of change per unit time.

(2) *Amount of change*=number of gm. mols. changed.

(3) *Active mass=molecular concentration.** This may be expressed as number of gm. mols. per unit volume.

EXAMPLE.—If 32 gms. of hydrogen peroxide in 120 c.cs. of water are decomposing, and in 5 secs. there are 30 gms. left undecomposed, the active mass was originally $32 \div (34 \times 120)$ gm. mol. per c.c., and the initial rate of decomposition being proportional to this was $k \times 32 \div (34 \times 120)$. After 5 secs. the active mass has fallen to $30 \div (34 \times 120)$ gm. mol. c.c. and the rate of decomposition to $k \times 30 \div (34 \times 120)$. The average rate of change during this period of 5 secs. is $(\frac{32}{34} - \frac{30}{34}) \times \frac{1}{120} \times \frac{1}{5}$ gm. mol. per sec. for each c.c. of the solution.

(4) Since the rate of change is varying continuously as a reaction proceeds, the idea of an " average rate " is of no value unless the time interval is very small, so that the notation of the calculus is employed when stating the law of mass action mathematically. Thus, if we start with a gm. mols. of hydrogen peroxide per unit volume and after t secs. there are $a-x$ gm. mols. per unit volume undecomposed, the rate of change is then $k(a-x)$, and this will cause a further minute change in the active mass represented by dx in the course of

heterogeneous owing to the marked catalytic effect of the walls of the containing vessel, but this can often be ignored (*cf.* para. 8, where $PCl_5 \rightleftarrows PCl_3 + Cl_2$ is treated as though it was a homogeneous reaction).

* This is an assumption that will have to be qualified later (see p. 239).

a very small time interval represented by dt. Thus, $\frac{dx}{dt}=k(a-x)$ is the expression used for stating the rate of change at this instant.

There are alternative ways of symbolising the molar concentration, such as $C_{H_2O_2}$ or $[H_2O_2]$. The latter convention (square brackets) is now in general use and will be adopted in the succeeding pages of this book. In other words, for the rate of decomposition of hydrogen peroxide we write

$$\frac{dx}{dt}=k[H_2O_2]$$

where dx is the change in molar concentration which will occur in a small time interval dt.

(5) If two or more molecules are involved in a reaction, the reaction velocity is proportional to the active mass of each of them. Thus, in the reaction alcohol+acid→ester+water, the rate of ester formation is $k\times$[alcohol]$\times$[acid]. And in the reaction $2HI\rightarrow H_2+I_2$ (which is really $HI+HI\rightarrow H_2+I_2$) the rate is $k\times[HI]\times[HI]$ or $k\times[HI]^2$. This is because two molecules are involved, although they are both of the same kind.

Speaking generally, if n molecules are reacting and their active masses are C_1, C_2, C_3 . . . C_n, the rate of reaction is $k\times C_1\times C_2\times C_3\times$ . . . C_n.

If the measured rate of reaction indicates that there is one molecule only on the left-hand side of the equation, *e.g.* $H_2O_2\rightarrow H_2O+\frac{1}{2}O_2$, the reaction is termed "first order." If two molecules are involved, *e.g.* $2HI\rightarrow H_2+I_2$ or $CH_3COOH+C_2H_5OH\rightarrow C_2H_5COOCH_3+H_2O$, it is termed "second order," and so on.*

An example will show one way in which the "order of a

* The terms "monomolecular," "bimolecular," etc, formerly used to designate the order of a reaction are best avoided, so frequently do complicating circumstances make it impossible to deduce from the experimentally determined order the actual number of molecules reacting. For example, the decomposition of phosphine on heating ($4PH_3\rightarrow P_4+3H_2$) is found to be a "first order" reaction when carried out in a glass vessel owing to the very great catalytic effect of the walls of the vessel.

reaction " can be deduced from the velocity measurements. Consider the case of hydrogen peroxide decomposing in the presence of a catalyst. We wish to find out whether $\frac{dx}{dt}$ is proportional to $[H_2O_2]$ or to $[H_2O_2]^2$. If the former is correct we know that $\frac{dx}{dt}=k(a-x)$, and this, on integration, gives $\frac{1}{t}\log_e\frac{a}{a-x}$=a constant. (This is often referred to as " the monomolecular law.") We can substitute our measured values of x and t in this expression and see if we get a constant. If not, we can try the next alternative, thus if $\frac{dx}{dt}\propto[H_2O_2]^2$, we have $\frac{dx}{dt}=k(a-x)^2$, which, on integration, gives $\frac{1}{t}\cdot\frac{x}{a(a-x)}$ =a constant. This can be tested in the same way.

(6) *Velocity Constants.*—We have written $\frac{dx}{dt}=k(a-x)$ as the expression of the proportionality between rate of reaction and active mass. The value of k determines the actual velocity and is called the " velocity constant." In an equilibrium system we must have two velocity constants since two velocities are involved. Thus, for the system

$$FeCl_3+3NH_4CNS\rightleftarrows Fe(CNS)_3+3NH_4Cl$$

the rate of the forward reaction is $k_1\times[FeCl_3]\times[NH_4CNS]^3$ and that of the back reaction is $k_2\times[Fe(CNS)_3]\times[NH_4Cl]^3$. When the system is in equilibrium these two rates must be equal, but k_1 and k_2 (the two velocity constants) are not equal.

NOTE.—Although these are called " constants," they vary with the temperature, for we have already noted that increased temperature means increased reaction velocity.

(7) *Equilibrium Constants.*—When a system is in equilibrium the opposing reactions must be occurring with equal velocities so that we can equate the two velocities and arrive at the composition of the mixture in terms of a new constant called the " equilibrium constant."

Thus in the system alcohol+acid$\rightleftarrows$ester+water we shall

have $k_1 \times [\text{alcohol}] \times [\text{acid}] = k_2 \times [\text{ester}] \times [\text{water}]$ when equilibrium is attained. But k_1 and k_2 are both constant, so that $\frac{k_1}{k_2}$ will be constant. Calling this K we shall have

$$K = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]}$$

where K is the equilibrium constant for this system.

5. Experimental Verification of the Law of Mass Action.—There are two different methods: (*a*) The **dynamic method,** in which the velocity of a practically irreversible change is measured, and the result compared with that deduced from the active masses of the reagents ; (*b*) The **static method,** in which a system is allowed to come to a state of equilibrium. The composition of the mixture is then determined experimentally and compared with deductions from the law of mass action.

(*a*) The former is clearly the more direct method and it was carried out as long ago as 1850 by *Wilhelmy,* who proved experimentally that the rate of inversion of cane sugar * was proportional to its active mass. The decomposition of hydrogen peroxide is another monomolecular reaction which can be used for this purpose. The concentration of hydrogen peroxide remaining at the end of various time intervals is determined (by permanganate titration, with due precautions to prevent interference with the main reaction), and the values of x and t substituted in the equation $\frac{1}{t} \log_e \frac{a}{a-x} = k$. A constant value for k would verify that reaction velocity $\propto [H_2O_2]$.

Constant temperature is essential during experiments on

* Cane sugar when dissolved in water decomposes slowly into glucose and fructose. The rate is easily measured if a dilute acid is added to act as a catalyst. The water is present in such large relative quantity that its active mass may be considered as constant and so the reaction $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ may be treated as monomolecular. The change is called the " inversion " of cane sugar owing to the optical properties of the solution becoming altered or " inverted " during the reaction. It was by measuring this optical property with an instrument called a polarimeter that Wilhelmy determined the amount of cane sugar inverted in a definite time interval.

reaction velocity, and a thermostat must be employed in all cases.

NOTE.—If the values of x be plotted graphically against the values of t, a smooth curve results. The slope of this curve at any point gives the value of $\frac{dx}{dt}$ for any value of x (see Fig. 41). If these values of $\frac{dx}{dt}$ plotted against $a-x$ give a straight line, then $\frac{dx}{dt} \propto a-x$. The law of mass action states that this should be the case for a monomolecular reaction.

(*b*) The static method involves analysing a system in equilibrium, and this must be done without displacing the equilibrium. It was noted on p. 152, that this can often be done by ordinary chemical analysis *at low temperatures*, since the displacement of equilibrium will then take place too slowly to cause serious error. The results obtained by *Berthelot* and *Péan de St. Gilles*, in 1862, will illustrate the method. They started in the first place with ethyl alcohol and acetic acid, and secondly with ethyl acetate and water, but found that the same equilibrium mixture of these four substances resulted in each case. Equilibrium was arrived at by keeping the mixture for a long period at a comparatively high temperature, for even at 200° C. it requires about 24 hours. The mixture was then cooled to room temperature and the acetic acid estimated by titration with standard baryta water.

Now we have seen that $\frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]}$ must be constant if the law of mass action is correct, and it was this constancy which they verified experimentally. Let us substitute some values for the active masses of these substances and try to follow their argument.

Suppose they started with 1 gm. mol. of alcohol and 1 gm. mol. of acid, and found in the equilibrium mixture $1-x$ gm. mol. of acid remaining. It follows that x gm. mol. of acid and alcohol have reacted and that x gm. mol. of water and ester must have been formed, so that if v is the volume of the whole mixture, the above fraction should be constant.

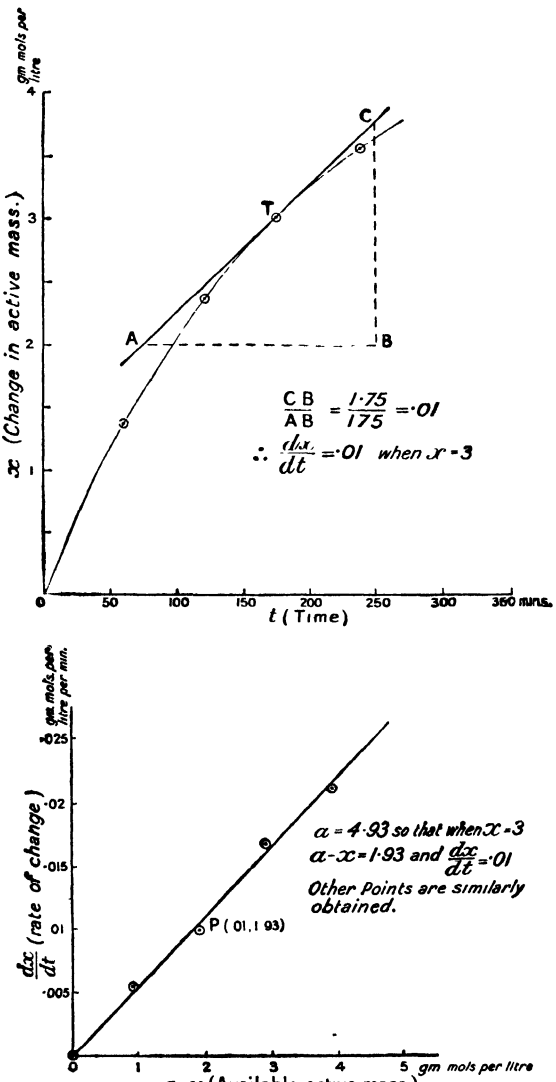


FIG. 41.—Experimental verification of the law of mass action.

$$\therefore \frac{\frac{1-x}{v}\times\frac{1-x}{v}}{\frac{x}{v}\times\frac{x}{v}} \text{ should be constant.*} \quad \text{Or } \frac{(1-x)^2}{x^2}=K.$$

They actually found in this case $x=\frac{2}{3}$, so that $\frac{(1-x)^2}{x^2}=\frac{1}{4}$.

They could now deduce the composition of the mixture which should result from mixing any proportions of alcohol and acid (or ester and water), on the assumption that

$$\frac{[\text{alcohol}]\times[\text{acid}]}{[\text{ester}]\times[\text{water}]}=\frac{1}{4},$$

and verify these conclusions experimentally. Thus, suppose they mixed 1 gm. mol. of acid and 8 gm. mols. of alcohol in v litres. When equilibrium was reached the concentrations of alcohol and acid would be $\frac{8-x}{v}$ and $\frac{1-x}{v}$ respectively, and of both ester and water $\frac{x}{v}$, so that

$$\frac{(1-x)\times(8-x)}{x\times x}=\frac{1}{4} \text{ or } x=\cdot 97.$$

Table IX. shows how completely the law is verified by their results.

TABLE IX.†

Original mixture		Equilibrium mixture	
		Observed.	Calculated from K=¼.
Gm. mols. acetic acid.	Gm. mols. ethyl alcohol.	Gm. mols. ethyl acetate.	Gm. mols. ethyl acetate.
1·0	0·05	0·05	0·049
1·0	0·50	0·414	0·423
1·0	2·00	0·858	0·850
1·0	8·00	0·966	0·970

6. Chemical Equilibrium.—Some important notes may be made on the results given above.

* The inversion of this fraction is to bring K=¼ (instead of 4), as in the historical data quoted in Table IX.

† Taylor, *ibid.* I. 334.

(*a*) Inspection of a chemical equation will show qualitatively the effect of altering the concentrations of reagents. Thus, in the case of alcohol+acid$\rightleftarrows$ester+water, an increase in [alcohol] will shift the equilibrium to the right (*cf.* p. 199). We may utilise this fact, if we wish to convert an acid into an ester, by using a large excess of alcohol.

(*b*) K is independent of the volume in this particular system, so that the dilution cannot affect the final equilibrium. It may, however, alter the rate at which the system reaches a state of equilibrium.

(*c*) Removal of any of the constituents of an equilibrium mixture will shift the equilibrium, and a reaction may be made to proceed to completion by this means. Thus, by sparking a mixture of nitrogen and hydrogen *in the presence of sulphuric acid,* the ammonia formed will be continually absorbed, $N_2+3H_2\rightarrow 2NH_3$, and an equilibrium system will not result. In a closed system all the substances represented in the equation must be present, and we can never get 100% conversion of reagents into products, though we may get very near to this.

" Removal from the sphere of action " is a phrase which needs understanding. At present we are only considering homogeneous systems; *i.e.* reactions in the gaseous or liquid phases (including solutions). Thus, the formation of a solid precipitate or the evolution of a gas would remove these substances from a reaction which was occurring in a liquid phase. The " closed space " to which we are constantly referring is therefore the space within the boundaries of the homogeneous system under consideration.

EXAMPLE.—Barium sulphate is nearly insoluble in water, and hence the reaction $K_2SO_4+Ba(OH)_2\rightarrow BaSO_4+2KOH$ proceeds nearly to completion. That it is reversible, however, was noted as long ago as 1801 by *Berthollet,* who, by digesting barium sulphate with large quantities of fresh caustic potash, converted it into baryta. Strictly speaking we ought to write $K_2SO_4+Ba(OH)_2\rightleftarrows BaSO_4+2KOH$, because there is always some barium sulphate in the solution.

7. Historical Note.—Long before there was any idea

that a state of equilibrium existed, *Mayow*, in 1674, was able to expel nitric acid from nitre by means of vitriol. He got the impression from this that the vitriol must be the stronger acid, an idea which is now known to be incorrect, for it was really the removal of the more volatile nitric acid vapour which caused the reaction to proceed. Also, *Baumé*, in 1760, succeeded in converting vitriolated tartar (K_2SO_4) into nitre (KNO_3) by acting on it with cold concentrated nitric acid, so that these two results form what is probably the first recorded example of a chemical change being reversible:

$$2KNO_3+H_2SO_4 \rightleftarrows K_2SO_4+2HNO_3.$$

It was evidently the alteration of the state of equilibrium of a system which first drew attention to the influence of reacting masses on chemical changes. *Berthollet* was so struck by the influence of reacting quantities on the products of a reaction, that he went so far as to doubt the law of constant composition. Apart from this incorrect appreciation of the facts, *Berthollet* showed a wonderful insight into the mechanism of chemical changes, and his *Researches into the Laws of Chemical Affinity*, written in 1799,* and his *Essay on Chemical Statics* (1803), are really astonishing, considering the time at which they were written. Thus, he writes: "The greater the relative quantity of the decomposing substance, the greater will be the effect produced"; and he also had a clear idea that precipitation from a solution would cause a reaction to proceed owing to removal of material from the solution.

8. The Influence of Pressure on Equilibrium Systems.—This was discussed briefly in para. 3, but we can now apply the law of mass action and so determine the magnitude of the change in the equilibrium system (if any), instead of merely the direction in which it occurs.

CASE I.—A reaction involving a change in volume; *e.g.* $PCl_5 \rightleftarrows PCl_3+Cl_2$. We have

$$K=\frac{[PCl_3]\times[Cl_2]}{[PCl_5]}$$

* It was read as a paper in Cairo in 1799, but not published until 1801. See Lowry, *Historical Introduction to Chemistry*.

or, substituting values for the active masses, as in the last paragraph,

$$K=\frac{\frac{x}{v}\times\frac{x}{v}}{\frac{1-x}{v}}=\frac{x^2}{(1-x)v}$$

Since K is constant, the value of x is seen to depend on v, and the composition of the equilibrium mixture can be calculated for any value of v when once K is determined.

NOTE.—It is clear that x decreases as pressure increases, since this tends to diminish v. This agrees with the observation of Wurtz (p. 151) that dissociation of phosphorus pentachloride was decreased by adding phosphorus trichloride at constant volume. Had this been added at the same partial pressure as it exerted in the original mixture (so that the volume increased) the dissociation of the pentachloride would have remained unchanged.

CASE II.—A reaction involving no change in volume; *e.g.* $N_2+O_2\rightleftarrows 2NO$. We have

$$K=\frac{[NO]\times[NO]}{[N_2]\times[O_2]} \text{ or } \frac{\frac{x}{v}\times\frac{x}{v}}{\frac{1-x}{v}\times\frac{1-x}{v}}=\frac{x^2}{(1-x)^2}$$

so that x is independent of the volume and therefore of the pressure.

9. Heterogeneous Systems.—In the foregoing paragraphs, the law of mass action has been applied to reactions occurring in one phase only; *e.g.* reactions between gases, or in solutions. It is only to such homogeneous systems that the law is strictly applicable, but by means of an assumption (which is justified by experimental facts) we can make use of it when investigating heterogeneous systems.

The assumption is that if a solid is reacting with a gas, it is really molecules of the substance in the vapour phase which are reacting. Now, as long as there is some solid present, the active mass of the molecules in the vapour phase may be

considered as constant, since the vapour pressure of a substance* is constant at a given temperature.

Thus, if calcium carbonate is heated in a closed space, a state of equilibrium is reached, represented by $CaCO_3 \rightleftarrows CaO + CO_2$, but it is the mixture of calcium carbonate and lime *vapours* which is in equilibrium with the gaseous carbon dioxide. Therefore as long as there is solid lime present, if molecules of lime vapour are removed they will be at once replaced by vaporisation; and if more lime molecules appear in the vapour, through dissociation of the calcium carbonate, they will at once condense to solid lime. Hence, the active mass of lime in the vapour phase remains constant. Similarly, $[CaCO_3]$ in the vapour phase is constant. We may therefore apply the law of mass action to the equilibrium in the vapour phase $CaCO_3 \rightleftarrows CaO + CO_2$. We find $K = \frac{[CaO] \times [CO_2]}{[CaCO_3]}$, which must accordingly lead to $[CO_2] = a$ constant. In other words, the active mass of carbon dioxide should be constant, at a given temperature, and independent of the quantities of solid lime or calcium carbonate present.

This is borne out by experiment, as long as there is some solid calcium carbonate and solid lime present. Of course if all the solid disappears (*e.g.* through continuous removal of carbon dioxide as it is formed), our assumption that $[CaCO_3]$ is constant cannot be valid.

The active mass of carbon dioxide can be measured by the pressure it exerts (this being the only gas present in measurable quantities), so that the experimental observation is that the carbon dioxide pressure is a constant depending only on the temperature. Thus:

Temperature in ° C. . .	547	625	745	812	865
Pressure in mms . . .	27	56	289	753	1333

This example and many similar are included in a general law

* All solids have a definite vapour pressure, or sublimation pressure, though this may be excessively small (see p. 55).

known as **Deville's law of dissociation pressure**: When any products of the dissociation of a solid are gaseous, the dissociation pressure is a function of the temperature only and is independent of the mass of solid present.

The use of a manometer (or pressure gauge) in the study of equilibrium systems is of great importance. The diagram (Fig. 42) indicates how it might be employed in this instance. The vessel A must be surrounded by a jacket which can be maintained at any desired temperature, and, with the stop-cock D closed, the pressure recorded by the manometer gives us the active mass of carbon dioxide at that temperature. If a pump be attached, we can prove that, although the carbon dioxide is continually removed, its active mass remains constant (through further dissociation of calcium carbonate) until all solid calcium carbonate has disappeared. Again, we can pump in carbon dioxide and observe that the carbon dioxide pressure does not rise until all solid lime has been converted into calcium carbonate.

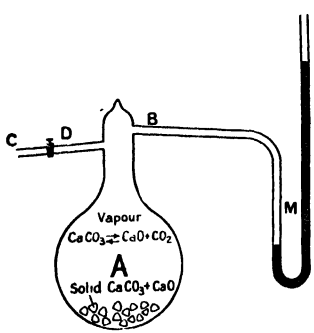


FIG 42.

We can now see why in "lime burning" on an industrial scale, a high temperature is used, together with a current of air to remove carbon dioxide as fast as it is formed.

By assuming that when a solution is in contact with a solid precipitate the active mass of the molecules of this substance **in the solution** is constant, we can apply the law of mass action in a similar manner to a system containing solid and liquid phases. Thus, in the system $BaCl_2 + K_2SO_4 \rightleftarrows 2KCl + BaSO_4$ we can assume $[BaSO_4]$ in solution is constant and deduce results which are in agreement with the facts (*cf.* p. 240).

10. The Phase Rule, derived in 1877 by *Willard Gibbs* from the laws of thermodynamics, is of particular value when investigating the equilibria in complex systems of many phases which cannot possibly be dealt with by the law of mass

action or by the rule of le Chatelier alone. It tells us how many different phases can possibly coexist under given conditions, and whether one or more of these will have to disappear if the conditions are altered. *E.g.* if the pressure is constant we can deduce from the phase rule that water and steam, water and ice, ice and water vapour (*i.e.* two phases) can coexist over a range of different temperatures; but that in order to get the three phases, water, ice, and water vapour, to coexist, the temperature and pressure would have to be fixed. The water (the only chemically distinct substance in this system—which is therefore termed a "one component system") is in this case said to have no "degrees of freedom," since neither temperature nor pressure can be varied without one phase disappearing. To make an intelligent study of the phase rule, we must be able to apply it to systems of two or more components and thus realise its value. This requires much more time than is available at this stage, and it is probably wiser to leave it altogether until it can be dealt with at some length.*

11. Catalysis.†—The name "catalyst" ‡ was given by *Berzelius* in 1835 to any substance which by its presence assisted a chemical change without being itself chemically altered at the end of the reaction. There were many examples known even at that early date (*e.g.* the action of platinum in accelerating combination between oxygen and hydrogen (*Davy*, 1817); and the decomposition of hydrogen peroxide in the presence of traces of solids such as manganese dioxide (*Thénard*, 1818)); but even now, after ninety years of research, we are still very doubtful "how they work." Various suggestions have been made to account for the action of catalysts, such as *Ostwald's* famous lubrication analogy §; the assumption of

* The student who has the time should read Findlay, *The Phase Rule*

† The student is strongly recommended to read *Catalysis* by Jobling, or *Catalysis in Theory and Practice* by Rideal and Taylor.

‡ From κατά and λύειν, "to loosen down."

§ If chemical affinity is the driving force of a reaction, then rate of reaction $= \frac{\text{driving force}}{\text{chemical resistance}}$, and a catalyst is supposed to act as a lubricant does to a piece of machinery; *i.e.* to lessen chemical resistance

unstable intermediate compounds; and the condensation of reacting gases on the surface of the catalyst. Modern chemists bring to their aid the terms "activation of molecules" and "adsorption on the catalytic surface," but we are still far from a satisfactory conclusion. We shall probably find that no single explanation will cover all cases. Let us turn to the facts.

(*a*) Catalysts alter the speed of reactions. They are termed **positive** or **negative** catalysts according to their effect on the reaction velocity. Thus, platinum **accelerates** the combination of oxygen and sulphur dioxide; sulphuric acid **retards** the decomposition of hydrogen peroxide.

(*b*) A catalyst is chemically unaltered at the end of the change. It may, however, be physically changed. Thus, crystalline manganese dioxide when accelerating the evolution of oxygen from potassium chlorate ends up as an amorphous powder, and the platinum grids used in ammonia oxidation become pitted on the surface after a time. It is, therefore, not claimed that the catalyst takes no part in the action, and there is good evidence in some cases that intermediate complexes are formed between the catalyst and one or other of the reagents. This may or may not be a chemical compound, but at any rate it is unstable and the catalyst is completely reformed.

(*c*) A catalyst can only alter the **rate** of a reaction, and cannot alter the composition of the resulting mixture. Hence, when two opposing reactions are concerned, both rates must be equally affected; equilibrium will be attained more quickly, but the same system will result as in the absence of the catalyst.

The unsolved question whether a catalyst can start a reaction or only alter the rate has already been mentioned.

(*d*) A catalyst need only be present in very small quantities. 1 gm. mol. of molybdic acid in 32 million litres definitely accelerates the reaction $H_2O_2+2HI \rightarrow 2H_2O+I_2$.* Note, however, that the magnitude of the effect produced depends very considerably on the amount of catalyst present. In most cases the **area of surface** exposed by the catalyst is the determining factor, and hence we find spongy platinum, platinised asbestos, or

* Findlay, *Physical Chemistry for Students of Medicine*, p. 153.

colloidal platinum used as catalysts in place of a sheet or lump of platinum.

The organic catalysts found in living organisms and termed **enzymes** are invariably colloidal in nature. They play a most important part in all life processes, but it is believed that they are merely complex carbon compounds which could be artificially synthesised if we knew their compositions. It is considered that such synthetic enzymes would behave just the same in test tubes as they do in living tissues.

(*e*) Catalysts are selective in action. A key will not fit every lock, and a catalyst will not affect every reaction. Platinum catalyses many reactions, and one or two other substances (such as nickel) have this power to a smaller extent; but some catalysts are limited to one specific reaction.* This is a well-marked characteristic of the enzymes.

(*f*) Catalysts are sensitive to " poisons," *i.e.* their efficiency is reduced by the presence of traces of certain substances. It is interesting to note that substances like arsenic, carbon monoxide, cyanides and mercury salts, which are poisonous to human beings, are often those which " poison " catalysts.

Substances which poison catalysts are termed **inhibitors,** inasmuch as they retard the action of the catalysts. On the other hand, the efficiency of a catalyst is often much increased by traces of other substances, termed **promoters.** A little molybdenum added to the iron used in the Haber process for accelerating $N_2+3H_2 \rightleftarrows 2NH_3$, increases the effect which the iron alone would have, to an extent out of all proportion to the amount added.

(*g*) The efficiency of a catalyst depends very much on its mode of preparation. In addition to the area of surface exposed, the actual nature of the surface is of importance. Thus, the efficiency of a nickel catalyst depends on the temperature at which the oxide is reduced when preparing the nickel.

(*h*) If a catalyst for a particular reaction is actually produced

* Sometimes the catalyst's function seems to be the opening up of one out of two or more possible reaction paths. Thus from carbon monoxide and hydrogen (water-gas) it is possible to obtain methane, methanol (CH_3OH), or higher alcohols, by using different catalysts and suitable temperatures and pressures.

as this reaction proceeds (so that the reaction velocity is continually increasing), the effect is termed autocatalytic. Thus, during the hydrolysis of an ester by water, an acid is formed which catalyses the hydrolysis.

12. Technical Importance of Catalysts.—How valuable would be an article which merely by its presence would increase our rate of working! Especially, if it never wore out! (Unfortunately many "negative catalysts" of this type exist; such as easy-chairs, wireless sets, and talkative people!) The chemical manufacturer, however, is in a happy position, for he can sometimes make use of a catalyst and speed up his output without extra cost.* But the full value of the catalyst is not this alone, for in many cases, a reaction would be practically impossible to carry out in its absence. This is because the only other way of accelerating a reaction to an extent which would make it commercially useful, would be by raising the temperature, and this in some cases tends to destroy the very products which are required. Thus, $2SO_2+O_2 \rightleftarrows 2SO_3+Q$ calories, so that a rise of temperature causes the equilibrium to shift to the left, decomposing the sulphur trioxide. Hence, heat must not be supplied if we wish to obtain the maximum yield of this substance. But at low temperatures, reaction velocity is so slow that the equilibrium state would never be reached and the manufacturer would have nothing to sell! This is where the catalyst comes in. *It enables a reaction to proceed, at comparatively low temperatures, at a speed which will give economically useful results, in cases where a rise of temperature would reduce the yield of the products of the reaction.*

Note that this will always be so with exothermic reactions, such as the contact process for sulphur trioxide; the Haber process for ammonia; Deacon's process for chlorine manufacture: $4HCl+O_2 \rightleftarrows 2Cl_2+2H_2O+Q$ cals.

When a reaction is endothermic (*e.g.* $N_2+O_2 \rightleftarrows 2NO-Q$) there is no need for a catalyst. In this case, the higher the

* In practice, catalysts have to be replaced from time to time, as their efficiency decreases after prolonged use, mainly through poisoning. Hence, the initial cost of a catalyst such as platinum has to be seriously considered, and cheaper ones are used if possible.

temperature the larger the yield of nitric oxide; hence the use of the electric arc in this method of fixing atmospheric nitrogen. In the Birkeland-Eyde furnace a temperature of about 3200° C. is said to be reached.

Even with a catalyst, the manufacturer is between the devil and the deep sea. Low temperature—slow yield; high temperature—poor yield. The only solution is a compromise. That temperature is found which with the catalyst gives the best yield in a given time; *i.e.* the "**optimum**" working temperature. Thus, with $2SO_2+O_2 \rightleftarrows 2SO_3$ the optimum temperature is about 400° C. when platinised asbestos is the catalyst. The reaction chamber has actually to be cooled to prevent the heat produced during the reaction raising the temperature above this optimum value!

Imagine the views of a manufacturer who has spent large sums on fuel and then finds that low temperatures would have increased his profits! He might be inclined to regard "theoretical chemistry" more favourably in the future!

Another point arises in connection with the use of catalysts. If a stream of gases is being passed rapidly over a catalyst with a view to removal of the products from the sphere of action (*vide* notes on the law of mass action), the rate of flow must be carefully regulated. There will obviously be an optimum rate of flow, at which the maximum value of the catalyst is obtained.

Empirical methods (trial and error) are largely employed in discovering the optimum conditions just mentioned, and the same is usually true of the mode of selecting the most suitable catalyst (see Fig. 43). There are in the latter case a few guiding rules, such as the probability of forming unstable intermediate compounds, but in the main the choice is the result of much patient research.* Very seldom does a lucky accident occur, such as the breaking of a mercury thermometer which disclosed the suitability of mercury (in sulphuric acid) as a catalyst for

* There are at least fifteen different substances which will catalyse the reaction $2SO_2+O_2 \rightleftarrows 2SO_3$, though platinum is easily the most efficient. In searching for a less expensive catalyst of suitable efficiency, ferric oxide in the form of burnt pyrites has been used, and certain complex vanadium silicates are now coming into favour.

the oxidation of naphthalene—a step in the synthesis of indigo. Even this might have passed unnoticed if trained observers had not been present to take advantage of Dame Fortune's intervention.

13. Further Notes on Industrial Processes.—The manufacturer cannot afford to neglect the principles discussed in this chapter, as he has so often done in the past. To obtain maximum yields of his products he must allow the research chemist to discover the optimum working con-

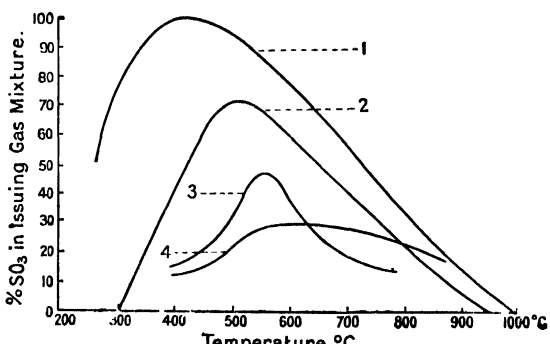


FIG. 43.—The efficiency of catalysts.

The curves refer to the contact process for the manufacture of sulphuric acid:

Curve 1. Platinised asbestos catalyst.
Curve 2. Same catalyst but with high-speed flow of gases.
Curve 3. Ferric oxide catalyst (pyrites cinders).
Curve 4. Broken porcelain catalyst.

ditions. The effect of temperature and catalysts has been referred to, but pressure and other factors must be considered as well.

(*a*) *Use of High Pressures.*—This is clearly unnecessary for an equilibrium like $N_2+O_2 \rightleftarrows 2NO$ which is unaffected by pressure, but in some cases increase of pressure will increase the proportion of the product required in the final mixture. Thus, ammonia synthesis, $N_2+3H_2 \rightleftarrows 2NH_3$, was originally carried out by *Haber* at low pressures, but a French chemist named

Claude has considerably improved upon this by working at a pressure of 1,000 atmospheres.*

The following data show the effect of pressure on the yield of ammonia.

Pressure in atmospheres (temperature 450° C.)	10	100	300	600	1000
% NH_3 in equilibrium mixture	2	17	36	54	69

(*b*) *Application of the Law of Mass Action.*—A good example is seen in the contact process for sulphuric acid. The proportion of sulphur dioxide converted into sulphur trioxide is clearly increased by making the oxygen concentration larger, for $2SO_2+O_2 \rightleftarrows 2SO_3$. This is made use of in practice, but since air is used instead of pure oxygen the best results are found when $\frac{[SO_2]}{[O_2]}=\frac{2}{3}$; with a larger proportion of air, the diluent effect of the nitrogen affects matters.

(*c*) *Other Factors.*—Removal of products from the sphere of action is often important (*vide* remarks on lime burning, p. 204). Sudden cooling is sometimes made use of to slow down undesirable reactions: *e.g.* in the arc process for fixing nitrogen, $N_2+O_2 \rightleftarrows 2NO$, the nitric oxide would dissociate on leaving the arc if it were not rapidly chilled.

APPENDIX

1. The Influence of Moisture on Chemical Changes

Traces of moisture have a marked catalytic effect on many reactions; *e.g.* on the combination of hydrogen and oxygen or of carbon monoxide and oxygen when sparked; or of hydrogen and chlorine in sunlight. In these cases exceptional methods of "activation" are needed to bring about reaction when the

* It is not always economical to work at high pressures even though the yield may be increased thereby. The contact process, for example, $2SO_2+O_2 \rightleftarrows 2SO_3$, is carried out at atmospheric pressure.

gases are perfectly dry; and the thermal dissociation of ammonium chloride and the combination of hydrogen chloride and ammonia seem to be completely prevented under these circumstances. See Smith, *The Effect of Moisture on Chemical and Physical Changes*, for further details.

Since ionic reactions are practically instantaneous (the ions being free to move in the solvent and meet oppositely charged ions) the effect of an ionising solvent like water can be readily understood, but it is no longer believed that all reactions are between ions, or that an ionising solvent is an essential part of a chemical change.

2. Some Important Reversible Reactions

(*a*) *Thermal Dissociations* of NH_4Cl; PCl_5; N_2O_4; HI; $CaCO_3$; NO; NH_3. (The last three are of technical importance.)

(*b*) *Reactions met with in Qualitative Analysis.*

$BiCl_3+H_2O \rightleftarrows BiOCl+2HCl$; $CdCl_2+H_2S \rightleftarrows 2HCl+CdS$;
$SnCl_2+H_2O \rightleftarrows Sn(OH)Cl+HCl$; $2SbCl_3+3H_2S \rightleftarrows 6HCl+Sb_2S_3$;
$CaCl_2+H_2C_2O_4 \rightleftarrows 2HCl+CaC_2O_4$.

(*c*) *Miscellaneous.*

$C_2H_5OH+CH_3COOH \rightleftarrows C_2H_5COOCH_3+H.OH$;
$FeCl_3+3NH_4CNS \rightleftarrows Fe(CNS)_3+3NH_4Cl$;
$SO_2+I_2+H_2O \rightleftarrows H_2SO_4+2HI$;
$NaCl+NH_4HCO_3 \rightleftarrows NaHCO_3+NH_4Cl$ (Solvay process);
$3Fe+4H_2O \rightleftarrows Fe_3O_4+4H_2$.

3. Some Examples of Catalytic Action (Positive Catalysts)

1.	Decomposition of potassium chlorate	Manganese dioxide.
2.	Decomposition of hydrogen peroxide	Colloidal metals or manganese dioxide.
3.	Combination of dry gases (*e.g.* hydrogen and chlorine)	Traces of moisture.
4.	Oxidation of hydrogen or of alcohol	Spongy platinum.
5.	Hydrolysis of esters	Dilute acids.
6.	Inversion of cane sugar	Dilute acids, or the enzyme invertase.

7. Conversion of starch to sugar (hydrolysis)	The enzymes diastase and ptyalin.
8 Fermentation of sugar (glucose) . .	The enzyme zymase.

Technical Uses.

9. Haber's synthesis of ammonia . .	Iron (with a promoter such as molybdenum)
10. Contact process for sulphur trioxide	Platinised asbestos.
11. Chamber process for sulphuric acid	Oxides of nitrogen.
12. Deacon's process for chlorine . .	Cupric salts.
13. Hydrogenation of oils (*e.g.* in margarine synthesis)	Finely divided nickel.
14. Hydrogenation of aldehyde (synthetic alcohol)	Finely divided nickel.
15. Methyl alcohol from water-gas . .	Metallic oxides.

Catalysts are also employed in the synthesis of indigo and rubber; the removal of hydrogen sulphide from coal gas; the preparation of hydrogen from water gas; the preparation of formaldehyde for artificial resins; as accelerators in vulcanisation; and in the materials of incandescent gas mantles and gas fires to promote more rapid combustion of the gas.

DEMONSTRATIONS.—1. Reversible changes and the effect of conditions on equilibrium systems. It is suggested that some of the preliminary demonstrations mentioned on p. 162 be repeated at this stage. The action of heat on nitrogen peroxide or phosphorus pentachloride, the action of water on bismuth chloride solution, and of hydrogen sulphide on cadmium chloride in hydrochloric acid solution can now be rediscussed with advantage.

2. Gladstone's experiment, showing the effect of varying concentrations of reagents on the system

$$3NH_4CNS + FeCl_3 \rightleftarrows Fe(CNS)_3 + 3NH_4Cl$$

should be carried out.

3. A "time reaction," or some other experiment to bring home the idea of definite speed in chemical changes, is essential.

4. Demonstrate the action of light on silver salts; a mixture of hydrogen and chlorine; a green leaf (afterwards tested for starch, by removing the chlorophyll with alcohol and placing in iodine solution).

5. The polarimeter might be shown and its action described.

6. Catalysis :—Davy's Glow Lamp shows the action of a platinum catalyst in a striking manner (a warmed platinum wire held above an alcohol-ether mixture accelerates the oxidation of the alcohol to such an extent that the heat of reaction makes the platinum white hot). The effect of manganese dioxide on hydrogen peroxide is worth showing The small-scale reproductions of the contact process for sulphur trioxide

and of Deacon's process for chlorine can be demonstrated at this stage with advantage. Discussion of the industrial processes and their efficiency is thereby rendered easier.

PRACTICAL WORK.—1. Investigate the effect of temperature on the products of decomposition of potassium chlorate.

2. Verify the reversibility of $K_2SO_4 + Ba(OH)_2 \rightleftarrows BaSO_4 + 2KOH$

3. Show that $HCl + NaNO_3 \rightarrow NaCl + HNO_3$ quantitatively if concentrated hydrochloric acid is continually added to heated sodium nitrate in a crucible; and that the reverse reaction proceeds quantitatively if concentrated nitric acid is kept present in excess and the hydrochloric acid removed by heating.

4. If a thermostat is available, a reaction velocity should be determined: *e.g.* the rate of decomposition of hydrogen peroxide; the rate of hydrolysis of an ester; or the rate of reaction between sulphuric acid and oxalic acid (see *School Science Review*, I. 142).

5. If a polarimeter is available, verify the law of mass action by measurements of the rate of inversion of cane sugar.

QUESTIONS.—1. Give an account of the historical experiments which led to our present ideas on the influence of reacting masses on chemical changes.

2. How can we measure reaction velocities? What information can be obtained in this way with regard to the order of a reaction?

3. Discuss the factors which affect the efficiency of (*a*) the Haber process for ammonia, (*b*) the contact process for sulphur trioxide.

4. What are the conditions which determine the composition of an equilibrium mixture of steam, iron, oxide of iron, and hydrogen? Suggest how the composition could be determined without disturbing the equilibrium.

5. Write a short essay on (*a*) the use of catalysts, (*b*) the action of light on chemical changes.

6. State the law of mass action. How can it be verified experimentally?

7. The rate of decomposition of oxalic acid in the presence of sulphuric acid was studied by titrating with potassium permanganate samples of the solution of equal volume withdrawn at definite intervals. The following results were obtained: *

Time in hours . .	0	13·08	15·33	17·08	19·08	21·00	22·17
Vol. of permanganate required in c.cs	21·0	10·5	9·4	8·6	7·7	7·0	6·5

Show that the reaction is monomolecular.

8. A 3% solution of hydrogen peroxide is decomposing under the influence of a catalyst and 250 c.cs. of oxygen are evolved (measured at N.T.P.) from 50 c.cs. of the solution in 40 secs. What is the average rate at which this solution is decomposing?

* Hammick and Prichard, *S.S.R.* I 142.

9. At 357° C. the equilibrium mixture of hydrogen iodide and its dissociation products consists of 1·445 mols. of hydrogen, 0·935 mol. of iodine; and 9·550 mols. of hydrogen iodide per litre. Calculate the composition of the mixture which would be obtained if 5 mols of hydrogen and 3 mols. of iodine per litre were heated to this temperature.

CHAPTER XII

CHEMICAL ENERGY. THERMOCHEMISTRY

1. Conservation and Dissipation of Energy.—Energy is defined as "capability of doing work" and chemical energy is one of the many forms in which it exists. Thus, we have already noted (p. 11) that during chemical changes chemical energy is transformed into other forms of energy (such as heat energy, electrical energy), and vice versa. Also, we know that the total quantity of energy in the universe is constant (the law of conservation of energy), so that when one form disappears an equal amount of some other form is always produced.

For example, the energy absorbed from sunlight by a green leaf converts carbonic acid into starch, and so chemical energy is stored up in the tree. When we burn coal we are reconverting this into heat energy.

All changes met with in practice are opposed by something analogous to friction. This always acts in opposition to the change even when the direction of the latter alters. The work done against these frictional forces is invariably converted into heat, and thus energy is lost for practical purposes, the heat being dissipated into space. It follows that the quantity of heat energy in the universe is gradually increasing and the total quantity of useful energy must accordingly be decreasing. This remark is based on observed facts, and it is usually termed the "law of dissipation of energy," or "degradation of energy." It leads us to the conclusion that perpetual motion is impossible, since all the available energy must sooner or later be dissipated in the form of heat.

EXAMPLE.—In driving a dynamo, the heat produced by

the current in the coils represents so much wasted energy, for it is not converted into electrical energy. If we reverse the change and use electrical energy to drive a motor we again waste energy in heating the coils. In other words, no machine has an efficiency as great as 100%.

Even in chemical changes, some energy is wasted in this sense. The conversion of chemical energy into electrical energy in the Daniell cell is, however, nearly perfect, and nearly all the chemical energy can be reobtained by reversing the process.

2. The Value of Thermochemical Measurements.—We cannot measure the total energy in a system, but we are able to measure changes in energy. This can be done by carrying out the change in a calorimeter in such a way that all the energy changed is converted into heat. The heat produced is measured by its effect on the temperature of a given mass of water.

It would seem at first sight that if a chemical change took place in a calorimeter we could always measure the change in chemical energy by observing the heat evolution (the **thermal effect of the reaction**). This, however, would not be the case if any external work had been performed during the action, for energy would have been absorbed for this purpose. The quantity so absorbed would, of course, be lacking in the total energy output which we measure, in the form of heat.

EXAMPLES.—(1) When zinc dissolves in sulphuric acid, the hydrogen evolved *does work* against the pressure to which it is subjected. This needs a supply of energy, and this energy is not, therefore, converted into heat.

(2) If hydrogen and oxygen are exploded and the result is water in the liquid state, energy will have been evolved (as latent heat) during condensation of the steam. The measured heat evolution is therefore greater than the heat of reaction between these two gases.

Thus, we may write $U=Q+A$ where U is the total energy change, Q the measured heat evolution, and A the energy which has been used in performing external work but has not been converted into heat.

Now, the practical value of an energy supply is the quantity of work which can be got from it, and the " available " or " free energy " of a system is defined as the maximum quantity of

external work which can be obtained from it under ideal conditions. The total energy content of a system therefore consists of "free energy" and "bound energy," the latter being dissipated during changes in the form of heat. It is the free energy which supplies the driving force behind a chemical change and therefore measures the "chemical affinity" of the reaction. *Reactions only proceed spontaneously in such a direction that the free energy decreases;* just as a ball only rolls *downhill*, for in that way its potential energy decreases.*

It can be proved by applying the laws of thermodynamics, that at ordinary temperatures the bound energy must be comparatively small, and therefore U (the total energy) will be an approximate measure of A (the free energy). Hence, if we convert into heat all the energy which is changed during a reaction (working at constant volume to avoid external work being performed), the *thermal effect of the change will be an approximate measure of the free energy which the system has lost;* i.e. *the decrease in "chemical energy."*

NOTE.—The relation is only approximate. Changes do sometimes occur spontaneously in which although the free energy *decreases*, the total energy *increases: e.g.* when a solid dissolves in water with absorption of heat.

Hence, as a general rule:

(1) Exothermic reactions † indicate a decrease in chemical energy, or rather, free energy.
(2) Systems tend to change so that their potential energy or free energy becomes a minimum.
(3) A stable system has a small free energy content.
(4) Energy is absorbed when endothermic compounds are formed, so that these are usually unstable.
(5) Exothermic compounds are comparatively stable.

It is clear that the heats of formation of compounds, or the heats of reaction (*i.e.* thermochemical data), give us much

* If energy be supplied from external sources a reaction may proceed in the reverse direction (just as a ball can be carried uphill), but this will not occur "spontaneously"

† The terms "exothermic" and "endothermic" were explained on p. 190.

useful information with regard to the stability of compounds or systems.

3. Thermochemical Measurements.—If we wish to measure the heat given out by a hot solid in cooling, we drop it into a known mass of cold water in a calorimeter and take the final temperature of the mixture.* We use exactly the same method in measuring the heat evolved in a chemical action, for the heat is given to a known mass of water in a calorimeter, and the final temperature is noted.

Specially designed calorimeters are usually employed: *e.g.* gas calorimeters for use when gases are to react; bomb calorimeters intended to withstand high pressures; and calorimeters in which a substance can be burnt so as to determine its "heat of combustion," or its "calorific power." † The principle of the method is the same in every case. An ordinary copper calorimeter can be employed for reactions between solids or liquids if no gaseous products are formed; *e.g.* for determining the heats of neutralisation of acids and bases.

4. Terms employed in Thermochemistry.—It is customary to calculate the heat evolved by the changes in gm. mol. wts. of substances, denoting the results by $+Q$ if heat is evolved, and $-Q$ if heat is absorbed. Thus, we distinguish:

Heat of reaction, heat evolved when reaction occurs between the weights of substances represented by a chemical equation.

Heat of formation of a compound, heat evolved when 1 gm. mol. of a compound is formed from its elements.

Heat of combustion, heat evolved when 1 gm. mol. of a substance is burnt.

Heat of solution, heat evolved when 1 gm. mol. of a substance dissolves in a solution which is so dilute that further dilution produces no further heat change.

* Physics books must be consulted for the details of calorimetry experiments. The precautions necessary in order to obtain accurate results in a specific heat determination apply equally to all experiments based on mixing hot and cold substances in a calorimeter.

† The term "calorific power" is used for fuels, and is the heat evolved when unit mass of the fuel is burnt.

NOTE.—If the substance is dissolved in a nearly saturated solution, the heat evolved is the theoretically correct heat of solution (see p. 83). On dilution a further heat change occurs (heat of dilution), which will include heat of ionisation if the substance ionises. The sum total of these gives the practical definition of heat of solution given above.

Heat of neutralisation, heat evolved when 1 gm. molecule of a monobasic acid is neutralised; or, more generally, when 1 gm. equivalent of an acid or alkali is neutralised (*i.e.* weights corresponding to HCl, NaOH, $\frac{1}{2}H_2SO_4$, $\frac{1}{2}Ba(OH)_2$, etc.).

Results obtained for heats of neutralisation are of great importance. On the one hand they lead to a knowledge of the basicities of acids; of the relative strengths of acids, and of bases (see p. 245). On the other hand they give us convincing evidence in favour of the ionic hypothesis, owing to the nearly constant value obtained when any strong acid is neutralised by a strong base (see p. 180).

NOTES.—(1) Since change of state involves latent heat absorption or evolution, we must always state whether our substances are solid (s), liquid (l), or gas (g). Thus

$$H_2(g)+I_2(s)=2HI(g)-12{,}800 \text{ cals.}$$

(2) If elements are used which exist in different allotropic forms we must state which form we are using, for they have different free energy contents. Thus,

$$2C \text{ (graphite)}+2O_2(g)=2CO_2(g)+188{,}000 \text{ cals.}$$

(3) If much water is present (*i.e.* a dilute solution employed) this must be stated, since heat of solution is involved. Thus $NH_3(g)+HCl(g)=NH_4Cl(g)+42{,}100$ cals., but

$$NH_3aq+HClaq=NH_4Claq+12{,}500 \text{ cals.}$$

5. Hess' Law of Constant Heat Summation (1841).—This law, which could be deduced from the law of conservation of energy, states that:

The heat evolved in a reaction depends only on the initial and final stages and is independent of the intermediate steps.

EXAMPLE.—If we start with water, hydrochloric acid gas, and ammonia gas, we can obtain a solution of ammonium chloride in two distinct ways. Hess' law states that the total heat evolved will be the same whichever way is adopted.

Thus		Or	
(1) Mix the two gases	$Q=+42,100$	(1) Dissolve $NH_3(g)$ in water	$Q=+8,400$
(2) Dissolve the product in water	$Q=-3,900$	(2) Dissolve $HCl(g)$ in water	$Q=+17,300$
		(3) Mix the two solutions	$Q=+12,500$
Total heat change	$Q=+38,200$	Total heat change	$Q=+38,200$

6. Indirect Determinations of Heats of Formation or Heats of Reaction.—Hess' law may be used in order to calculate heats of formation from thermochemical data involving the compound and its elements. This is useful in cases where direct synthesis of the compound in a calorimeter is impossible or inconvenient.

EXAMPLE.—We wish to know the heat of formation of methane. Now

$$CH_4(g)+2O_2(g)=CO_2(g)+2H_2O(l)+211,930 \text{ cals.};$$
$$C(\text{graphite})+O_2(g)=CO_2(g)+94,800 \text{ cals.};$$
and
$$2H_2(g)+O_2(g)=2H_2O(l)+136,000 \text{ cals.}$$

Let Q be the heat of formation of methane. We can imagine that it is first made and then burnt, the total heat evolved being $Q+211,930$ cals. But if we started with the same ingredients (graphite, hydrogen, and oxygen) we could arrive at the same end products with a heat evolution of $94,800+136,000$ cals.

$$\therefore Q+211,930=94,800+136,000$$
or
$$Q=+18,870 \text{ cals.}$$

Therefore methane is exothermic, and 18,870 cals. are evolved in forming 1 gm. mol. of it from graphite and hydrogen.

However complicated the problem, the same principle can always be made use of: imagine two ways of proceeding from the initial to the final stages and equate the total heat

evolved in the two cases. One of these will of course contain the unknown heat of reaction required.

EXAMPLE.—To determine the heat of reaction

$$Zn + CuSO_4aq = ZnSO_4aq + Cu.$$

It is known that the heats of formation of dilute solutions of copper sulphate and zinc sulphate are +198,400 cals. and +248,500 cals. respectively.

We have for our two alternative paths:

(1) $Zn + (Cu + S + 2O_2 + Aq) = Zn + CuSO_4(aq) + 198{,}400$ cals.
and $Zn + CuSO_4aq = ZnSO_4aq + Cu + Q$ cals.

Total heat evolved $= Q + 198{,}400$ cals.

and (2) $Cu + (Zn + S + 2O_2 + Aq) = Cu + ZnSO_4aq + 248{,}500$ cals.
so that $Q + 198{,}400 = 248{,}500$, or $Q = + 50{,}100$ cals

DEMONSTRATIONS.—1. Show the production of heat, light, and electrical energy from chemical energy and vice versa.

2. The work done by an expanding gas might be demonstrated by its effect on the mercury column in a manometer.

3. Show any types of calorimeter which may be available and discuss the precautions necessary in using them.

PRACTICAL WORK.—1. A specific heat or latent heat determination should be carried out in order to point out the essential features of calorimetry.

2. Heats of solution, and heats of neutralisation should be determined. If different members of a class use different acids and bases the results may be compared and discussed.

3. Determine the relative strengths (avidities) of sulphuric and nitric acid.

4. Determine the basicity of sulphuric acid, given that the neutralisation of caustic soda evolves approximately 14,000 calories.

QUESTIONS.—1. Why is perpetual motion considered to be impossible? Distinguish between the conservation and the dissipation of energy.

2. Why are thermochemical measurements important? Explain the difference between the total energy change which occurs as the result of a chemical action, and the free energy change.

3 Describe in detail how you would determine the heat of neutralisation of *N* nitric acid by *N* caustic potash

4. Calculate the heat of formation of carbon monoxide from the following data. Heat of combustion of carbon (amorphous) = 97,300 cals ; heat of combustion of carbon monoxide = 68,300 cals

5. Calculate the heat of formation of formic acid if its heat of combustion is 69,400. The heats of combustion of hydrogen and carbon are 68,400 and 97,300 cals. respectively.

6. The heat of combustion of acetylene is 310,000 cals. If the heats of combustion of hydrogen and carbon are as in Question 5, show that this substance is probably unstable.

7. Calculate the heat of solution of anhydrous copper sulphate from the following data. Heat of formation of $CuSO_4$ = 183,000 cals. ; heat of formation of $CuSO_4aq$ = 198,000 cals.

CHAPTER XIII

ELECTROCHEMISTRY. APPLICATIONS OF THE IONIC THEORY

1. Ionic Migration. Transport Numbers.—In order to account for Faraday's second law, the ionic theory assumes that as each univalent anion is discharged at the anode a univalent cation is simultaneously discharged at the cathode.* It is not supposed, however, that the anion and cation move towards the electrodes with equal velocities under the influence of the applied E.M.F. In consequence, the concentration of the electrolyte near the electrodes alters as electrolysis proceeds, —a phenomenon which was investigated experimentally by *Hittorf* in 1855. From his measurements, as we shall see, Hittorf was able to obtain the relative speeds with which the two ions were migrating (or moving towards the electrodes). An analogy may be useful in order to see how the ions can move at different speeds and yet be discharged in equal numbers. A crowd is being "moved on" by a policeman, and people

* To simplify the discussion in this paragraph, only binary electrolytes are considered; *i.e.* those which yield two ions only; *e.g.* NaCl $\rightleftarrows Na^{\cdot} + Cl'$. Also the ions referred to are all univalent. The argument can, however, be extended to cover electrolytes which yield two or more ions of any valency.

crossing the road from left to right are moving more rapidly than those crossing from right to left. The left-hand pavement will in consequence become relatively less crowded than the right-hand one. This will still be the case if at intervals people are simultaneously removed from the two pavements, through shop doors.

To understand Hittorf's work we must first consider a

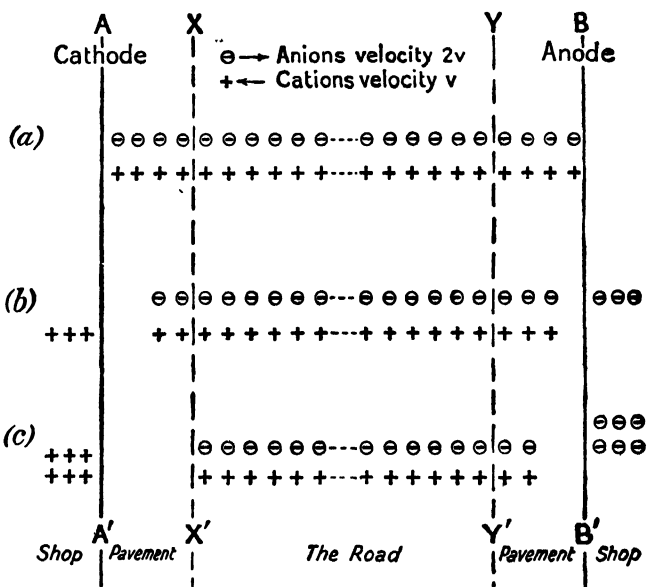


FIG. 44.—The movement of ions during electrolysis.

simple illustration; *e.g.* an electrolyte whose anion moves twice as fast as its cation. In Fig. 44 we see at (*a*) the state of affairs before the E.M.F. is applied. In order to consider changes in concentration **near the electrodes,** dotted lines XX′ and YY′ are drawn; between these the main body of the solution will not have altered in concentration by the time our imaginary measurements are completed. The E.M.F. is now applied and electrolysis commences. After a certain

interval the ions will have reached positions represented by (*b*), and a little later by (*c*).

It will be seen that as 2 anions leave AX (the cathode compartment) and enter BY (the anode compartment), 1 cation leaves the cathode compartment and enters the anode compartment. Any ion without a partner becomes discharged, and it will be seen that equal numbers of ions are simultaneously discharged at A and B. It can be seen that the concentration of the electrolyte in AX falls off twice as fast as it does in BY. In other words:

$$\frac{\text{fall in concentration round the cathode}}{\text{fall in concentration round the anode}} = \frac{2}{1} = \frac{\text{speed of anion}}{\text{speed of cation}}.$$

By means of moving strips of card on which equally spaced ions are painted, we can verify in a similar manner that $\frac{\text{fall in concentration round cathode}}{\text{fall in concentration round anode}}$ is always equal to $\frac{\text{speed of anion}}{\text{speed of cation}}$, as long as the concentration of the body of solution between X and Y remains unaltered.

EXAMPLE.—If $\frac{\text{fall of concentration round cathode}}{\text{fall of concentration round anode}} = \frac{5}{4}$, it follows that as 4 cations leave the anode compartment, 5 anions must have simultaneously left the cathode compartment, and 9 ions will be discharged at each electrode during this interval.

Hittorf measured the changes in concentration round the electrodes, taking care to leave the main body of the solution undisturbed, as far as possible, by stirring or diffusion. His measurements were made quickly, before electrolysis had caused concentrations to alter at any distance from the electrodes. He argued that the amount of electricity carried in unit time from one electrode to the other depended on the charge which each ion carried and on its velocity. That is to say, he imagined the anions transporting negative electricity to the anode and cations transporting positive electricity to the cathode, each ion transporting a fraction of the total. He assumed that during the passage of unit quantity of electricity the anion

would transport a fraction n of it, and the cation the remaining fraction $1-n$. These fractions he called **transport numbers** (also known as "migration ratios"), and since the ionic charge is a constant, they can clearly depend only on the ionic speeds.

Hence $$\frac{n}{1-n}=\frac{\text{speed of anion}}{\text{speed of cation}} \text{ or } \frac{U_a}{U_k}.$$

NOTES.—(1) $\frac{n}{1-n}+1=\frac{U_a}{U_k}+1$. Hence, $n=\frac{U_a}{U_a+U_k}$ and $1-n=\frac{U_k}{U_a+U_k}$. The total quantity of electricity transported is proportional to U_a+U_k, and the transport numbers show the fraction carried by anions and cations respectively.

(2) Only **relative ionic speeds** are obtained by these measurements.

(3) Transport numbers vary with the temperature. They tend to become equal as the temperature rises ($n=1-n=\frac{1}{2}$).

(4) Transport numbers vary slightly with the concentration of the solution when this is greater than ·2N, and so values given always refer to dilute solutions. Some values are given below:

TABLE X.—TRANSPORT NUMBERS FOR N/10 SOLUTIONS AT 18° C.*

	n (for anion).	$1-n$ (for cation).
HCl	·172	·828
KNO_3	·497	·503
KCl	·508	492
$AgNO_3$	528	·472
NaCl	617	383

Hittorf's work remained neglected for nearly thirty years, until *Arrhenius* became aware of its importance. The measurement of transport numbers gives us some idea of what is happening in a solution during electrolysis. Thus, the changes in concentrations round the two electrodes during the electrolysis of cadmium iodide prove to us that cadmium, as well as iodine, is moving to the anode. This supports the idea that the solution contains a complex anion (probably $CdI_4'' + Cd^{\bullet\bullet} \rightleftarrows 2CdI_2$). Similar evidence for the existence of complex ions in solutions of potassium silver cyanide, $KAg(CN)_2$,

* Taylor, *ibid.* I. 546.

potassium ferrocyanide, $K_4Fe(CN)_6$, sodium platinichloride, Na_2PtCl_6, and in Fehling's solution, is given by the fact that the second metal is in each case found to be moving towards the anode as well as the "acid radical." This assumption of **complex ions** is in agreement with the chemical behaviour of these solutions (see p. 233).

1a. True Transport Numbers. Solvation of Ions.—*Washburn* has modified Hittorf's method in order to correct for a bodily shift of the solvent towards one of the electrodes (see *J.A.C.S.* **33,** 322, 1909, and **37,** 698, 1915), due to one of the ions carrying with it more of the solvent than the other. His values, which may be regarded as "True Transport Numbers," do not differ much from Hittorf's numbers when solutions are very dilute, but the differences become appreciable when concentrations increase. These experiments prove beyond doubt that most ions are to some extent solvated. The importance of this lies in the fact that the attached solvent molecules increase the size of the ion (and thus its mobility), and also form a protective "atmosphere" round it which affects the electrical forces on it due to neighbouring ions. Thus the conductivity of the electrolyte is affected and also the tendency for the ions to cling together as "doublets" (see p. 230).

2. Ionic Conductivities. Kohlrausch's Law.—From his measurements of molecular conductivity in 1876, *Kohlrausch* was led to the important generalisation that the conductivity was the additive effect (or sum) of the "conductivities" of the ions. His method may be seen from the following figures: *

λ_∞ for	$NaNO_3$ = 106·45 ;	KNO_3 = 114·55 ;	$RbNO_3$ = 118·15.
λ_∞ for	NaCl = 96·95 ;	KCl = 105·05 ;	RbCl = 108·65.
Differences	9·50 ;	9·50 ;	9·50.

And λ_∞ for	KNO_3 = 114·55 ;	KCl = 105·05 ;
λ_∞ for	$NaNO_3$ = 106·45 ;	NaCl = 96·95 ;
Differences	8·10 ;	8·10.

It can be seen that replacing NO_3' by Cl' has the same effect

* These figures are actually taken from conductivity measurements in methyl alcohol as solvent (Frazer and Hartley, *Proc Roy Soc*, A. **109,** 351, 1925). They show more clearly than any others the constant differences due to the exchange of one ion for another.

on the equivalent conductivity whatever the cation used, and also replacing $K^{\bullet}$ by $Na^{\bullet}$ has the same effect whatever anion is present. From results similar to these it can be inferred that each ion is playing its part independently (Kohlrausch's law is usually referred to as the **law of independent ionic migration**).

Hence, if λ_k and λ_a are the **ionic conductivities** we may write

$$\lambda\infty = \lambda_k + \lambda_a.$$

We can determine the values of λ_k and λ_a by combining our knowledge of $\lambda\infty$ with the transport numbers for the two ions.

3. Ionic Conductivities or Mobilities.—The following examples will illustrate the method of determining λ_k and λ_a.

EXAMPLE I.—For a solution of potassium chloride we find that $\lambda\infty = 130{\cdot}11$, and Hittorf's transport numbers are ·497 for $K^{\bullet}$ and ·503 for Cl'. Hence, $·497 \times 130{\cdot}11$ of the conductivity must be due to $K^{\bullet}$ and the remainder to the Cl'. This gives 64·67 ($=\lambda_k$) and 65·44 ($=\lambda_a$) as the ionic conductivities of $K^{\bullet}$ and Cl' respectively.

EXAMPLE II.—By electrolysing a silver nitrate solution, Hittorf found

$$\frac{\text{fall in concentration round cathode}}{\text{fall in concentration round anode}} = \frac{·130}{·117}, \text{ and so}$$

$$\frac{\text{speed of } NO_3'}{\text{speed of } Ag^{\bullet}} = \frac{130}{117}.$$

Hence, $\frac{130}{117+130}$ or ·52 of the current is carried by the NO_3' and $\frac{117}{137+130}$ or ·48 by the $Ag^{\bullet}$. But $\lambda\infty$ for silver nitrate $=115$ at 18° C., and so, $\lambda_k = ·48 \times 115 = 55{\cdot}2$ and $\lambda_a = ·52 \times 115 = 59{\cdot}8$, which gives us the ionic conductivities of $Ag^{\bullet}$ and NO_3' respectively.

It is clear that the values of λ_k and λ_a are proportional to the velocities of the ions, and it is for many purposes convenient to consider these numbers (the ionic conductivities) as representing ionic velocities in some arbitrary units. They are,

therefore, usually found in books of reference under the heading of **mobilities** (see Table XI.).

The **absolute mobility of an ion** is its speed in cms. per sec. when the potential difference between electrodes 1 cm. apart is 1 volt. N.B.—If the potential difference between electrodes l cms. apart is E volts then $\frac{E}{l}$ is called the potential gradient, and the velocity of an ion will of course depend upon this.

The absolute mobility of an ion must be proportional to its mobility (or ionic conductivity), and it can be proved that mobility = F × absolute mobility, where F is a constant and is equal to 96,500 (the charge on 1 gm. equivalent of a univalent ion). Hence, we can calculate absolute mobilities, and the results are shown in the table.

TABLE XI.*—THE MOBILITIES OF SOME COMMON IONS AT 18° C.

Ion.	Mobility (or ionic conductivity).	Absolute mobility in cms. per sec. per unit potential gradient.
$H^{\cdot}$	314	·00325
OH'	174	·00178
$K^{\cdot}$	64·6	·00068
$Na^{\cdot}$	43·4	·00045
$Ag^{\cdot}$	54·0	·00057
Cl'	65 5	·00068
NO_3'	61 8	·00064

NOTES.—(*a*) The mobility of an ion varies with the temperature. *E.g.* for $H^{\cdot}$ the value is 314 at 18° C. and 350 at 20° C. It is also to be clearly understood that the mobilities are obtained from measurements with solutions so dilute that the conductivity is λ_∞. (*b*) The values for the absolute mobilities are in good agreement with those obtained by direct measurements of moving boundaries (p. 181). (*c*) The relatively large mobility of the hydrogen ion should be noted. (*d*) The slowness with which the ions move under the influence of an E.M.F. indicates that they meet with very great resistance to motion. It has been calculated that a force of 38,000,000

* These values are taken from a recent compilation (Taylor, *Treatise on Physical Chemistry*, I. 540) and may be found to differ from values obtained in the examples in para. 3, which were based on earlier and less accurate measurements.

kgms. wt. is required to move 1 gram of potassium ions with unit velocity.*

4. Indirect Determinations of λ_∞.—With weak electrolytes experimental difficulties make the direct measurement of λ_∞ impossible (*vide* curve for acetic acid on p. 174). But the value of λ_∞ must be known before we can calculate α (the degree of ionisation) from conductivity measurements. Hence, for weak electrolytes we calculate λ_∞ from the mobilities of the ions ($\lambda_\infty = \lambda_k + \lambda_a$); and so obtain its value in an indirect manner.

EXAMPLE.—To determine λ_∞ for acetic acid. We know that all sodium salts are strong electrolytes, and hence can determine experimentally λ_∞ for sodium acetate. Its value is 78·1. Now the mobility of $Na^\cdot$ is 43·4, so that $\lambda_a = 78{\cdot}1 - 43{\cdot}4 = 34{\cdot}7$ (the mobility of the acetate ion). Hence, λ_∞ for hydrogen acetate (acetic acid) $= 314 + 34{\cdot}7 = 348{\cdot}7$, since the mobility of $H^\cdot$ is 314.

5. Determinations of Solubilities of nearly Insoluble Substances.—A substance like silver chloride has a solubility too small to be measured by weighing or chemical analysis. The specific conductivity of a saturated solution of silver chloride can, however, be measured, and from this electrical conductivity measurement we are able to calculate the concentration of the solution; *i.e.* the solubility of the salt.

We may assume that the solute will be 100 % ionised (for the solution will be extremely dilute) and therefore $\lambda\infty$ can be calculated from the mobilities of the ions. Thus, $\lambda\infty$ for silver chloride $= 54{\cdot}0 + 65{\cdot}5 = 119{\cdot}5$. Now κ (the specific conductivity) is found to be $1{\cdot}33 \times 10^{-6}$ (when the conductivity due to the water itself has been deducted), so that if V is the dilution, or volume in c.cs. containing 1 gm. equivalent of silver chloride, we have $\lambda\infty = 1{\cdot}33 \times 10^{-6}$ V.

$\therefore$ $1{\cdot}33 \times 10^{-6}\ V = 119{\cdot}5$ or $V = 9 \times 10^7$ c.cs.

$\therefore$ 9×10^4 litres of solution contain 1 gm. equivalent of silver chloride, AgCl, $= 108 + 35{\cdot}5$ gms.,

$\therefore$ the solubility is ·0016 gm. per litre.

In this way the solubilities of many of the most "insoluble" substances have been determined: *e.g.* silver chloride (AgCl), $1{\cdot}1 \times 10^{-5}$ gm. mol. per litre; silver iodide (AgI), $1{\cdot}3 \times 10^{-8}$ gm

* Taylor, *ibid.* I. 542.

mol. per litre; cupric sulphide (CuS), $9{\cdot}2 \times 10^{-23}$ gm. mol. per litre; barium sulphate ($BaSO_4$), $1{\cdot}1 \times 10^{-5}$ gm. mol. per litre.

6. The Equilibrium between Ions and Unionised Molecules.—*Arrhenius* assumed that this could be treated as an exact parallel with an equilibrium between gaseous molecules and their dissociation products, the rule of le Chatelier and the law of mass action being thus applicable to such "systems." We must see to what extent this is justified.

(*a*) *Temperature and Ionisation.*—A rise in temperature decreases the viscosity of the solvent, and it is not surprising to find that the mobilities of the ions are increased under these circumstances. In most cases this results in increased conductivity. But, if the electrolyte is not completely ionised, the temperature change may alter the number of ions as well as their mobilities, and the conductivity is in fact found to be decreased in some cases and increased in others by a rise in temperature. Arrhenius, applying le Chatelier's Rule, related this to a positive or negative Heat of Ionisation.

(*b*) *Application of the Law of Mass Action.*—A solution of an electrolyte XY is supposed to contain the equilibrium mixture $XY \rightleftarrows X^{\cdot} + Y'$, from which we deduce that increase in $[X^{\cdot}]$ or $[Y']$ would cause the formation of more XY, and vice versa.* This principle, applied in a qualitative manner, will explain a great many of the reactions which take place in solutions, and its use in analytical chemistry is largely responsible for the popularity of the ionic hypothesis. The quantitative applications will be dealt with in later paragraphs.

7. Qualitative Applications of the Ionic Theory.—(a) *Precipitation by means of Reagents.*—At a given temperature

* In strong electrolytes XY molecules do not exist according to modern views, yet we continue to write equilibrium equations of this type while awaiting more definite knowledge. An alternative $X^{\cdot}Y' \rightleftarrows X^{\cdot} + Y'$ was suggested on p. 156 (footnote), the group $X^{\cdot}Y'$ representing a pair of ions (called an "electrically neutral doublet") in close contact, and held together by electrostatic attraction. This "doublet" only differs from a "molecule" because there has been no actual transfer of electrons from one ion to the other (see p. 270) to produce a "chemical bond" between uncharged atoms. In subsequent pages "molecules" occuring in ionic equilibria should be treated in this sense.

the concentration of unionised molecules in a solution cannot exceed a certain "solubility value" * without precipitation occurring (see pp. 72–3). If, therefore, we have in solution a system $X^{\bullet}+Y' \rightleftarrows X^{\bullet}Y'$, and can by any means (such as addition of $X^{\bullet}$ or Y') cause [XY] to exceed its "solubility value," precipitation is bound to occur.

EXAMPLE.—The maximum concentrations of unionised molecules in solutions of the chlorides of silver mercury(ous) and lead are very small, but the values for the chlorides of calcium, copper(ic) and other metals are very much greater. Hence, if we add Cl' (by the addition of hydrochloric acid or a solution of any chloride) to a solution containing $Ag^{\bullet}$, $Hg^{\bullet}$ or $Pb^{\bullet\bullet}$ the solubility values for silver chloride, mercurous chloride and lead chloride are certain to be exceeded. If, however, the solution contained any other cation, such as $Ca^{\bullet\bullet}$ or $Cu^{\bullet\bullet}$, the concentration of $CaCl_2$ or $CuCl_2$, resulting from the addition of Cl', would not reach the solubility value, and precipitation would not occur. In this way analytical separations can be brought about.

It is clear, moreover, that a solution of **any sulphate** will cause precipitation from **any solution containing a barium salt,** for $Ba^{\bullet\bullet}+SO_4'' \rightleftarrows BaSO_4$ represents the state of affairs in the solution and the solubility value for barium sulphate is so small that it is bound to be exceeded.

NOTE.—An "insoluble" substance is one for which a very small concentration of unionised molecules reaches the limiting "solubility value." In para. 9 it will be shown that this is related to the product of the concentrations of the ions present (or "solubility product") so that a small "solubility product" is regarded as indicating "insolubility."

(b) *Use of Excess of Reagents.*—If a solution contains silver and calcium we can separate the silver by adding hydrochloric acid and precipitating silver chloride. But $Ag^{\bullet}+Cl' \rightleftarrows AgCl$, so that if we increase [Cl'] we tend to increase [AgCl] and further precipitation of silver chloride must occur. In this way the quantity of silver remaining in the solution can be

* The measured solubility of the solute will be greater than this, for it will include the weight of solute present as ions.

reduced to a minimum.* For this reason, reagents are always added in excess of the quantity represented by the chemical equation, when maximum precipitation is desired.

(c) *Addition of a "Common Ion."*—If we add either concentrated hydrochloric acid or caustic soda solution to a solution of sodium chloride, we are adding Cl' or $Na^{\bullet}$, and increasing the concentrations of ions which are already present in the solution; *i.e.* "common" ions. But $Na^{\bullet}+Cl' \rightleftarrows NaCl$. Hence, [NaCl] will tend to increase in either case, and if the solution was originally saturated then precipitation will occur.

EXAMPLES.—(1) Hydrochloric acid gas passed into brine causes precipitation of pure sodium chloride. A concentrated solution of caustic soda produces the same result.

(2) The addition of brine to a solution of sodium stearate (soap) causes precipitation of the latter owing to the increase in $[Na^{\bullet}]$. This is often referred to as the "salting out" of the soap, but in this case the effect is also due in part to coagulation of the colloidal soap by the addition of the electrolyte sodium chloride.

(3) A precipitate of barium sulphate which is to be weighed must not be washed with water but with dilute sulphuric acid. The common ion SO_4'' tends to keep the $BaSO_4$ unionised, whereas with water $BaSO_4 \rightarrow Ba^{\bullet\bullet}+SO_4''$, which would result in solution and therefore loss of some of the precipitate.

(d) *Suppression of Ions.*—In a solution of ammonia we have $NH_4^{\bullet}+OH' \rightleftarrows NH_4OH$. Addition of ammonium chloride, NH_4Cl, will cause $NH_4^{\bullet}+OH' \rightarrow NH_4OH$ owing to the increase in $[NH_4^{\bullet}]$. The result is a decrease in $[OH']$, so that this ion is said to have been suppressed.

This is made use of in separating iron, aluminium, and chromium, from magnesium and manganese. The hydroxides of the first three have very small solubility products, but for the last two the values are a little larger. The value of $[OH']$ in a solution of ammonia, NH_4OH, is sufficient to cause preci-

* It can never be quite complete, for the solution will always remain saturated. The error thus introduced in gravimetric analysis is very small for substances which like silver chloride have very small solubility products.

pitation of all five hydroxides, but if suppressed by the addition of ammonium chloride it will be too small for the solubility products of the hydroxides of magnesium and manganese, $Mg(OH)_2$ and $Mn(OH)_2$, to be exceeded, and only the first three will be precipitated.

(c) *Solubility of Salts in Acids.*—A salt like calcium phosphate, which is nearly insoluble in water, dissolves readily in hydrochloric acid. The ionic explanation is based on the fact that the salt is derived from a weak acid, hydrogen phosphate being little ionised in solution. Hence, we have in contact with water $Ca_3(PO_4)_2 \rightleftarrows 3Ca^{\bullet\bullet} + 2PO_4'''$ in very small concentrations, but on addition of $H^{\bullet}$ (from the acid) we get $3H^{\bullet} + PO_4''' \rightleftarrows H_3PO_4$ and the latter is very little ionised. In other words $[PO_4''']$ is lowered by the addition of $H^{\bullet}$, and consequently $Ca_3(PO_4)_2 \rightarrow 3Ca^{\bullet\bullet} + 2PO_4'''$ owing to the displacement of the equilibrium. The reduction in $[Ca_3(PO_4)_2]$ owing to this further ionisation leaves the solution unsaturated so that more solid dissolves. This will continue until all is dissolved, provided that sufficient acid is added.

The salt of any weak acid will for the same reason dissolve in strong acids even though it is nearly insoluble in water. *E.g.* calcium oxalate dissolves readily in hydrochloric acid.

(f) *Complex Ion Formation.*—The reactions of a solution indicate the nature of the ions present. A solution of potassium ferrocyanide gives no precipitate of iron hydroxide when ammonia is added, and therefore neither $Fe^{\bullet\bullet}$ nor $Fe^{\bullet\bullet\bullet}$ can be present. The solution known as Fehling's solution * contains the element copper, yet no precipitate of copper hydroxide is obtained with caustic soda. Hence, it does not contain $Cu^{\bullet\bullet}$. Similarly, we do not believe that Nessler's solution † contains

* Fehling's solution is a reagent used as a test for reducing agents such as glucose. It is made by mixing solutions of copper sulphate, sodium potassium tartrate (Rochelle salt) and caustic soda. Solutions of many sugars, such as glucose, reduce it on warming to red insoluble cuprous oxide.

† Nessler's solution is used as a test for ammonia. It is an alkaline solution of mercuric iodide in potassium iodide and gives a yellow coloration with minute traces of ammonia.

$Hg^{\bullet\bullet}$; or that the dark blue solution of cupric hydroxide in ammonia contains $Cu^{\bullet\bullet}$.

N.B.—The absence of precipitates in the cases quoted does not prove the complete absence of the ions mentioned, but it shows that the concentrations of these ions (if present) must be exceedingly small. *E.g.* ammoniacal solutions of copper salts do give a precipitate of cupric sulphide with hydrogen sulphide, but they give none of the other $Cu^{\bullet\bullet}$ reactions. The solubility product of cupric sulphide is so small that $[Cu^{\bullet\bullet}]$ is sufficient to cause precipitation.

The metal in all these cases is supposed to form part of a **complex ion,** an assumption which accounts quite satisfactorily for the absence of the simple metallic cations. Thus, we suppose potassium ferrocyanide to ionise into $4K^{\bullet}$ and $Fe(CN)_6''''$, which agrees with the ordinary idea of calling it a salt of hydrogen ferrocyanide ($H_4Fe(CN)_6$). We suppose Fehling's solution to contain a complex copper-tartrate anion; Nessler's solution a complex HgI_4'' anion; and cuprammonium salts (as their name indicates) a complex cuprammonium cation ($Cu(NH_3)_4^{\bullet\bullet}$). These views are in harmony with the behaviour of these solutions on electrolysis, for measurements of transport numbers indicate which way a particular element is moving during electrolysis. Thus, we find that the solution of silver cyanide in potassium cyanide used in silver plating contains silver as well as cyanogen in the anion, for both these migrate to the anode on electrolysis.* Complex ion formation is also assumed to account for the solubility of zinc hydroxide or aluminium hydroxide in caustic soda (sodium zincate and aluminate are produced, the metal forming part of a complex anion), $Zn(OH)_2 \rightleftarrows Zn^{\bullet\bullet} + 2OH' \rightleftarrows ZnO_2'' + 2H^{\bullet}$, and the addition of caustic soda suppresses $H^{\bullet}$ thus, $H^{\bullet} + OH' \rightarrow H_2O$. The solubility of zinc hydroxide or copper hydroxide in ammonia is similarly accounted for by the assumption of a complex cation formed at the expense of the simple metallic ions.

It will be noted that the colours of some of these solutions

* Secondary reactions then occur which result in the silver being finally deposited at the cathode. This is not silver which has migrated to the cathode, but comes from $K + KAg(CN)_2 \rightarrow 2KCN + Ag$.

afford further evidence for the existence of new ions. *E.g.* the dark blue of cuprammonium salts is quite different from the pale blue due to $Cu^{\bullet\bullet}$.

(g) *Neutrality and Hydrolysis.*- Litmus used to be regarded as a standard indicator, for it gives its neutral or halfway colour with water. Hence the term "neutral" was taken to mean "neutral to litmus." It is, however, a term which should never be employed without stating the indicator referred to, for even water—a strictly neutral liquid as we shall see in a moment—is "acid to phenolphthalein" and "alkaline to methyl orange." The term "neutral salt" is also to be avoided, for normal salts are often not neutral to litmus: *e.g.* sodium carbonate turns it blue; ammonium chloride turns it red; and the "acid salt," sodium bicarbonate, is "neutral to litmus."

Pure water is an equilibrium mixture consisting of

999·9999982 gms. of H_2O,
·0000001 gm. of $H^{\bullet}$,
and ·0000017 gm. of OH' per litre.

This corresponds to values for $[H^{\bullet}]$ and $[OH']$ of 10^{-7} gm. equivalents per litre—values which have been arrived at in many different ways. The equality of $[H^{\bullet}]$ and $[OH']$ is inevitable since $H^{\bullet}+OH' \rightleftarrows H_2O$, and this makes water a truly neutral substance.

A solution with $[H^{\bullet}]>10^{-7}$ is acid with reference to water, but solutions with $[H^{\bullet}]<10^{-7}$, although alkaline with reference to water, have nevertheless a definite "degree of acidity" or concentration of hydrogen ions.

Why are solutions of all normal salts not neutral to litmus (*i.e.* neutral with reference to water)? The answer to this is that the equilibrium $H^{\bullet}+OH' \rightleftarrows H_2O$ may be displaced by the addition of the anion of a weak acid, or the cation of a weak base. In these cases $[H^{\bullet}]$ or $[OH']$ will be suppressed respectively owing to the formation of unionised acid or base molecules, and therefore the solution will no longer have $[H^{\bullet}]=[OH']=10^{-7}$.

EXAMPLES.—Sodium carbonate is the salt of a weak acid, H_2CO_3. Hence, on adding CO_3'' to water we get

$$2H^{\bullet}+CO_3''\rightarrow H_2CO_3$$

with consequent suppression of $[H^{\bullet}]$. The $Na^{\bullet}$ remains unaffected since caustic soda is a strong base and largely ionised, but $H_2O\rightarrow H^{\bullet}+OH'$ owing to the removal of $H^{\bullet}$. The solution ends up with much more OH' than $H^{\bullet}$ and is therefore alkaline to litmus.

Clearly, *potassium cyanide, sodium acetate and all such salts of weak acids will give solutions with alkaline reaction to litmus.*

Similarly, ammonium chloride is the salt of a weak base NH_4OH, so that when it is dissolved in water the following changes occur: (1) $NH^{\bullet}_4+OH'\rightleftarrows NH_4OH$ proceeding largely to the right, and (2) $H_2O\rightarrow H^{\bullet}+OH'$ owing to this removal of $H^{\bullet}$. The solution therefore ends up with much more $H^{\bullet}$ than OH', and so it will be acid to litmus.

The equilibria in solution may all be represented on one diagram if desired, thus:

$$\begin{array}{ccc} NH_4Cl\rightleftarrows NH^{\bullet}_4+Cl' & & \\ & + & \\ & OH'+H^{\bullet}\rightleftarrows H_2O & \\ & \uparrow\downarrow & \\ & NH_4OH & \end{array}$$

omitting $H^{\bullet}+Cl'\rightleftarrows HCl$ which is nearly 100 % $H^{\bullet}+Cl'$ and therefore unimportant.

Clearly, *any salt of a weak base such as copper sulphate, ferric chloride, ammonium chloride will be acid to litmus for a similar reason.*

NOTE.—In any aqueous solution the equilibrium

$$H^{\bullet}+OH'\rightleftarrows H_2O$$

must be taken into account. The concentration of H_2O is relatively so large, however, that it may be considered as constant, and we are mainly concerned with changes in acidity brought about by variations in $H^{\bullet}$.

The acid or alkaline reaction of these solutions to litmus is said to be due to **hydrolysis**. *E.g.* sodium carbonate is said

to be hydrolysed in solution. The term hydrolysis means a decomposition brought about by water,* and the old-fashioned way of regarding the above phenomena was to suppose that the water had decomposed the salts thus:

$$Na_2CO_3 + 2HOH \rightarrow 2NaOH + H_2CO_3.$$

The strong base (it was thought) would more than compensate for the action of the weaker acid. The ionic explanation is distinctly more satisfactory.

8. The Dilution Law.—In a solution of a binary electrolyte we have assumed the existence of an equilibrium mixture $XY \rightleftarrows X^{\bullet} + Y'$. If we apply the law of mass action to this in a quantitative manner we deduce that $\frac{[X^{\bullet}] \times [Y']}{[XY]} = \text{a constant}$ (*cf.* p. 196). The constant (K) is termed the **dissociation constant,** for it enables us to calculate the degree of dissociation of XY at any given dilution. If the solution contains 1 gm. mol. of solute in v litres, and α is the degree of ionisation we have $[XY] = \frac{1-\alpha}{v}$; $[X^{\bullet}] = \frac{\alpha}{v}$; and $[Y'] = \frac{\alpha}{v}$, and therefore by substitution $\frac{\alpha^2}{(1-\alpha)v} = K$. Expressed in terms of concentration, and with $\frac{\lambda_c}{\lambda_0}$ substituted for α, this becomes $\frac{\lambda_c^2 \cdot C}{\lambda_0(\lambda_0 - \lambda_c)} = K$, the expression given on p. 175, usually known as *Ostwald's Dilution Law.* The results of experiment were found to be in good agreement as long as ionic concentrations were small. Thus it is applicable to weak electrolytes in all but very concentrated solutions, but not to strong electrolytes except when extremely dilute; *e.g.* when v is 10,000 litres or more (concentrations less than ·0001 *N*). Table XII. shows the validity of the law when a weak electrolyte is employed, the figures in the last column being obtained after applying a correction to the value of α for the varying viscosity of the solution. Table XIII. shows how hopeless it is when applied to a strong elec-

* Do not confuse this with hydration, which is combination with water.

trolyte at ordinary dilutions. The discovery that in such cases $\lambda \propto \sqrt{c}$ (Kohlrausch's Law, see p. 175), a relation incompatible with Ostwald's Dilution Law, showed that strong electrolytes must receive separate treatment and led to the theory of complete ionisation which has already been mentioned.

TABLE XII.– The Ionisation of Acetic Acid at 25° C.*

V (the dilution in litres).	α (from conductivity measurements).	K (calculated from the dilution law).	K (calculated from a modification of the dilution law).
·334	·001595	0000077	0000165
·989	·003636	·0000140	·0000184
5·371	·009806	·0000181	0000190
10·753	·01382	·0000180	·0000185
24·875	·02163	·0000192	·0000195
63·260	·03350	·0000185	0000186

TABLE XIII.– Ionisation of Potassium Chloride at 25° C†

V in litres.	α	K
1	·7565	2·350
10	·8624	·5405
500	·9723	·0681
1,000	·9802	·0485
5,000	·9912	·0223
10,000	·9936	·0154

Notes on the Dilution Law.—(1) If α is small, $1-\alpha$ is nearly unity, so the expression reduces to $\frac{\alpha^2}{v}=K$, or $\alpha \propto \sqrt{v}$. (2) Ionisation is complete when $\alpha=1$. This will happen when $v=\infty$ (infinite dilution). (3) The dissociation constant depends on the temperature, for this affects the value of α. (4) Tables of Dissociation Constants for weak electrolytes are given in reference books, and we can then calculate their degrees of ionisation at any dilution. To show the magnitude of these quantities a few are given on p. 247. It should be clear that a strong electrolyte like HCl or KOH has not got a dissociation constant since the dilution law does not apply.

8a. Strong Electrolytes. The "Activity Concept." Qualitative applications of the Law of Mass Action to ionic equilibria had been so successful (see para. 8) that the failure to apply it quantitatively to strong electrolytes at ordinary

* Taylor, *ibid.* I. 556. † Taylor, *ibid* I. 547.

dilutions was surprising. Yet it would give satisfactory results when dealing with very small ionic concentrations, such as are to be found, for example, in solutions of nearly insoluble substances (see para. 9). A growing belief in the idea that strong electrolytes were completely ionised at all dilutions made it clear that "ionic concentration" * had lost its original meaning. It was pointed out that Guldberg and Waage in deducing the Law of Mass Action had used a thermodynamic term which they had called the "active mass," and that possibly the substitution of molecular or ionic concentrations for this was not always justified. This view has now been accepted, and when applying the law we should substitute for the "active mass" of a molecule or ion a term called its "*activity*." †

In some cases the "activity coefficient" (see footnote) may be nearly unity, so that the "activity" will be sensibly equal to the molecular (or ionic) concentration. Good agreement will then result if such concentrations are used when applying the law. This has been the case throughout Chapter XI., and it will be met with again in the next paragraph.

In general, then, when considering the equilibrium $XY \rightleftarrows X^{\bullet} + Y'$ we must write:

$$K = \frac{(\text{activity of } X^{\bullet}) \times (\text{activity of } Y')}{(\text{activity of } XY)} \quad \text{or simply} \quad K = \frac{a_1 a_2}{a_3}.$$

9. The Solubility Product of an Electrolyte.—If a precipitate of silver chloride is formed in a solution, we shall have $Ag^{\bullet} + Cl' \rightleftarrows AgCl$ for the equilibrium between the ions and unionised molecules remaining in the solution. Since the ionic concentrations are excessively small, for such an "insoluble" substance, these may be substituted for "activities," and so

* Although there may be a state of equilibrium between ions and "neutral doublets" (see footnotes, pp. 156 and 230), this can only be treated qualitatively, for very few of the ions are supposed to be in close enough contact to form a "doublet."

† There is a relation between the "activity" of an ion and its "concentration" of the type $a = \gamma[A^{\bullet}]$, where γ is termed the "activity coefficient," but γ is not a constant. A full understanding of the "activity concept" is impossible without resorting to thermodynamics.

$\frac{[Ag^{\bullet}]\times[Cl']}{[AgCl]}$ = a constant. Now [AgCl] in a saturated solution must be the solubility value, and therefore constant. Hence **the product $[Ag^{\bullet}]\times[Cl']$ must be constant.** It is called the **solubility product,** and is that value of the product of the ionic concentrations which will cause the solution to become saturated.

If we increase either $[Ag^{\bullet}]$ or [Cl'] by any means (*e.g.* by the addition of a common ion), we tend to increase the product beyond this maximum value. In other words, more silver chloride will be formed, the solution will become momentarily supersaturated, and precipitation will then occur.

EXAMPLE.—The solubility of silver chloride is ·0016 gm. per litre (p. 230) or $1{\cdot}1\times10^{-5}$ gm. mol. per litre. But at such extreme dilution [AgCl] will be negligible compared with $[Ag^{\bullet}]$ and [Cl']. Hence we can write $[Ag^{\bullet}]=1{\cdot}1\times10^{-5}$ and $[Cl']=1{\cdot}1\times10^{-5}$. Therefore the solubility product is $1{\cdot}1\times10^{-5}\times1{\cdot}1\times10^{-5}$, or $1{\cdot}2\times10^{-10}$.

If, therefore, to a solution containing Cl' (*i.e.* any chloride) we add $Ag^{\bullet}$ (in the form of silver nitrate), precipitation will occur when $[Ag^{\bullet}]\times[Cl']$ reaches the value $1{\cdot}2\times10^{-10}$. It follows that a substance with a small solubility product will be nearly insoluble and readily precipitated.

The experimentally measured solubility of a substance like silver chloride will be diminished by adding a common ion, for since $[Ag^{\bullet}]\times[Cl']$ remains constant the value of $[Ag^{\bullet}]$ must decrease if [Cl'] is increased. Hence, the weight of silver (and therefore of its chloride) in solution will be decreased.

EXAMPLE.—Solubility of silver acetate in water at 25° C. =·0660 gm. mol. per litre. If sodium acetate solution is added, of concentration ·653 gm. mol. per litre, some silver acetate is precipitated and the solubility is reduced to ·0167 gm. mol. per litre. The addition of silver nitrate produces a similar effect.

10. The Ionic Product of Water.—In pure water we have $H^{\bullet}+OH' \rightleftarrows H_2O$. Applying the law of mass action $\frac{[H^{\bullet}]\times[OH']}{[H_2O]}=K$, and $[H_2O]$ is relatively so large that it may be considered as constant. Hence, $[H^{\bullet}]\times[OH']$ must be

constant. But $[H^\bullet]-[OH']=10^{-7}$, so that this product has the value 10^{-14}. It is commonly referred to as K_w, the ionic product of water. It varies with the temperature, being $\cdot 46\times10^{-14}$ at 15° C. and $3\cdot8\times10^{-14}$ at 40° C.

Now, in any aqueous solution $[H^\bullet]\times[OH']$ must have this value, so that in a $\frac{N}{10}$ solution of sodium acetate, in which for example $[H^\bullet]=10^{-9}$, $[OH']=\frac{10^{-14}}{10^{-9}}=10^{-5}$. This solution has therefore $[OH']>10^{-7}$ (the value in water), and is commonly termed an alkaline solution. At the same time it has a definite "degree of acidity,"—a concentration of hydrion of 10^{-9} gm. equivalent per litre.

11. The Degree of Hydrolysis of a Strong Electrolyte.—If XY is the salt of a weak acid, then in solution we have the following system in equilibrium:

$$\begin{array}{ccc} XY & \rightleftarrows & X^\bullet+Y' \\ & & + \\ H_2O & \rightleftarrows & OH'+H^\bullet \\ & & \downarrow\uparrow \\ & & HY \end{array}$$

the result of which gives large values for [HY] and [OH'], and comparatively small values for $[H^\bullet]$ and [Y']. We may omit from our discussion all except $Y'+H_2O\rightleftarrows HY+OH'$, for this shows the extent to which hydrolysis has occurred; and XY being largely ionised to start with, $X^\bullet$ remains unaffected by the hydrolysis. Now we have noted that $[H_2O]$ is practically constant, so by applying the law of mass action to the system we get $\frac{[OH']\times[HY]}{[Y']}$=a constant (at a given temperature).* This constant K_h is called the "hydrolysis constant," for it shows the degree of hydrolysis (*i.e.* the fraction of XY hydrolysed) at any given

* A useful form of this expression is $\frac{[\text{base formed}]\times[\text{acid formed}]}{[\text{unhydrolysed salt}]}=K_h$, where it is assumed that the salt and the strong base are completely ionised and the weak acid completely unionised.

dilution. This will be seen more clearly if we let x be the fraction hydrolysed, when the above reduces to $K_h = \frac{x^2}{(1-x)v}$. The degree of hydrolysis always increases with rise in temperature.

It can be shown that $K_h = \frac{K_w}{K_{acid}}$ (where K_w is the dissociation constant for water, and K_{acid} the dissociation constant of the weak acid HY), and it follows from this that

$$[H^\bullet] = \sqrt{K_A \times K_w \times v}.$$

This expression may be used for calculating the degree of acidity in a solution of any salt of a strong base and weak acid.

E.g., for $\frac{N}{10}$ sodium acetate, $[H^\bullet] = \sqrt{\cdot 18 \times 10^{-4} \times 10^{-14} \times 10}$

$= 1 \cdot 4 \times 10^{-9}$ gm. equivalent per litre.

A similar discussion applies to salts of weak bases and strong acids. The hydrolysis may in such cases be represented by

$X^\bullet + H_2O \rightleftarrows XOH + H^\bullet$, so that $K_h = \frac{[H^\bullet] \times [XOH]}{[X^\bullet]}$ or

$\frac{[\text{base formed}] \times [\text{acid formed}]}{[\text{unhydrolysed salt}]} = K_h$ The base is in this case considered to be unionised, and the acid and salt completely ionised.

It can be shown that in this case $K_h = \frac{K_w}{K_{base}}$ and $[H^\bullet] = \sqrt{\frac{K_w}{K_B \times v}}$.

E.g., for $\frac{N}{10}$ ammonium chloride, $[H^\bullet] = \sqrt{\frac{10^{-14}}{2 \cdot 3 \times 10^{-5} \times 10}}$

$= \cdot 7 \times 10^{-5}$ gm. equivalent per litre.

The degree of hydrolysis of salts of weak bases and weak acids, *e.g.* aniline acetate, is practically independent of the dilution, but it depends upon both K_A and K_B.

Determination of the Degree of Hydrolysis of a Salt.—An example will illustrate the method. Experimental measurements of $[H^\bullet]$ (carried out as described in para. 12) give a value for $\frac{N}{10}$ ammonium chloride of $\cdot 7 \times 10^{-5}$ gm. equivalent

per litre (agreeing with the calculated value above). Now the degree of hydrolysis is $\frac{[\text{acid formed}]}{[\text{total salt}]}$, so that in this case we have $\frac{\cdot 7 \times 10^{-5}}{\cdot 1} = 7 \times 10^{-5}$ or ·007 %. Hence, in $\frac{N}{10}$ ammonium chloride, ·007 % of the salt molecules have been hydrolysed.

12. The Relative Strengths of Acids.—When comparing the strengths of two acids we must take care that both are fairly treated. If one is more volatile than the other, our method must not involve removing the more volatile acid in the form of vapour or it will not have a fair chance to show its strength. Again, if one acid is less soluble than the other the conditions of the experiment must not allow the less soluble acid to be precipitated and thus removed from the sphere of action. The fact that sulphuric acid expels nitric acid from nitrates does not show that the former is the stronger acid, for the nitric acid being more volatile is not able to compete with it on equal terms. As a matter of fact nitric acid is a stronger acid than sulphuric acid (see below). Hence, in all methods of comparing strengths of acids, chemical analysis must be avoided, and **physical measurements** made use of whenever possible, for these do not involve the removal of any substances from the systems under examination.

The methods adopted may be summarised as follows:

I. *Partition Methods.*
   (*a*) Thermal measurements.
   (*b*) Volume change measurements.

II. *Determinations of* $[H^{\bullet}]$.*
   (*a*) From degree of ionisation by electrical conductivity measurements.
   (*b*) From degree of ionisation by osmotic measurements (freezing point depression, etc.).
   (*c*) From measurements of E.M.F. (potentiometric method).
   (*d*) By using calibrated indicators.

* As pointed out on p. 179 it is probably $[H_3O^{\bullet}]$ which is actually measured.

NOTE.—Table XIV. shows the relative strengths of a few acids as determined by three different methods. The same "order" is given by each method, although exact numerical agreement is lacking, and this was regarded by Ostwald as vindicating the ionic hypothesis on which Methods II. and III. were based, for Method I. is quite independent of such assumptions (see below). Unfortunately his third method based on the catalytic effects of acids on certain reactions (such as the inversion of cane sugar) has proved to be unsound, and it must now be regarded as of historical interest only. He assumed that this catalytic effect was entirely due to the [H•] which the acid introduced. The work of Dawson (see *J.C.S.* **103,** 2135, 1913, and **105,** 1426, 1915) has shown that not only the hydrogen ions, but other ions present, and even undissociated acid molecules, may possess catalytic activity. Hence no reliable information as to [H•] can be expected from experiments of this nature.

TABLE XIV.—RELATIVE STRENGTHS OF ACIDS IN *N* SOLUTIONS.

Acids examined.	Thermal measurements of partition.	Degree of ionisation from electrical conductivity.	Catalytic effect on the inversion of cane sugar.
Hydrochloric . .	100	100	100
Nitric	100	99·6	100
Sulphuric . . .	49	65 0	53·6
Monochloracetic .	9	4 9	4 8
Acetic	3	1 4	0 4

The Methods in Detail.—I. *The Partition Method.*—If two acids are mixed in equivalent quantities and enough of a base is added to neutralise only one of them, the base will be shared by the two acids in proportion to their strengths.

Julius Thomsen, to whom this method is due, used the term "avidity" (or greediness for base) instead of "strength." His work was done ten years or more before Arrhenius' ionic hypothesis, and gave the first available data for comparing the strengths of different acids.

The partition of the base between the two acids must be determined by physical measurements to avoid disturbing the

mixture. *Thomsen* employed thermal measurements. He determined Q_1 the heat of neutralisation of acid A alone; Q_2 the heat of neutralisation of acid B alone; * and Q_3 the heat developed when a mixture of A and B was partly neutralised by 1 equivalent of base. Now if acid A had reacted with x equivalents of base, then acid B would have reacted with $1-x$ equivalents and $Q_3 = xQ_1 + (1-x)Q_2$. Hence, from Q_1, Q_2 and Q_3 he could determine the ratio of x to $1-x$; *i.e.* the relative acidities of the two acids.

Ostwald noted the volume change V_1 occurring when A was neutralised alone; V_2 when B was neutralised alone; and V_3 when the mixture of A and B was partly neutralised, thus arriving at the partition by dilatometric measurements.

The partition method remains at the present day the most satisfactory method for comparing the strengths of strong or moderately strong acids, owing to the failure of the ionic hypothesis when applied quantitatively to strong electrolytes.

II. *Determinations of* $[H^\bullet]$.—The acidity of a solution (or strength of an acid in solution) is, according to the ionic hypothesis, measured by its hydrion concentration.

Since $HX \rightleftarrows H^\bullet + X'$ represents the system in equilibrium, the value of α (the degree of ionisation) at a given dilution v gives us for $[H^\bullet]$ the quotient $\frac{\alpha}{v}$. Thus, if an acid is 2 % ionised in $\frac{N}{10}$ solution $[H^\bullet] = \frac{\cdot 02}{10} = \cdot 002$ gm. equivalent per litre. Hence, we can determine $[H^\bullet]$ from conductivity measurements $\left(\alpha = \frac{\lambda_v}{\lambda_\infty}\right)$, or from the i value obtained by freezing point depression or other osmotic measurements $\left(i = \frac{1-\alpha+n\alpha}{1}\right)$.

The value of $[H^\bullet]$ for a solution can also be very accurately determined by electromotive force measurements. A specially designed electrode containing unionised hydrogen (known as

* We have noted that all strong acids have *nearly* the same heat of neutralisation. If they had *exactly* the same heat of neutralisation they would be equal in strength.

a hydrogen electrode) is immersed in the solution. The difference of potential between this and the hydrogen ions in the solution is measured with a potentiometer, and from this $[H^\bullet]$ can be calculated.

The use of indicators is discussed in para. 20.

Approximate values for $[H^\bullet]$ can be obtained at a given dilution V by a single determination of λ_v without determining $\lambda\infty$ (a matter of importance owing to the difficulty of determining $\lambda\infty$ directly). Referring to Kohlrausch's law we see that for all acids $\lambda\infty$ is equal to mobility of $H^\bullet$ + mobility of the anion, and the latter is always comparatively small (see p. 228). Hence, we may consider that $\lambda\infty$ is approximately equal to mobility of $H^\bullet$, and so approximately the same for all acids; an assumption which is borne out by the tendency for all acids to become equal in strength at infinite dilutions. Therefore, $\alpha=\frac{\lambda_v}{\lambda\infty}$ becomes approximately $\alpha=\frac{\lambda_v}{314}$; so that measurements of λ_v for two acids can be used for comparing their degrees of ionisation.

13. The Relative Strengths of Bases.—These can be determined by exactly similar methods; *e.g.* by the partition of an acid between two bases, or by measurements of $[OH']$ in the solutions.*

NOTE.—If $[H^\bullet]$ is determined experimentally, $[OH']=\frac{10^{-14}}{[H^\bullet]}$.

14. The Strength of an Acid at Various Dilutions.—In the case of weak acids the dilution law may be applied and $K_A=\frac{\alpha^2}{(1-\alpha)v}$. Since $[H^\bullet]=\frac{\alpha}{v}$ it is clear that the dissociation constant K_A will enable us to calculate $[H^\bullet]$ at any given dilution.

* In the case of bases like ammonia and the amines, the alkaline character of their solutions must be due to their ability to remove $H^\bullet$ from the water. Thus $NH_3+H_2O=NH_4^\bullet+OH'$. It is now considered that bases act as "proton-acceptors" in contrast with acids which are "proton-donors," as mentioned on p. 179.

TABLE XV.

DISSOCIATION CONSTANTS.

Dissociation constants of acids K_A		Dissociation constants of bases K_B	
Acetic acid	$1{\cdot}8\times10^{-5}$	Ammonia	2×10^{-5}
Boric acid	$6{\cdot}5\times10^{-10}$	Aniline	$1{\cdot}1\times10^{-10}$
Benzoic acid	$6{\cdot}7\times10^{-5}$	Pyridine	$2{\cdot}3\times10^{-9}$
Hydrocyanic acid	$4{\cdot}7\times10^{-10}$	Urea	$1{\cdot}5\times10^{-14}$
Phenol	$1{\cdot}3\times10^{-10}$		
Acetic acid	·000018	Ammonia NH_3	·00002
Monochloracetic acid	·00155	Methylamine $NH_2(CH_3)$	·0005
Trichloracetic acid	1·21	Dimethylamine $NH(CH_3)_2$	·0007
Cyanacetic acid	·0037	Aniline $NH_2(C_6H_5)$	$1{\cdot}1\times10^{-10}$
Aminoacetic acid	$3{\cdot}4\times10^{-10}$		

NOTES.—(1) The nature of the anion decides the strength of the acid, and substitution in organic acid radicals has a very marked effect. It can be seen that replacing H by Cl, CN, or C_6H_5 increases the strength of an acid; on the other hand, replacing H by NH_2 decreases the acid properties (or confers basic properties). Similar remarks apply to bases (see the substituted ammonias or amines in the above table).

(2) Polybasic acids appear to ionise in stages. Thus, $H_2CO_3 \rightleftarrows H^\bullet + HCO_3'$ and $HCO_3' \rightleftarrows H^\bullet + CO_3''$. Hence, two dissociation constants are given for carbonic acid: $K_{A_1}=3\times10^{-7}$, and $K_{A_2}=6\times10^{-11}$. Similar remarks apply to H_3PO_4, H_2S and other polybasic acids. The values for K_{A_1}, K_{A_2}, etc., show the extent to which ionisation occurs in each stage. In this way we can explain why Na_3PO_4 is hydrolysed to a much greater extent than Na_2HPO_4, for H_3PO_4 is a much weaker acid than $H_2(HPO_4)$.

15. The Practical Importance of Measurements of [H•].—Acidity and alkalinity are no longer vague terms applied to solutions, for the degree of acidity can now be precisely determined by the methods we have just described. The success of many industrial processes is dependent upon a careful control of the degree of acidity in the solutions

employed, and great progress has been made since the adoption of these methods of measuring [H•].*

Thus, the dairy farmer finds that the bacteria which cause the souring of milk, or those which are used in making cheese, only flourish in solutions whose degrees of acidity lie between certain limits. The brewer and the leather tanner have to control the degree of acidity in their solutions. The agricultural expert finds that certain species of plants grow best when [H•] for the soil water has a definite value. Even the distribution of snails depends upon this factor! The biochemist must keep [H•] for his culture solutions to definite values if he wishes his bacteria to flourish. The doctor also can learn a great deal from a knowledge of the degree of acidity in various body fluids, for our health is regulated to a large extent by this factor. It is found, for example, that the activities of living cells cease altogether if [H•] is $>10^{-6}$ or $<10^{-8}$; the normal value for blood is about $10^{-7\cdot4}$ and it varies as a rule between $10^{-7\cdot3}$ and $10^{-7\cdot5}$. The extreme limits found in human blood have been $10^{-7\cdot0}$ and $10^{-7\cdot5}$, and this amazingly constant value is brought about by the regulating action of certain salts, such as sodium bicarbonate, which are said to act as " buffers " against changes in [H•].

Finally, we may mention the numerous titrations which are necessary in analytical work, involving the use of indicators. *Clark* † gives a list of 158 indicators which can be used, and the choice of the correct indicator to use in any particular case involves a knowledge of the changes in [H•] which occur during the titration. The behaviour of indicators must now be discussed.

16. The Action of Indicators.‡—An indicator like litmus,

* The bacteriologist or industrial worker wishes to obtain a value for [H•] as quickly and easily as possible. Hence the methods always adopted involve either the use of indicators (see p 254) or the measurement of E.M.F.

† Clark, *The Determination of Hydrogen Ions.*

‡ These remarks only apply to indicators such as methyl orange which change colour during the titration of an acid by an alkali. They do not apply to indicators like starch or potassium chromate which during a titration form coloured compounds with reagents in the solution and thus show the " end point."

methyl orange, or phenolphthalein, shows by a colour change when a solution is more acid or less acid than one in which it shows its halfway colour. Thus, the halfway colour of methyl orange is orange; it is pink in more acid solutions and yellow in less acid solutions. The colour changes are due to changes in $[H^\bullet]$ in the solution, and each indicator shows its halfway colour when $[H^\bullet]$ has a definite value: *e.g.* 10^{-4} for methyl orange; 10^{-7} for litmus; 10^{-10} for phenolphthalein.

It can be seen that water is neutral to litmus, acid to phenolphthalein and alkaline to methyl orange if we judge neutrality by halfway colour. If we say that a solution is "neutral" we mean that $[OH'] = [H^\bullet] = 10^{-7}$; but we may speak of a solution as "neutral to phenolphthalein" if it has a value for $[H^\bullet] = 10^{-10}$.

The ionic explanation of the action of indicators is that they are weak acids or weak bases the degrees of ionisation of which are altered by changes in $[H^\bullet]$ or $[OH']$. Thus, an indicator in solution may consist of $H^\bullet + X' \rightleftarrows HX$ and addition of $H^\bullet$ will cause $H^\bullet + X' \rightarrow HX$; or if it is $Y^\bullet + OH' \rightleftarrows YOH$ then addition of OH' will cause $Y^\bullet + OH' \rightarrow YOH$. Since an increase in $[H^\bullet]$ causes a corresponding decrease in $[OH']$ and vice versa we need only fix our attention on changes in $[H^\bullet]$.

It is next assumed that the unionised indicator molecule has a different colour from that of the ions it produces,* so that a change in the equilibrium mixture will cause a colour change. Thus, if HX is pink and X′ is yellow, the effect of adding an acid to this indicator ($H^\bullet + X' \rightarrow HX$) would be to change it from yellow (X′) to pink (HX).

* A modification of this theory is necessary in some cases. The ions may perhaps be the same colour as the unionised molecules, so that we must then assume that the indicator can exist in two tautomeric forms having different colours. If one of these forms will ionise and the other will not, and there is a state of equilibrium between molecules of the two forms in the solution, the theory outlined above can be applied as before. Thus, we should have $\underset{\text{pink}}{XH} \rightleftarrows \underset{\text{yellow}}{HX} \rightleftarrows \underset{\text{yellow}}{H^\bullet + X'}$, and this system would obviously change from yellow to pink on the addition of an acid: $\underset{\text{pink}}{XH} \leftarrow \underset{\text{yellow}}{HX} \leftarrow \underset{\text{yellow}}{H^\bullet + X'}$.

to pink. Or if YOH is pink and $Y^{\bullet}$ is colourless, an acid will change the indicator ($Y^{\bullet}+OH' \leftarrow YOH$) from pink to colourless.
colourless pink

It is clear that such indicators will give their halfway colour when 50 % ionised. With methyl orange, for example, when $[H^{\bullet}]=10^{-4}$ there will be 50 yellow X' ions for every 50 pink HX molecules, so that the mixture will look orange.

17. Changes in $[H^{\bullet}]$ during Titrations. The Choice of Indicators.—We wish the "end point" to be indicated when chemically **equivalent quantities** of acid and alkali have been mixed. **The resulting solution will have a definite degree of acidity and the correct indicator to use will be the one which shows its halfway colour for this value of $[H^{\bullet}]$.**

EXAMPLE.—$\frac{N}{10}$ ammonia is to be titrated with $\frac{N}{10}$ hydrochloric acid. We wish the end point to be shown when ammonium chloride is present in solution; *i.e.* when there is no excess of either reagent. Now $[H^{\bullet}]$ for $\frac{N}{10}$ ammonium chloride is 7×10^{-5}, so that litmus would be pink and phenolphthalein colourless at this stage. If the latter indicator were used, the end point would not be reached until $[H^{\bullet}]=10^{-10}$ and there would be considerable excess of ammonia present. On the other hand methyl orange is not far from its halfway colour when $[H^{\bullet}]=7\times10^{-5}$, so that a nearly correct end point will be obtained.

Similarly, for titrating a weak acid like oxalic acid with a strong base we must use phenolphthalein in preference to methyl orange, for the end point in this case is reached when $[H^{\bullet}]<10^{-7}$, and methyl orange would change colour when there was a large excess of acid present. With strong acids and bases, the end point is reached when $[H^{\bullet}]=10^{-7}$ (approximately), and all three indicators can be used without serious error. Fig. 45 shows these conclusions graphically.

NOTE.—It will be easier to understand these paragraphs if a series of solutions be placed in beakers and indicators added as shown on next page. (A white background is advisable and

I.	$\frac{N}{10}$ hydrochloric acid	$\frac{N}{10}$ aniline hydrochloride.	$\frac{N}{10}$ ammonium chloride.	$\frac{N}{10}$ sodium chloride.	$\frac{N}{10}$ sodium acetate.	$\frac{N}{10}$ potassium cyanide.	$\frac{N}{10}$ caustic soda.	Methyl orange in each.
II.	,,	,,	,,	,,	,,	,,	,,	Methyl red in each.
III.	,,	,,	,,	,,	,,	,,	,,	Litmus in each
IV.	,,	,,	,,	,,	,,	,,	,,	Phenolphthalein in each.
V.	,,	,,	,,	,,	,,	,,	,,	B.D.H. Universal Indicator in each.
VI.	Solution with $[H^{\cdot}]=10^{-1}$	Solution with $[H^{\cdot}]=10^{-3}$	Solution with $[H^{\cdot}]=10^{-5}$	Solution with $[H^{\cdot}]=10^{-7}$	Solution with $[H^{\cdot}]=10^{-9}$	Solution with $[H^{\cdot}]=10^{-11}$	Solution with $[H^{\cdot}]=10^{-13}$	Any indicator.

row I. should be at a higher level than row II., etc., to give an uninterrupted view. The "B.D.H. Universal Indicator" will be referred to presently; also the standard solutions in row VI. The scheme can easily be abbreviated if desired (see Plate IV.).

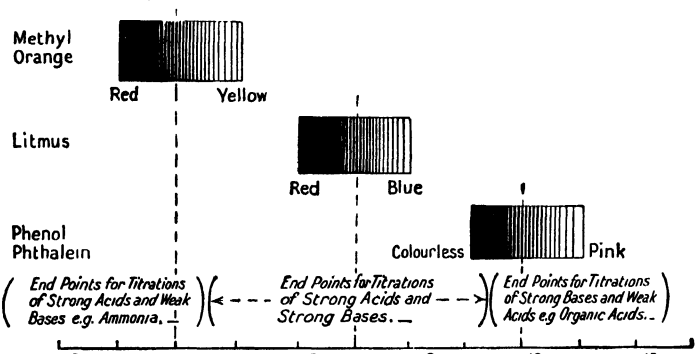
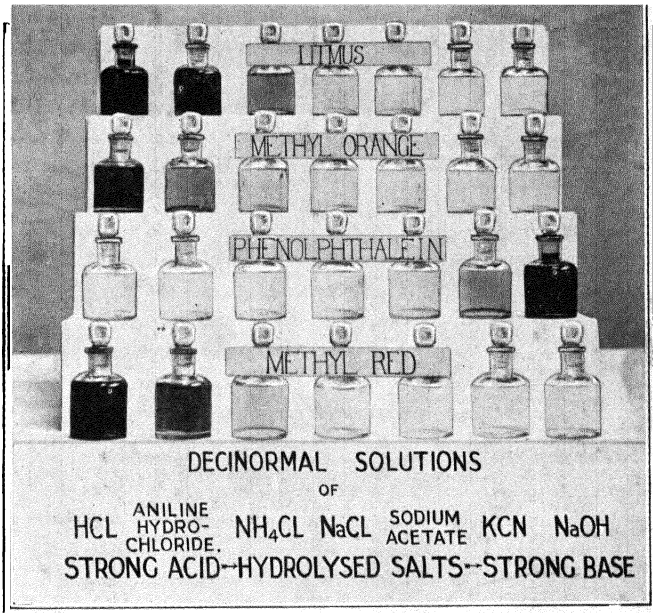


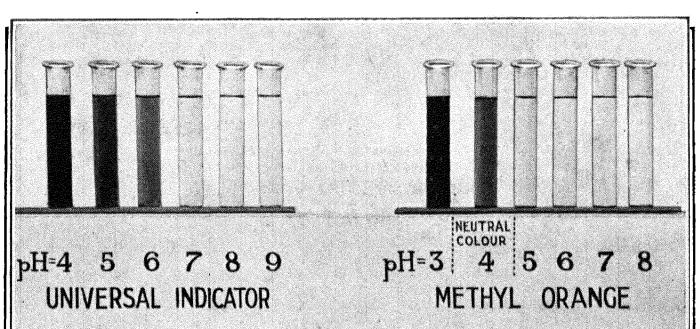
FIG. 45.—The range of an indicator.

18. The Range and Sharpness of an Indicator.—In any solution containing an indicator there is a mixture of the two different coloured forms, but the eye cannot distinguish between colours which are nearly the same. It takes a change of about 10 % of one form into the other to produce a **visible** colour change. *E.g.* when 90 % of methyl orange is in the yellow form the eye will distinguish no pinkness, and when it is 10 % in the yellow form the eye will see only pinkness. Hence, the effective range of the indicator, between the limits of which the eye can see its colour altering, lies between those values of $[H^{\bullet}]$ which will bring it from (10 % A + 90 % B) to (90 % A + 10 % B) if A and B are the different coloured forms. By considering the dissociation constant of the indicator itself, it can be shown that these limiting values of $[H^{\bullet}]$ are 10 times and $\frac{1}{10}$th the value giving the halfway tint.*

* A reprint of an article by Brig.-Gen. H. Hartley in the *School Science Review* is sold by John Murray (1*s.* 1*d.* post free), under the title *The Study of Indicators and the Law of Mass Action.* This gives a fuller treatment than is possible here and includes a proof of this statement.



Hydrolysis and the choice of Indicators.



Determination of the hydrion concentration of a solution

The range of an Indicator

Photo : Bromhead, Clifton.

PLATE IV. APPARATUS FOR DEMONSTRATING THE USE OF INDICATORS

Hence, the **range** for methyl orange is 10^{-3} to 10^{-5};
" " " litmus 10^{-6} to 10^{-8};
" " " phenolphthalein 10^{-9} to 10^{-11}.

Methyl orange in solutions more acid than $[H^{\bullet}]=10^{-3}$ is therefore pink, and in solutions less acid than $[H^{\bullet}]=10^{-5}$ it is yellow. Between these two limits there is a gradual colour change through a halfway "orange" at $[H^{\bullet}]=10^{-4}$. (See Fig. 45.)

The change in colour is brought about by definite changes in $[H^{\bullet}]$ and unless a small change in $[H^{\bullet}]$ produces a big change in colour the end point will not be sharp.

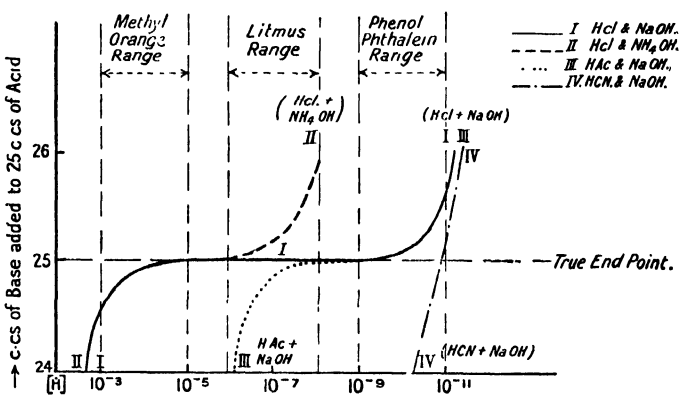


FIG. 46.—Titrations of $\frac{N}{10}$ solutions of acids and bases.

We may plot curves showing how $[H^{\bullet}]$ varies during a titration, as we increase the amount of alkali run into a given quantity of acid, and we shall then get results similar to those shown in Fig. 46.

In Curve I. (strong acid and base) we see that a very small change in the volume of acid **in the neighbourhood of the end point** produces a big change in $[H^{\bullet}]$. This will result in a big colour change and therefore a sharp end point.

In Curve II. (weak base and strong acid) and Curve III. (weak acid and strong base), and especially in Curve IV. (very weak acid and strong base), we see that even in the neighbourhood of the end point the curves are comparatively steep, so that a considerable volume of acid must be added to produce that change in $[H^\bullet]$ which will be recognised by a visible colour change. End points cannot be sharp in these cases even though the correct indicator is chosen.

19. $[H^\bullet]$ and pH.—The value of $[H^\bullet]$ is always very small, and it is convenient for many reasons to use a number to express the degree of acidity of a solution which is the logarithm of $\frac{1}{[H^\bullet]}$. This is termed the **hydrogen ion exponent** and it is represented by pH.

Thus if $[H^\bullet]=10^{-7}$ . . . . $p\text{H}=7$.

$[H^\bullet]=10^{-9}$ . . . . $p\text{H}=9$.

$[H^\bullet]=5{\cdot}63\times10^{-8}$ . . $p\text{H}=\log\frac{1}{5{\cdot}63\times10^{-8}}=7{\cdot}25$.

The range of methyl orange is therefore from pH=3 to pH=5, with halfway colour at pH=4.

NOTE.—As pH decreases, acidity increases and vice versa, a solution with pH=3 being more acid than one with pH=5.

20. The Use of Indicators for Measurements of $[H^\bullet]$.—If we could obtain solutions of known pH (or $[H^\bullet]$) and place therein various indicators, we could note the colour of each for a given pH value. This would in fact be calibrating our indicators, for if we used them afterwards on unknown solutions, we could tell the pH of them from the colour obtained. This is just what the busy man likes to do. He is given an indicator and a colour chart, places the indicator in his solutions and reads the value of pH from the chart. An ingenious combination of indicators has been devised which gives approximate values for pH in any solutions between pH=4 and pH=11. The Universal Indicator made by British Drug Houses, Ltd., gives the following results:

Colour.	*p*H
Red	4
Orange red	5
Orange	6
Greenish yellow	7
Green	8
Greenish blue	9
Violet	10
Reddish violet	11

For more accurate values, a single indicator must be used and calibrated accurately over the required range.

The preparation of standard solutions of known *p*H is a necessary step towards calibrating an indicator. Theoretically we could do this by adding to water calculated quantities of either a strong acid (HCl) or strong base (NaOH). *E.g.* $\frac{N}{10,000}$HCl has $pH=4$ (since it can be regarded as completely ionised at this dilution and therefore must contain 1 gm. of $H^{\bullet}$ in 10^4 litres). In practice, however, such a solution is much too sensitive to atmospheric or dissolved carbon dioxide, and to alkali from the glass, and it would not keep its calculated *p*H value for long. For standard purposes we must therefore use a "buffer" which will prevent rapid changes in *p*H, and we will explain the action of a buffer by considering the effect of adding some sodium acetate to acetic acid. The system in solution is $H^{\bullet}+Ac' \rightleftarrows HAc$, and there is a large concentration of Ac' due to the sodium acetate. If we add to this solution a few drops of a strong acid, such as would, if added to acetic acid alone, cause a big increase in $[H^{\bullet}]$, we shall get the added $H^{\bullet}$ reacting with Ac' thus: $H^{\bullet}+Ac' \rightarrow HAc$, so as to keep $\frac{[H^{\bullet}]\times[Ac']}{[HAc]}=K_A$. In other words, the value of $[H^{\bullet}]$ will not increase very much as long as there is large excess of Ac' present. Hence, a **buffer solution** usually contains a weak acid and a reserve of the anion supplied from a salt of this acid; *e.g.* boric acid and borax.

It is possible to calculate from the dissociation constant of an acid the value of *p*H which will be obtained by mixing it with one of its salts.

Gm. mols. of acetic acid per litre.	Gm. mols. of sodium acetate per litre.	*p*H.
·185	·015	3·6
·164	·036	4·0
·126	·074	4·4
·080	·120	4·8
·042	·158	5·2
·019	·181	5·6

These values may be plotted graphically, and from the curve we can read off quickly what mixture is required to obtain a

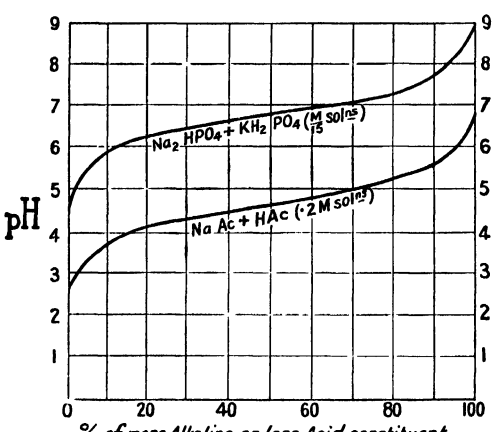


FIG. 47.—The preparation of solutions of known pH.

solution of definite *p*H. (See Fig. 47.) A great many such buffer solutions are available, but the sodium acetate-acetic acid mixture works well for solutions of *p*H between 3 and 6 and the Na_2HPO_4—KH_2PO_4 mixture for solutions of *p*H between 5 and 7.

Reliance is not placed entirely on these calculations, for

the solution when prepared is standardised by E.M.F. measurements which give pH with great accuracy. In fact, this method (the potentiometric method) * is always employed in preference to indicators when accuracy is required, owing to the difficulty of matching two colours with any exactness.

21. Electrochemistry.—The preceding paragraphs in this chapter have dealt with applications of the ionic hypothesis, and they have dealt almost entirely with aqueous solutions, the behaviour of solutions in other solvents being left for a more advanced course. The subject of electrochemistry, however, covers a much wider field than this, for it includes a study of the energy problems involved when electrical energy is obtained from chemical energy, or vice versa.

Since the beginning of the nineteenth century, when *Volta* designed the first electric cell, the two sciences have been firmly linked. The chemist uses electrical energy for electrolytic purposes, and the physicist employs chemical changes in his batteries for producing electrical energy.

Davy in 1807 seems to have been the first to identify chemical affinity with attraction between oppositely electrified atoms, and in 1812 *Berzelius* is found remarking that " Every chemical action is fundamentally an electrical phenomenon . . . Electricity is the first cause of all chemical action." The modern electron theory of matter leads us to suppose that this remark is in all probability correct.

The student of chemistry must therefore make a very complete study of the science of electricity if he is to get an insight into the mechanism of chemical changes. The theory of the voltaic cell forms the starting point of the " mutual science " of electrochemistry. This leads to the phenomenon of polarisation, and the necessity for a definite decomposition voltage which must be exceeded before electrolysis can proceed; *e.g.* for N hydrochloric acid with platinum electrodes 1·35 volts. It is then learnt that this decomposition voltage (or discharge potential) is the sum of two electrode potentials characteristic of the elements (or radicals) appearing at the electrodes. These have an important bearing on the control of chemical changes

* Findlay, *Physical Chemistry for Students of Medicine* gives details.

by electrolytic methods Electrolytic separation of metals is thus made possible, as in the refining of copper. The possibility of oxidising or reducing compounds by electrolytic methods must also be considered, as in the preparation of persulphates by electrolysing sulphates. This has important technical applications, and is largely concerned with the current density or $\frac{\text{current}}{\text{area of electrode surface}}$. Enough has been said to show that at the end of this brief course of physical chemistry we are still only at the beginning of a serious study of the subject. The foundations have been laid, but there is still a great deal to be done before we can realise the immensity of the building which has grown upon them.

DEMONSTRATIONS.—1. Show a model with moving strips of card to illustrate transport numbers.

2. Show qualitative experiments to illustrate solubility product and common ion effect, such as precipitation of silver acetate from a saturated solution by adding either silver nitrate or sodium acetate.

3. Show qualitative experiments to illustrate suppression of ions, solubility of salts in acids, and complex ion formation.

4. Show the movement towards the anode of the dark blue boundary between Fehling's solution and sodium tartrate during electrolysis. Comparison with a pale blue copper sulphate—sodium sulphate boundary moving towards the cathode, gives very convincing evidence for the existence of a complex ion in the Fehling's solution.

5. The hydrolysis of salts and the behaviour of indicators should be illustrated by the demonstration suggested on p. 251.

British Drug Houses, Ltd., supply materials (together with information in the form of a graph) from which solutions of known pH can be quickly and cheaply made up.

6. Titrate acids with strong and weak bases using the B.D.H. Universal Indicator. Hence derive curves showing how pH varies with the volume of acid added.

7. The phenomenon of polarisation should be illustrated, and the back E.M.F. of a simple voltaic cell measured.

PRACTICAL WORK.—1. Qualitative analysis reactions which can be interpreted ionically should be carried out.

2. Prepare pure sodium chloride from brine by precipitation with hydrochloric acid gas.

3. Determine the *p*H of solutions of normal salts by means of the universal indicator, and so draw conclusions as to the strengths of the acids and bases composing these salts.

4. Titrate strong and weak acids with caustic soda and ammonia, using various indicators, and discuss the results.

5. Titrate phosphoric acid with caustic soda and various indicators and discuss the results. Prepare the three sodium phosphates and determine *p*H for *N* solutions of each.

6. Determine the relative strengths of acids by the thermometric measurement of partition; or with weak acids by Methods II. and III.

QUESTIONS.—1. In a $\frac{N}{10}$ solution of sodium chloride the transport number of the anion is ·617. What does this mean? What information as to the nature of a solution can be obtained from measurements of transport numbers?

2. What is meant by the "mobility" of an ion? Distinguish between this and "absolute mobility." If $\lambda_\infty = 109{\cdot}0$ for sodium chloride solution, and the transport number for the anion is ·604, what are the mobilities of $Na^{\cdot}$ and Cl'?

3. How is λ_∞ determined for a weak electrolyte? Calculate λ_∞ for monochloracetic acid from the following data: λ_∞ for sodium monochloracetate $= 117{\cdot}3$; mobility of $H^{\cdot} = 314$, of $Na^{\cdot} = 43{\cdot}3$.

4. Determine (*a*) the solubility, (*b*) the solubility product of silver bromide from the following data: the specific conductivity of a saturated solution of silver bromide is $\cdot 06 \times 10^{-6}$ mho (allowance having been made for the conductivity of the water); mobilities $Ag^{\cdot} = 54{\cdot}0$, $Br' = 67{\cdot}7$.

5. Explain in terms of the ionic hypothesis (*a*) the separation of copper from iron in qualitative analysis, (*b*) the use of ammonium chloride in qualitative analysis, (*c*) the solution of calcium oxalate in hydrochloric acid, and its reprecipitation by ammonia, (*d*) the precipitation of solid barium chloride when concentrated hydrochloric acid is added to a concentrated solution of barium chloride.

6. Write an essay on "complex ions and the evidence for their existence."

7. By applying the law of mass action to the equilibrium between ions and unionised molecules in a solution derive the dilution law. If K_A for benzoic acid is $6{\cdot}7 \times 10^{-5}$ calculate (*a*) the degree of ionisation, (*b*) the concentration of hydrion in a $\frac{N}{100}$ solution.

8. The ionic product of water is 10^{-14} at 25° C. What does this

mean? A solution has $[H^+]=2\cdot5\times10^{-6}$. Determine the values of $[OH']$ and pH for this solution. What volume of $\frac{N}{1000}$ caustic soda will exactly neutralise 100 c.cs. of it?

9. Why is a solution of sodium benzoate alkaline with respect to water? If K_A for benzoic acid is $6\cdot7\times10^{-5}$ calculate the degree of hydrolysis of sodium benzoate in $\frac{N}{100}$ solution. $K_w=10^{-14}$.

10. Summarise the methods by which the strengths of acids can be compared.

11. Describe in detail how you would compare the strengths of $\frac{N}{10}$ caustic soda and $\frac{N}{10}$ baryta.

12. Write an essay on " indicators and their use."

13. Explain with the help of curves the changes in $[H^+]$ which occur during the titration of N HNO_3 with N NaOH.

14. What is a " buffer solution " ? How can an indicator be calibrated for use as a check on the value of $[H^+]$ in a given solution?

PART IV.—THE BUILDER'S TASK

CHAPTER XIV

THE NATURE OF MATTER

1. The fascinating question of what is inside the atom cannot be answered in a few pages. No doubt when it is answered we shall be well on our way towards an " explanation " of all chemical and physical changes, and a stage nearer the completion of our temple of science. It is true that great progress has been made recently, but there are still large gaps to be seen in our building; thus, the nature of solutions and the mechanism of chemical changes are still not understood. Even the scaffolding seems none too secure in places; the ionic hypothesis, for example, when applied to strong electrolytes, has had to be drastically revised. But, on the whole, the work is proceeding satisfactorily, and we may pause awhile to look at some of the recent additions.

It will be necessary in this limited space to state and make use of many experimental results without giving any account of how they have been obtained, and even then only a few of the more important lines of progress can be mentioned.*

2. The Passage of Electricity through Gases.—At low pressures gases will conduct the electric current, and curious phenomena were observed as long ago as 1878 by *Sir Wm. Crookes* when working on these lines. He was able to prove

* The following books are recommended for reading at this stage: Kendall, *At Home among the Atoms;* Russell, *The ABC of Atoms;* Sullivan, *Atoms and Electrons;* Butler, *The Chemical Elements;* Cranston, *The Structure of Matter;* Caven, *Atoms and Molecules;* Aston, *Isotopes;* Thomson (G. P.), *The Atom.* For more advanced treatment see Andrade, *The Structure of the Atom;* and Sidgwick, *The Electronic Theory of Valency.*

the existence of a stream of negatively charged particles proceeding from the cathode which he called **cathode rays**. In 1897, *Sir J. J. Thomson* established that these were excessively small (the mass of each being about $\frac{1}{1800}$ of the mass of a hydrogen atom); that they all carried the same electric charge; and that they were travelling at a very high speed, which was about one-third that of light. He called them **electrons** (using a word invented in 1891 by *Johnstone Stoney*). Now *Townsend* has proved the charge on each electron to be the same as that carried by univalent ions during electrolysis, so this quantity of electricity is clearly of fundamental significance. The electron is in fact considered to be the **unit of negative electricity.** The unit of positive electricity was not identified until much later (see para. 6).

3. Radioactive Elements were investigated from 1895 onwards by *Becquerel, Mme. Curie, Soddy* and others. They were found to be spontaneously disintegrating, and emitting streams of positively charged helium atoms (known as α particles); streams of electrons (known as β particles); and radiation of very high frequency (known as γ rays). A relatively enormous amount of energy is evolved during disintegration. Thus, 1 gm. of radium produces 156 c.cs. of helium in a year and the energy output is about 100 calories per hour. The result of disintegration is that the atom of a radioactive element changes into an atom of another element. *E.g.* thorium in course of time changes into lead.

The discovery of this spontaneous transmutation of the elements caused much excitement, and it has been followed by even more startling results in recent times—artificial transmutation of the elements. This was first achieved by *Sir Ernest Rutherford* in 1919, who bombarded nitrogen atoms with charged helium atoms (α particles). He found that the nitrogen disintegrated into helium and hydrogen, and since that time many examples of transmutation have been noted. None, of course, has any commercial value, owing to the amount of energy which has to be employed.

NOTE.—The word "disintegrated" is purposely used in place of "decomposed," for we still claim that nitrogen is an

element (see reasons given in para. 7). The change must not therefore be regarded as an ordinary chemical change or decomposition.

Attempts to place the radioactive elements (uranium, thorium, radium, ionium and many others) in the periodic table led *Soddy* to a wonderful explanation of their disintegration which has since been amply verified. Before we can understand this we must consider briefly the electronic conception of valency which *Soddy* made use of and which was put forward by *Sir J. J. Thomson* in 1904.

4. Valency according to the Electron Theory.—Thomson assumed that an atom would consist of rings of electrons embedded in a sphere of uniform electrification, and he showed that it could only be a stable structure as long as the number of electrons in each ring did not exceed some definite value. Thus, if we imagine an atom being built up by the gradual addition of electrons to a positive "nucleus," * we are to believe that as soon as we have "filled up" a ring to its maximum capacity the next electron added would start a new ring. Thomson considered that *every atom would strive to reach a state of maximum stability by gaining or losing electrons in such numbers as to leave its outer ring "full up." The number of electrons so gained or lost would measure its valency*. This view gave a ready interpretation of the periodic table (see below), and it is now generally accepted.

Between 1916 and 1922, mainly through the researches of *Bohr*, *Langmuir*, *Lewis* and *Bury*, it was established that *the "stable structures" suggested by Thomson were the atoms of the inert gases*, and that in these the electrons were arranged as follows: He 2; Ne 2, 8; A 2, 8, 8; Kr 2, 8, 18, 8; Xe 2, 8, 18, 18, 8; Rn 2, 8, 18, 32, 18, 8. Every other atom strives to reach one of these stable states. Thus, an atom like chlorine having seven electrons in its outer ring needs only one more to

* It has been shown that Thomson was wrong in regarding the positive charge as occupying the whole volume of the atom. It is now believed to be contained in a minute "nucleus" around which the "valency electrons" mentioned above revolve in complicated orbits (see p 266).

reach the argon structure. In picking it up it becomes a univalent negative ion $Cl \rightarrow Cl'$. Again a magnesium atom with two electrons in its outer ring will *lose* two electrons (becoming thereby a bi-valent positive ion $Mg \rightarrow Mg^{\cdot\cdot}$) in order to reach the neon structure. Chlorine ions and magnesium ions are thus seen to be stable structures. The outer ring of electrons is full up in each case.

Now, since the number of electrons required to fill the outer ring appears to be eight in every case (after helium), the periods of eight in Mendeleef's Table are easily explained. Thus sodium with one electron in its outer ring reproduces the properties of lithium, which has similar structure; chlorine resembles fluorine with seven electrons in the outer ring; and so on.

N.B.—If both positive and negative valencies are shown by the same element they usually add up to 8; *e.g.* nitrogen in NH_3 and N_2O_5.

Finally it will be noted that short and long periods are accounted for by the necessary filling up underlying rings from 8 to 18 or 32 before additions can be made to the outer ring.

5. Soddy's Disintegration Hypothesis.—It appeared that if an atom lost an electron, its valency would increase by one, and it would move from one group of the periodic table to the group preceding it. Thus, Group II. contains bivalent atoms of magnesium calcium, and mercury; loss of an electron would reduce their electropositive valency to 1, so that they would have to take their place in Group I. with sodium, potassium, and gold. Now loss of electrons does not appreciably alter the mass of an atom, but during radioactive disintegration α particles are sometimes shot out as well. These are helium atoms of mass 4 and they carry two positive charges, so that each α particle lost means 4 units less mass in the atom, and a change in valency in the opposite direction to that produced by loss of an electron; *i.e.* a movement towards the right of the periodic table. Again, the decrease in atomic weight would tend to take the element from the bottom to the top of the table. Hence, it appeared to *Soddy* that by means of such changes, an atom could possibly come to occupy the position of some

other element in the table. An atom of uranium (atomic weight 238) by losing 8 α particles and 6 electrons could in this way become an atom of lead (atomic weight 206), and we know that uranium does turn into lead! Moreover it should be possible for several different elements to end up in the same place in the periodic table by disintegration of this kind, but they would in such cases differ in the masses of their atoms. Thus: lead from uranium $=238-8\times4=206$; lead from thorium $=232-6\times4=208$. There was already one case known of two elements differing only in radioactive properties, but so similar in all chemical properties that they could not be separated when mixed (ionium and thorium), so that the notion of two different elements occupying the same place in the periodic table was not altogether new.

Soddy coined the word "isotopes" * for such cases. The lead from thorium and the lead from uranium were therefore called isotopes of lead; they differ in atomic weight, but are chemically identical. Ordinary lead has an atomic weight $=207{\cdot}2$, so that unless this is another isotope it must be a mixture of these two. Hence we arrive at the notion that an element may be a mixture; *i.e.* some of its atoms may be of one isotope, and some of another. Chlorine is now known to possess atoms of mass 35, and atoms of mass 37. The chlorine which the chemist always handles however (even in compounds), has the constant atomic weight of 35·46, so that this is regarded as a **mixed element** in which the proportions of the isotopes is always the same. A **pure element** is one in which all the atoms are identical.

The existence of these isotopes has been verified by sifting out the atoms of different masses from the mixtures which exist in ordinary matter, by means of electrical and magnetic fields. It was in 1912 that *Sir J. J. Thomson* first applied **positive ray analysis** (as it has been called) to this problem, and neon was at once shown to be mixed—consisting of atoms of mass 20 and 22 in such proportions as to give the chemical (or mean) atomic weight 20·20. From 1919 onwards *Aston*, at the Cavendish Laboratory in Cambridge, has

* ἴσος—τόπος (the same place).

developed this experimental method, and with his **mass spectrograph** has shown that most of the elements are mixed. Mercury, for example, has at least six isotopes, and tin as many as eight.

The old idea that an element is characterised by all its atoms being the same, and of definite weight, must clearly be abandoned. Indeed, it is possible to separate an element into its isotopes on a small scale by taking advantage of the difference in their masses (by diffusion). So that after all an element may be a mixture, and it can also disintegrate into other elements, much as a compound does! What then is an element? Before we can answer this we must introduce the "proton."

6. The Nucleus. Protons.—All matter contains electrons. What else is present? It must, whatever it is, carry positive charges of electricity, and also constitute the mass of the atom, for the atom is electrically neutral, and electrons are negatively charged and of practically no mass. The work of *Sir Ernest Rutherford* has established that all atoms are complicated structures consisting of a very minute nucleus, in which the mass of the atom is concentrated, and rings of electrons round the nucleus, which are responsible for the atom's chemical properties—valency, reactivity, etc. The nucleus itself is a complex structure (except in the hydrogen atom) although it is so small, being made up of units of positive electricity (called **protons**) and units of negative electricity (electrons). The whole nucleus will thus have a net positive charge if it contains more protons than electrons, and since the whole atom is electrically neutral this must be balanced by the negative charge due to all the electrons outside the nucleus (the "valency electrons"). **Now the unit of positive electricity (or proton) has been shown to be the nucleus of the hydrogen atom.** Hydrogen is the only element whose atomic nucleus contains no electrons. The ordinary uncharged hydrogen atom is therefore made up of one proton and one valency electron. Loss of the latter converts it into a univalent electropositive ion.

All matter is therefore made up of the same "bricks," as

Aston has put it,—protons and electrons; * and **the mass of the atom is the mass of all the hydrogen nuclei in it, which is numerically equal to the number of protons. Also it is clear that the number of valency electrons is equal to the net nuclear charge** (see Fig. 48).

EXAMPLE.—An atom of lithium (atomic weight 7) has 7 protons and 4 electrons in its nucleus. The net nuclear charge of +3 is balanced by the charges on the 3 electrons outside, two in the first ring and one in the outer ring. It is therefore an electropositive univalent element (see Fig. 48).

NOTE.—If the atomic weight of an element is the sum of the masses of all the hydrogen nuclei in its atom, we should expect all atomic weights to be whole numbers (H=1). The atomic weights considered must, however, be those of the actual atoms (or isotopes) and not the mean or chemical atomic weights determined by chemical analysis. Aston's mass spectrograph has enabled him to determine the masses of the isotopes directly, and with very few exceptions they are found to be whole numbers, when allowance is made for certain explicable deviations.

7. Atomic Number.—If the elements are arranged in the order in which they appear in the periodic table, we can number them from 1 to 92 (allowing gaps for undiscovered elements) in going from hydrogen to uranium. The number assigned to any element in this way is termed its "atomic number." †

Thus:

H	He	Li	Be	B	C	N	O	F	Ne	Na	etc.
1	2	3	4	5	6	7	8	9	10	11	

* This affords wonderful confirmation of earlier speculations, such as the alchemists' ideas as to the common ingredients of matter which needed only the "philosopher's stone" to transmute one kind into another. The hypothesis of Prout (1815) that all elements had whole number atomic weights (being in fact condensed hydrogen atoms) was nearer the mark, and Sir Wm. Crookes, with his suggested "protyle" as the primordial substance from which all matter was evolved (1886), perhaps the nearest of all.

† Uranium is the heaviest element known at present, and it is therefore believed that there are 92 elements altogether. Only two of these now remain undetected (Nos. 85 and 87).

The atomic number is found to have a very fundamental significance. It is in fact **equal to the net nuclear charge.** This startling result was arrived at in 1911 by *Van den Broek* following experimental work by *Barkla* and by *Rutherford*, who were working on quite different lines. It is quite securely established, though the evidence cannot be discussed here. Fig. 48 indicates the fact diagrammatically.

It should now be clear that isotopes are atoms which have the same net nuclear charge (*i.e.* same atomic number and position in the periodic table), but different actual numbers of protons in the nucleus. The atomic weights will therefore be different but the atomic numbers the same.* An atom of mass 3 with only 1 electron in the nucleus would have atomic number 2 (an isotope of helium). It would be univalent, having 3 electrons outside the nucleus.

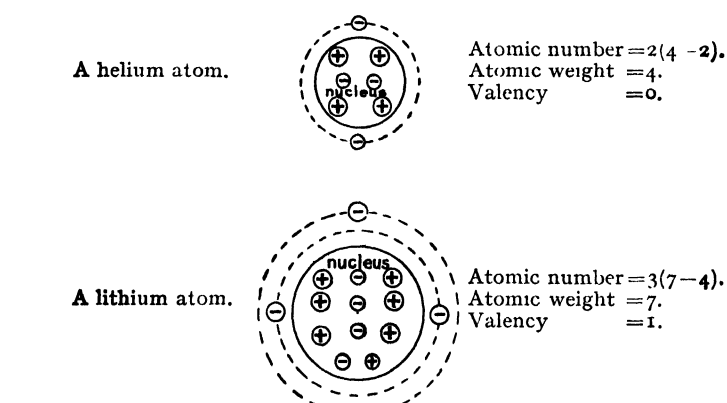


FIG. 48.

SUMMARY.—(1) Nuclear protons confer mass on the atom.

(2) Net nuclear charge decides the atomic number and the number of electrons outside the nucleus.

(3) The electrons outside the nucleus fix the chemical

* The reverse is also possible. Two elements of different atomic number but the same atomic weight are termed isobares.

properties of the atom. **Atomic number is therefore the fundamental characteristic of an element.**

(4) Radiations emitted by elements under certain conditions and recognised by their spectra (see below) are due to vibrations of the valency electrons. These spectra are therefore characteristic of the element.

Hence, **an element** *is composed of atoms which have a definite atomic number, definite valency and other chemical properties, and which produce definite spectra. By these it can be identified. Its atoms do not necessarily all possess the same mass or the same radioactive properties, for these depend upon the composition of the nucleus. An element is therefore not necessarily homogeneous or indivisible, and the mass spectrograph will reveal the presence or absence of isotopes.*

8. Experimental Determination of Atomic Numbers.—We can determine the net charge on the nucleus of an atom, and so arrive at the probable nature of the element, by determining experimentally its **atomic number.** The method was devised by *Moseley* in 1913, whose brilliant researches were unfortunately terminated by the war. He established that the atomic number of an element was proportional to the square root of the frequency of the radiations which its atoms could be made to emit under certain circumstances. The frequency of these radiations was very great, so that they constituted what are known as X-rays. Thus, an element when suitably excited emits X-rays of a definite frequency, and Moseley's law is that the atomic number $\propto \sqrt{\text{frequency of X-rays emitted}}$. Measurement of the X-ray frequency therefore constitutes the experimental work necessary for determination of the atomic number.

Moseley's work proved beyond doubt that the periodic table of Mendeléef was rather a lucky fluke. If the atomic weights of the elements were not in most cases nearly proportional to their atomic numbers this table would never have existed, and we must remember that Mendeléef's atomic weights were the chemical or mean atomic weights, not the actual relative weights of the atoms. As a matter of fact argon and potassium, tellurium and iodine, cobalt and nickel

did come out of place in his table. Moseley's work showed that the order stated is the correct order of their atomic numbers though not of their atomic weights.

NOTE.—When an element is rendered incandescent it emits radiations of frequency less than X-rays. These give rise to line spectra which also afford means of identifying elements, as they are due to its valency electrons. They do not give any direct clue to the value of its atomic number.

9. The Electron Theory and Chemical Change.—All matter appears to be composed of electric charges, and attraction between opposite charges would thus account for the clinging together of atoms. Each atom is supposed to be trying to adjust the number of its electrons to the stable number, which is found in the inert gases (see p. 263). It does this by accepting elcctrons from other elements, or by giving some away, and in so doing the neutral atom becomes a charged ion. Two ions of opposite sign would cling together by electrostatic action, unless kept apart in some way, such as by the solvent action of water. Thus, a sodium atom has one electron in its outer ring, and a fluorine atom has seven. The result is called a " polar " compound (sodium fluoride) in which the positively charged sodium ion is holding the negatively charged fluorine ion. The analysis of the crystal structure of sodium fluoride has actually verified the existence of these ions as the particles forming the space lattice, inasmuch as both the sodium and fluorine particles are found to have 10 electrons outside the nucleus, and their atomic numbers are 11 and 9 respectively.

This type of combination is said to be due to electrovalency (the actual " chemical change " is the electron transfer ; what follows is electrical attraction) ; but there is another type of combination in which two atoms mutually share one or more pairs of electrons. Thus, in O_2, or the " non-polar " compound CO_2, the " bonds " which hold the atoms together are real " chemical bonds," unlike the electrical forces holding the $Na^{\cdot}$ and F' of sodium fluoride. These atoms will not come apart so as to form oppositely charged ions, and the term " co-valency " is employed to indicate that we believe in this case that some of the electrons are shared by the atoms concerned.

10. Conclusion.—Modern research proceeds faster than we can follow. In these pages many fascinating developments have of necessity been left completely untouched, such as the quantum theory applied to chemical problems; the relation between physical properties and chemical constitution; and the co-ordination theory of valency developed in accordance with modern views. The object of this book has been to stimulate questions and a thirst for more knowledge, so that its incompleteness will have been justified if at this point the reader desires to know more about matter and its properties.

ANSWERS TO NUMERICAL QUESTIONS

Chapter	II. p. 10.	No. 2.	380,300.
		No 4.	108.
„	III. p. 31.	No. 6.	At. wt. 48·0; valencies 3 and 4; formulæ for oxides: Ti_2O_3 and TiO_2.
		No. 7.	113·7.
		No. 8.	118·8.
„	VII. p. 123.	No. 6.	28 cms.
		No. 7.	39.
		No. 8.	59·9 cms.
		No. 9.	11·80 mms.
„	IX. p. 163.	No. 7.	122·4.
		No. 8.	184.
		No. 9.	263.
		No. 10.	30·86; 80 %; 100·062° C.
		No. 11.	Composition by weight: 88·8 % As_4O_6; 11·2 % As_2O_3.
		No. 12.	194·4.
„	X. p 186.	No. 1.	·00033.
		No 5.	92·3 %.
„	XI. p. 214.	No. 8.	112×10^{-7} gm. mol. per c.c. per sec.
		No. 9.	Hydrogen 2·21 gm. mols. per litre. Iodine 0·21 gm. mol. per litre Hydrogen iodide 5·58 gm. mols. per litre.
„	XII. p. 221.	No. 4.	+29,000 cals.
		No. 5.	+96,300 cals.
		No. 6.	Heat of formation is −47,000 cals.
		No. 7.	+15,000 cals.
„	XIII. p. 259.	No. 2.	43·2 and 65·8.
		No. 3.	388 mhos.
		No. 4.	$9·3 \times 10^{-5}$ gm. per litre; $2·4 \times 10^{-13}$.
		No. 7.	7·9 %; ·00079 gm. equivalent per litre.
		No. 8.	4×10^{-8}; 5·60; 0·25 c.cs.
		No. 9.	·012 %.

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