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RECENT ADVANCES IN GENERAL CHEMISTRY

BY

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PREFACE

In recent years there have been highly important developments in a number of fields in the borderland between physical chemistry, on the one hand, and inorganic or organic chemistry, on the other hand; some of these subjects, which may be included under the title of "General Chemistry," have been reviewed in the chapters of the present volume. The book is intended as a companion to the writer's "Recent Advances in Physical Chemistry," and it is meant to appeal to the same type of reader, namely university students, both of graduate and undergraduate standing, and those who have left the university but wish to keep abreast of recent progress in chemistry. The increasing pressure of modern conditions leaves little time, either to professional chemists, to teachers or to students, for a comprehensive study of the original literature, or even of the monographs on special topics which are published from time to time. It has been the object of the writer to condense the large amount of material available and to present it in a simple and palatable form. To workers in the various fields considered the treatment may often appear to be over-simplified; although this is the only course open in a book of the present type, the useful purpose may be served of arousing the interest of those who prefer to approach a difficult subject by way of an elementary introduction. A list of selected references is given at the end of each chapter for those who wish for further information; review papers and monographs are specially marked with an asterisk.

The style of the book is similar to that of the "Recent Advances in Physical Chemistry"; the author has been gratified by the knowledge that chemists of all grades have found the latter useful in various ways, and it is hoped that the "General Chemistry" will prove equally popular. Although the two books may be read quite independently, there are frequent cross

references from one to the other; as far as possible, however, material required for the understanding of the subject matter of any chapter is given in a preceding one of the same volume. The chapter on "Solubility," which was omitted from the second edition of "Recent Advances in Physical Chemistry," has been revised and included in the present work as a result of requests from many quarters. The section on "Acid–Base and Salt Catalysis" has also been transferred to allow space for necessary expansion; both these chapters fit in well with the scope of this book.

A cursory examination may give the impression of the presence of many mathematical symbols; the extent of the actual mathematics is, however, quite small. The inclusion of some equations and formulæ is inevitable, but wherever possible an effort is made to give the physical significance of any expression of which the meaning is not directly obvious. Some explanation is perhaps necessary for the chapter on "Statistical Methods"; the subject is undoubtedly a difficult one, but the fundamental ideas are simple, and a knowledge of these is essential to an understanding of the chemistry of hydrogen and of modern theories of reaction velocity. Both these subjects are already having an important influence, and it is safe to prophesy that a great deal more will be heard in the near future of the "partition function" concept.

The author wishes to acknowledge his indebtedness to several valuable monographs of which he has made free use in the compilation of this book and which have greatly minimised the labour involved; amongst these special mention must be made of Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen"; Hildebrand, "Solubility"; Moelwyn-Hughes, "Kinetics of Chemical Reactions in Solution"; and Rice and Rice, "Aliphatic Free Radicals." Thanks are also due to Professor P. M. S. Blackett, F.R.S., Professor J. Chadwick, F.R.S., Dr. V. E. Cosslett, Dr. P. I. Dee, Dr. A. Farkas, Dr. G. P. S. Occhialini, Dr. J. T. Randall, and the Royal Society, for permission to reproduce figures, and to a number of others, especially Dr. C. D. Anderson and Professor H. C. Urey, whose work has been used in the preparation of the diagrams. The writer must again

express his gratitude to his wife for her assistance in correcting the proofs and for her help in innumerable ways.

Finally, the author would like to take this opportunity to place on record his high appreciation of the courtesy and consideration which he has always received from the publishers, Messrs. J. & A. Churchill Ltd., and of the helpful co-operation of the printers, The Whitefriars Press Ltd.

S. G.

SHEFFIELD.

CONTENTS

CHAP.		PAGE
	PREFACE	v
I.	ATOMIC DISINTEGRATION	1
II.	STATISTICAL METHODS	53
III.	ORTHO- AND PARA-HYDROGEN	98
IV.	DEUTERIUM AND ITS COMPOUNDS	136
V.	ELECTRON DIFFRACTION BY GASES AND VAPOURS	189
VI.	SOLUBILITY	229
VII.	THE MECHANISM OF REACTIONS IN SOLUTION	269
VIII.	ACID–BASE AND SALT CATALYSIS	328
IX.	SIMPLE ORGANIC FREE RADICALS	377
	INDEX	425

RECENT ADVANCES IN GENERAL CHEMISTRY

CHAPTER I

ATOMIC DISINTEGRATION

THE investigation of atomic disintegration is generally regarded as the prerogative of the physicist, but the results obtained in the past few years in this connection are of such fundamental importance that a survey of them is desirable. The existence of new elementary particles has been brought to light, and hitherto unsuspected phenomena, such as those of artificial radioactivity, have been discovered which are of definite chemical interest and importance. Further, some surprising results have been obtained in connection with the atomic weights of the lighter elements.

DISINTEGRATION BY ALPHA-PARTICLES

Emission of Protons. In 1919 Rutherford noted that when fast-moving helium nuclei, that is α-particles, from a radioactive source, such as radium-*B* and -*C*, are passed through nitrogen gas, scintillations on a zinc sulphide screen indicated the formation of a number of new particles of long range. These particles were found to carry a single charge of positive electricity and to have a mass of unity; that is to say, they were hydrogen nuclei, or protons, resulting probably from the disintegration of the nitrogen nucleus consequent upon impact with the α-particles. The protons could not have been produced from hydrogen present as an impurity, since the maximum range of the particles obtained by the passage of α-rays through hydrogen gas was 28 cm., whereas the protons from nitrogen had a range up to 40 cm. in air. Later (1921, 1922, 1924) Rutherford and Chadwick, using an improved

apparatus, found that protons were liberated in the same manner from all elements between boron and potassium, inclusive, with the exception of carbon and oxygen, and possibly of lithium and beryllium. Kirsch and Petterson (1924, 1925) claimed to have disintegrated even these four elements to yield protons, and although there was some difference of opinion on this point, the main fact that artificial disintegration of matter had been achieved was beyond dispute.

Mechanism of Disintegration. Two obvious mechanisms for the process resulting in the liberation of protons are possible: (*a*) the nucleus of the disintegrated atom merely loses a proton ($^1_1$H) as a result of the severe impact it receives on collision with an α-particle ($^4_2$He); or (*b*) the α-particle enters the nucleus on impact and the resulting complex ejects a proton; for nitrogen these alternatives can be indicated by

$$(a) \qquad {}^{14}_{7}\mathrm{N} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{13}_{6}\mathrm{C},$$

and

$$(b) \quad {}^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{17}_{8}\mathrm{O},$$

where each symbol represents the nucleus of the corresponding element, the lower prefix giving the atomic number, that is, the net positive charge on the nucleus, and the upper prefix the mass number, that is, the whole number nearest to the isotopic atomic weight. In disintegration equations, of which those given above are typical, it is of course essential that the sums both of the positive charges, and of the mass numbers, should be the same before and after the disintegration process. If a nitrogen nucleus loses a proton, as in equation (*a*), it is evident that the residual nucleus must carry six positive charges, and so be an isotope of carbon; the mass is, however, 13 and so the product would be the ^{13}C isotope which is present to a small extent in ordinary carbon. Similarly, process (*b*) would give as product an oxygen isotope of mass 17; this is also present in normal oxygen.

A distinction between the alternative modes of disintegration was made possible by the work of Blackett (1925) and of Harkins (1928); these authors used the Wilson method of photographing "cloud tracks" in an expansion chamber, and from a large number of experiments a few tracks were found showing collisions

resulting in the liberation of protons. As in the work of Rutherford and Chadwick, there appeared to be only about twenty fruitful collisions for every million α-particles of 7 cm. range shot into the nitrogen; the disintegration is, therefore, a comparatively rare event. The tracks indicating a disintegrative collision showed that the α-particle disappeared and that two new tracks were formed: a long track, undoubtedly due to the proton, and a very much shorter one resembling that resulting from the elastic collision of an α-particle with a nitrogen nucleus. It appears, therefore, that in the disintegrating impact the atomic nucleus, *e.g.*, nitrogen, takes up the α-particle, discharges a proton and leaves a nucleus of mass number 17 and atomic number 8, that is, an oxygen nucleus, which gives the short track. The photographs also showed clearly that only one proton is produced at each impact, and so the mechanism of disintegration is the second of the two types discussed: the same kind of mechanism is apparently applicable to other atoms besides nitrogen.

Conservation of Mass and Energy. Further information concerning the disintegration process may be found in the following calculations based on the idea of the equivalence of mass and energy. In the disintegration of boron by α-particles of 3·6 cm. range it is very probable that the isotope of mass 10 is actually involved, giving rise to the proton; according to the views expressed above the process would be represented by

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

the product being an isotope of carbon. From mass-spectrographic determinations the atomic weights of ^{10}Be and ^{4}He are 10·0135 and 4·00216, respectively, making a total of 14·01566, and those of ^{1}H and ^{13}C are 1·00778 and 13·0039, adding up to 14·01168; there is thus a net loss of mass of 0·0040 in atomic weight units.* In the calculation given here and in other parts of this chapter, the masses of the nuclei should, strictly speaking, be employed, since these are actually involved in the processes discussed. It is a matter of convenience, however, to use the

* It will be seen later (p. 28) that the atomic weights used here are probably incorrect, but the substitution of the corrected values makes very little difference to the net mass lost in the process under consideration.

actual isotopic atomic weights, as obtained from mass-spectroscopic or other investigations. This merely means that the weights of the " orbital " electrons are added to the weights of the nuclei : the number of electrons being the same on both sides of any disintegration equation, the additional weights cancel. The mass of 0·0040 units which has disappeared in the boron disintegration must have been converted into energy, equivalent to mc^2 ergs, m being the mass lost and c the velocity of light in cms. per sec. In order to convert the energy in ergs into electron-volts, the units generally employed in this work, the former value is multiplied by $300/e$, where e is the electronic charge, $4{\cdot}77 \times 10^{-10}$ e.s.u. The mass lost in the disintegration under discussion is consequently equivalent to $3{\cdot}6 \times 10^6$ electron-volts; and the hydrogen and carbon nuclei which result should have this amount of energy in excess of that originally present on the boron and helium nuclei. The energy of the boron is negligible, but that of the α-particle is appreciable and is known from its range, which is related to its velocity. A number of observations have been made of the ranges, and hence of the energies, of the protons expelled from boron by α-particle bombardment and the values, although varying somewhat amongst themselves, indicate that the excess energy carried by them is of the order calculated from the masses of the nuclei involved in this disintegration. This agreement not only provides evidence for the mode of disintegration proposed, but also for the equivalence of energy and mass postulated by the theory of relativity.

It may be mentioned that the bombardment of elements by means of α-particles often gives rise to several groups of protons having different ranges and energies : the boron isotope ^{10}B, for example, gives at least three, and probably five, such groups.* One of these, consisting of the longest range and highest energy protons, corresponds to the disintegration just considered resulting in the formation of ^{13}C in its ground state ; a second group made up of protons of lower range and energy is believed to be due

* It has been stated that in addition to protons, the nuclei of deuterium are obtained by the bombardment of boron by α-particles, thus $^{10}_{5}B + {}^{4}_{2}He \longrightarrow {}^{2}_{1}D + {}^{12}_{6}C$.

to the fact that some of the energy remains on the ^{13}C nucleus, which is thus in an excited state. A study of the different groups of protons emitted during disintegration can hence throw some light on the energy levels within the atomic nucleus: so far relatively little information of this kind is available, but more will no doubt be forthcoming, and this may well prove to be of considerable value in elucidating the structures of nuclei.

Resonance Levels. Before an α-particle can enter the nucleus of an atom it must overcome an energy barrier, equivalent to a force of repulsion, around the nucleus. Experiment has shown, however, that during the bombardment of various elements there are certain stages, as the velocity of the α-particles is increased, their energies being still insufficient to permit them to pass over the top of the barrier, at which they undoubtedly pass *through* it, and give rise to proton emission. In between these stages the extent of disintegration is small. This effect has been ascribed to the presence of " resonance levels " in the nucleus of the atom which is struck by the α-particle, and that when the latter possesses energy equal to one of these levels passage through the barrier can occur. When the energy of the particle is more than sufficient for the barrier around the nucleus to be surmounted the extent of disintegration increases steadily with the speed. With magnesium, for example, emission of protons occurs continuously if the energy of the bombarding α-particles exceeds $6{\cdot}5 \times 10^6$ electron-volts, but below this value appreciable disintegration occurs only if the energies are $6{\cdot}3$ or $5{\cdot}7 \times 10^6$ electron-volts: the nucleus of magnesium evidently has resonance levels corresponding to these two values. Observations of this kind are also likely to be of value in contributing towards the eventual development of a theory of the structure of atomic nuclei.

THE NEUTRON

Discovery of the Neutron. In the course of an investigation of the effect of α-particles on atomic nuclei, by Bothe and Becker (1930), it was found that certain light elements, especially beryllium, when bombarded by α-particles from polonium, emitted a

radiation which appeared to be similar to γ-rays. Later observations by Bothe (1931), Joliot-Curie (1931) and Webster (1932) showed that their penetrating power was much greater than the radiations from any radioactive element, and Webster found that boron gave rise to rays of even greater penetrating power. These radiations were able to eject protons with considerable velocity from hydrogen, helium, carbon, air and argon (Joliot-Curie and Joliot, 1932; Chadwick, 1932), and from an analysis of the speeds and masses of the nuclei involved Chadwick showed that mere radiation could not have been responsible for the observed disintegration. He, therefore, put forward the suggestion that the so-called radiation discovered by Bothe and Becker consists of particles of mass nearly equal to that of the proton but having *no net charge*; these are the " neutrons " the existence of which, as a unit of nuclear structure, had frequently been postulated. Collision of neutrons with atomic nuclei is then responsible for the ejection of the high-velocity protons; this mechanism is in harmony with the observed speeds of the recoil atoms, as will be shown later. Chadwick considered the neutron to arise from the disintegration following the capture by a beryllium or boron nucleus of an α-particle; thus

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{0}n + {}^{12}_{6}\mathrm{C},$$

the symbol ${}^{1}_{0}n$ being used to represent the neutron, having no charge but unit mass.

Velocity of the Neutron. This suggestion can be partially verified by a consideration of the masses and velocities of the particles concerned. The beryllium nucleus may be assumed to consist of two α-particles and one neutron, and so the atomic weight of the ^{9}Be isotope would be $(2 \times 4{\cdot}00216) + {}^{1}n$, where ${}^{1}n$ represents the mass of the neutron; the mass of the helium atom corresponding to the captured α-particle is 4·00216 and its kinetic energy is equivalent to 0·00565 atomic weight units, making a total mass equivalent of $12{\cdot}01213 + {}^{1}n$ before disintegration. The atomic weight of ^{12}C is 12·0036, and so the difference, $(12{\cdot}01213 + {}^{1}n) - (12{\cdot}0036 + {}^{1}n) = 0{\cdot}00853$, which is equivalent to $7{\cdot}8 \times 10^{6}$ electron-volts, should appear as kinetic

energy divided between the carbon nucleus and the neutron. The maximum kinetic energy of the latter, ejected from beryllium, should thus be $7{\cdot}8 \times 10^6$ electron-volts, which would give it a velocity of about $3{\cdot}9 \times 10^9$ cm. per sec. Since the mass of a neutron must be almost the same as that of a proton it is reasonable to suppose that the maximum velocity of the two particles would be very similar ; the highest observed velocity for a proton is $3{\cdot}3 \times 10^9$ cm. per sec., and the supposition of a similar value for the neutron would be in harmony with Chadwick's views concerning its origin.

Production of Neutrons. The bombardment of beryllium gives about thirty neutrons per million α-particles, smaller yields being obtainable from lithium, boron, fluorine, neon, sodium, magnesium, aluminium and phosphorus. No element of higher atomic number has yet been made to yield neutrons by impact with α-particles : this may be due to the increased repulsion of the two positively charged nuclei, that is, to the increased height of the energy barrier round the nucleus to be entered. It is not improbable that if α-particles of higher energy become available the number of elements giving protons and neutrons may be increased.

Some isotopes can apparently disintegrate in two alternative ways, *e.g.*, ^{19}F and ^{27}Al, one giving a proton and the other a neutron ; thus

$$^{19}_{9}F + {}^{4}_{2}He \rightarrow {}^{22}_{10}Ne + {}^{1}_{1}H$$

and

$$^{19}_{9}F + {}^{4}_{2}He \rightarrow {}^{22}_{11}Na + {}^{1}_{0}n.$$

On the other hand, when boron is bombarded by α-particles the two isotopes disintegrate in different ways, as follows :

$$^{11}_{5}B + {}^{4}_{2}He \rightarrow {}^{14}_{7}N + {}^{1}_{0}n$$

and

$$^{10}_{5}B + {}^{4}_{2}He \rightarrow {}^{13}_{6}C + {}^{1}_{1}H.$$

A study of the extent of neutron emission brought about by α-particles of different energies shows that resonance levels exist which permit the passage of the particles through the energy barriers surrounding certain nuclei. With ^{9}Be, for example, the height of the barrier is apparently $3{\cdot}5 \times 10^6$ electron-volts, but strong neutron emission is observed with α-particles having

energies of 2·5 and 1·4 × 10^6 electron-volts. As in the emission of protons, some elements emit two or more groups of neutrons of different energies: these probably correspond to different states of the other nuclear product of the disintegration process. Neutron emission is sometimes accompanied by very penetrating γ-radiation; the energy liberated by the destruction of mass is frequently liberated in this form of high-frequency radiation.

Neutrons can be ejected from the nuclei of deuterium and of beryllium by means of γ-rays (Chadwick and Goldhaber, 1934) and even by X-rays (Szilard, Chalmers, *et al.*, 1934), and they are also obtained when certain elements are bombarded with high velocity protons or deuterons.* This latter aspect of the subject is discussed more fully at a later stage.

The Mass of the Neutron. The first calculations of the mass of the neutron (Chadwick, 1933) were made from the masses and energies involved in the disintegration of the ^{11}B nucleus of boron: as shown above, this involves a boron nucleus and an α-particle which give a neutron and a ^{14}N nucleus of nitrogen. The atomic weight of ^{11}B is 11·0110 and that of helium (α-particle) is 4·00216, which together with the mass equivalent of the energy of the latter, 0·00565 atomic weight units, give a total mass of 15·01881 before disintegration. The mass of the resulting nitrogen atom is 14·0080 and the kinetic energy of this and the neutron has been estimated to be 0·0061 and 0·0035 mass units, respectively (Feather, 1932). The net difference of mass, which should be that of the neutron, is consequently 1·0067. A number of other estimates have been made in an analogous manner by considering the energies and masses involved in disintegration processes, and all give results in fair agreement with that obtained originally by Chadwick. The most reliable value appears to be that of Chadwick and Goldhaber (1934); these authors found that γ-rays of sufficient energy were able to disintegrate a deuteron into a proton and a neutron; thus,

$$^2_1D + \gamma\text{-radiation} \rightarrow {}^1_1H + {}^1_0n.$$

* This is the name given to the nuclei of deuterium, the heavy isotope of hydrogen (see Chapter IV.). The deuteron has a mass of 2 and a unit charge, and is designated ^2_1D.

The γ-rays from polonium, having an energy of $1{\cdot}8 \times 10^6$ electron-volts, were unable to bring about this disintegration, but the high energy rays ($2{\cdot}62 \times 10^6$ electron-volts) from thorium-*C''*, the most energetic available, were quite effective. The energy of the resulting proton was found to be approximately $0{\cdot}25 \times 10^6$ electron-volts, and assuming that the neutron of almost equal mass carried the same energy, it is evident that energy of $2{\cdot}62 - 0{\cdot}5 = 2{\cdot}12 \times 10^6$ electron-volts is required to disintegrate the deuteron. If the atomic masses of deuterium and hydrogen are taken as 2·0136 and 1·0078, respectively, which are the older mass-spectroscopic values, and the binding energy of $2{\cdot}12 \times 10^6$ electron-volts is converted into its equivalent mass, namely, 0·0022 units, it follows that the mass of the neutron is $2{\cdot}0136 + 0{\cdot}0022 - 1{\cdot}0078 = 1{\cdot}0080$. It will be seen later (p. 29) that the atomic weights of hydrogen and deuterium used here may be somewhat low, and if the amended values are used the mass of the neutron becomes $1{\cdot}0084 \pm 0{\cdot}0003$.

Constitution of the Neutron and of Atomic Nuclei. When the neutron was first discovered it was believed to be a combination of a proton and an electron in one particle : if this were the case it should have a mass lighter than that of the hydrogen atom, the difference representing the binding energy of the proton and electron within the neutron. The mass of the latter, however, now appears to be at least equal to, if not greater than, that of the hydrogen atom ; further, according to modern quantum mechanics the hydrogen atom is the only possible combination of a proton and an electron, and so it is now generally accepted that the neutron is an individual and fundamental particle, and is not made up of any other known units.

Until recently the nuclei of atoms were believed to be constituted of protons and " cementing " electrons, the excess of protons over electrons being equal to the atomic number. The discovery of the neutron has led Heisenberg (1933) and others to propose the view that nuclei do not contain electrons, but are composed only of neutrons and protons : the number of the latter would be the same as the atomic number of the element, whereas the total of neutrons and protons would be equal to the mass number. It is

evident, therefore, that the discovery of the neutron has simplified and revolutionised the older ideas concerning nuclear structure.

Disintegration by Neutrons. Since a neutron is uncharged it produces very little ionisation in its passage through matter, but when it collides with a suitable nucleus the resulting recoil nuclei can be readily detected and photographed in the Wilson expansion chamber. A study of collisions under these conditions of neutrons with nitrogen nuclei has been made (Feather, 1932; Harkins, Gans and Newson, 1932), and at least two types of tracks were observed. The first was clearly due to the recoil of a nitrogen nucleus after being struck by a neutron without disintegration occurring; the range of the nucleus was 3·5 mm. in air, corresponding to a velocity of $4{\cdot}7 \times 10^8$ cm. per sec. If the recoil had resulted from a "head on" collision with a neutron of mass unity, then the velocity of the latter should have been $3{\cdot}5 \times 10^9$ cm. per sec.; this is in good agreement with the value already given as the maximum velocity of the neutron calculated by Chadwick. The second type of track definitely indicated disintegration, but a number of different kinds seem probable. In the first place evidence was obtained for the capture of the neutron by the nitrogen nucleus, and of the possible processes which might occur subsequently an analysis of the velocities and masses of the particles concerned showed the following to be the most probable:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}n \rightarrow {}^{11}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He}.$$

It may be noted that this disintegration is the reverse of the process whereby the neutron has been produced, namely, the bombardment of boron by α-particles.

Fluorine, neon, oxygen and other elements are apparently disintegrated in an analogous manner as a result of impact with neutrons, the latter being taken up and an α-particle liberated in each case. When slow neutrons collide with boron nuclei, there is reason to believe (Chadwick and Goldhaber, 1935) that the process

$$^{10}_{5}\mathrm{B} + {}^{1}_{0}n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{T}$$

occurs, where T represents the nucleus of tritium, the hydrogen isotope of mass number 3 (see p. 186). The disintegration in this instance is more complete than usual. A somewhat similar

breaking up is found to take place with lithium, the ^{6}Li isotope being involved ; thus

$$^6_3\text{Li} + ^1_0n \rightarrow ^4_2\text{He} + ^3_1\text{T}.$$

The energy released in this process should be about 5×10^6 electron-volts, and a singly charged particle having the range to be expected of one with a mass of 3, presumably the tritium nucleus, was observed, in addition to the α-particle which was ejected in the opposite direction.

The α-particles produced by collisions of atomic nuclei with neutrons generally form a number of groups of different energies : those with the highest energy have presumably passed over the top of the barrier which not only prevents the entry of α-particles into, but also their ejection from, the nucleus. The particles of lower energy apparently leave the combined nucleus formed by the original nucleus taking up an α-particle, *e.g.*, ^{15}N when ^{14}N engulfs a neutron, through one or other of its resonance levels. A knowledge of the energies of the emitted α-particles may thus be useful in the study of the structure of unusual nuclei, such as that of ^{15}N just mentioned.

Evidence of Helium Formation. Actual proof of the production of helium as a result of neutron bombardment of boron has been obtained by Paneth and Loleit (1935). Methyl borate vapour was submitted to the continuous action of neutrons for seven weeks : the ester was then removed by condensation and the residual gas, consisting mainly of hydrogen, was mixed with pure oxygen and passed over heated palladium. After removal of the residual oxygen by means of charcoal, cooled in liquid air, there remained $1{\cdot}8 \times 10^{-7}$ c.c. of gas which showed quite definitely the spectrum of helium.

Other Types of Disintegrations by Neutrons. In addition to the disintegration resulting in the ejection of an α-particle, neutron bombardment often leads to the liberation of a proton, sometimes together with energy in the form of γ-radiation, but the remaining nucleus is almost invariably of an unstable type which breaks up further spontaneously. For example, the impact of neutrons on the sodium ^{23}Na nucleus not only results in disintegration of the

type already discussed, but another process also occurs, namely,

$$^{23}_{11}\mathrm{Na} + {}^{1}_{0}n \rightarrow {}^{1}_{1}\mathrm{H} + {}^{23}_{10}\mathrm{Ne}.$$

The resulting isotope of neon ^{23}Ne is not one found in nature, and this is not surprising as it disintegrates at a definite rate giving off electrons; thus

$$^{23}_{10}\mathrm{Ne} \rightarrow {}^{0}_{-1}e + {}^{23}_{11}\mathrm{Na},$$

where $^{0}_{-1}e$ represents an electron, having almost zero mass and one negative charge. A sodium nucleus of isotopic weight 23 is regenerated in the process. It may be noted that with the ^{23}Na nucleus the disintegration giving α-particles also results in the formation of an unstable isotope, namely ^{20}F; the subject of these unstable species will be considered later.

There is some reason for believing that a neutron can, in certain instances, bring about disintegration of an atomic nucleus merely as a result of the impact and without being captured itself. Chadwick, Feather and Davies (1934) noted the formation in an expansion chamber of three tracks having a common origin, probably due to three α-particles from a non-capture collision of a carbon nucleus with a neutron; thus

$$^{12}_{6}\mathrm{C} \rightarrow 3\ {}^{4}_{2}\mathrm{He}.$$

This type of disintegration had been previously suggested in other cases, but the evidence was not generally accepted.

Another mode of interaction with neutrons, usually resulting in the formation of an unstable nucleus (see p. 41), which is particularly common with the heavy elements, results in a neutron being taken up by the bombarded nucleus without any particle being simultaneously emitted; thus

$$^{127}_{53}\mathrm{I} + {}^{1}_{0}n \rightarrow {}^{128}_{53}\mathrm{I},$$

the product, which is an unstable species, is isotopic with the original nucleus although one unit heavier in mass. In one or two instances it appears that the resulting nucleus is stable; the interaction process is then accompanied by γ-ray activity.

THE POSITIVE ELECTRON

Discovery of the Positron. Soon after the discovery of the neutron came the announcement of the identification of the long-

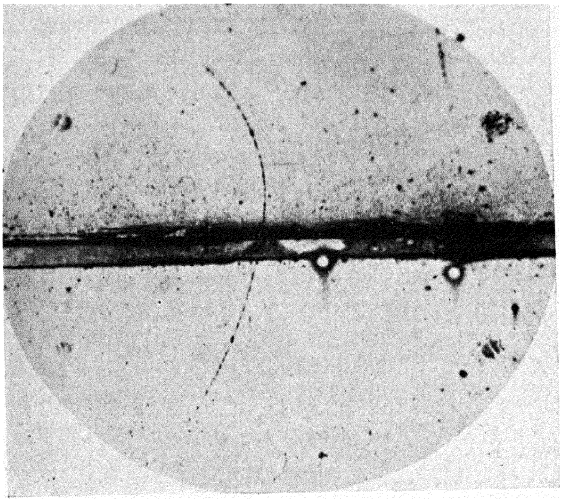


FIG. 1.—Cloud-track photograph of positron travelling upwards through a 6 mm. lead plate: this photograph led to the discovery of the positron. (After Anderson.)

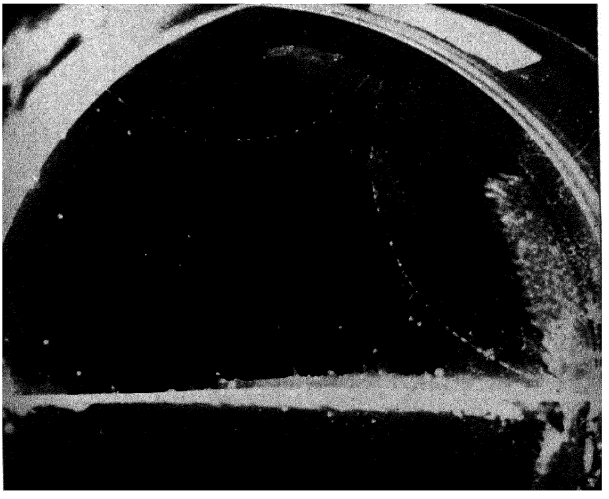


FIG. 2.—Electron–positron pair obtained by absorption of γ-rays by a lead target: the lower track is produced by the positron and the upper by the electron. Originating at one point the particles are deflected in opposite directions by a magnetic field. (After Chadwick, Blackett and Occhialini.)

[*To face p.* 13.

sought positively charged particle of small mass, similar to that of the electron. In the course of a study of the " cosmic " radiation, which consists of quanta, or photons, of high energy coming vertically to the earth from the depths of space, Millikan and Anderson had built a vertical Wilson cloud-chamber, arranged between the poles of a very powerful electromagnet. It was known that the cosmic rays could eject electrons from matter with high velocity, and the intense magnetic field was necessary in order to obtain appreciable curvature of the paths of these electrons. A lead plate of 6 mm. thickness was placed across the centre of the cloud-chamber with the object of finding the loss in energy of the charged particles in traversing the metal, and one of the ionisation photographs, obtained under these conditions, showed clearly that the particle producing the track must have been positively charged. The charge of the particle was determined from the fact that its curvature was less below the lead plate than above it, that is to say, its velocity was greater below the plate, so that it must have been moving upwards ; this being definitely established, and the polarity of the magnetic field being known, the direction in which the particle was deflected established the charge as being positive.

The surprising fact now emerged that the length of the path after the passage through the lead plate was at least ten times as great as the possible length of the path of the same curvature due to a proton. The positively charged particle, produced from matter by the action of the cosmic ray photons, must therefore have a much smaller mass than the proton, and the thickness of the ionisation track produced by it indicated a mass of the order of that of the electron. In this way Anderson (1932) obtained the first definite evidence for the existence of the positive electron, now generally called the " positron." These observations, originally made in California, were soon afterwards confirmed in Cambridge by Blackett and Occhialini (1933), who employed a cloud-chamber actuated by means of a relay which was set in action by the particles produced by the cosmic rays. Study of the positron tracks showed that the charge carried was within 10 per cent. and the mass within 20 per cent. of the corresponding values for the

negative electron.* It is important to record that whenever a positive electron is produced, it is always accompanied by one with a negative charge, so that in the magnetic field at least two tracks, deflected in opposite directions but emerging from the same point, are observed. There are generally more electron than positron tracks, many of the former being due to the extra-nuclear, *i.e.*, " orbital," electrons ejected from atoms which are present.

Production of Positrons by γ-Rays. The discovery of the positron led to search being made for other sources of these particles, and it was found that the absorption of γ-rays, for example from thorium-C'', by lead or other metal, resulted in the production of positrons. The penetrating γ-radiation, which accompanies neutron emission when beryllium is bombarded by α-particles, is also capable of liberating positrons when it is absorbed by matter (Anderson and Neddermeyer; Curie and Joliot; Meitner and Philipp; Chadwick, Blackett and Occhialini, 1933, 1934). It has been known for several years that in the scattering of high-energy γ-rays, the production of electrons is in excess of theoretical expectations based on the photo-electric and Compton effects; this anomalous, or " excess," absorption increases with the atomic number of the scattering element, and is about 20 per cent. of the total for γ-rays of $2{\cdot}6 \times 10^6$ electron-volts energy when lead is employed to scatter them. By the use of high-energy γ-radiation, obtained in certain artificial disintegration processes, the additional particle formation is actually several times greater than the scattering by the extra-nuclear electrons (Crane, Lauritsen, *et al.*, 1934). There is little doubt that this excess formation of electrons is to be attributed to the production of positive–negative electron pairs by the annihilation of the γ-ray photons.

Mass of the Positron. When the γ-rays from thorium-C'', having energy of $2{\cdot}6 \times 10^6$ electron-volts, were absorbed by lead or aluminium the maximum energy of the positive particles ejected, estimated by deflection in a magnetic field, was found to be $1{\cdot}6 \times 10^6$ electron-volts, although many had energies of less than

* The name " electron " is still generally retained for the negative electron, although some authors use the term " negatron."

half this value. The maximum energy of a positive–negative pair, being the sum of the separate energies for the two particles, was also $1{\cdot}6 \times 10^6$ electron-volts, although single electrons, presumably coming from outside the nucleus, had energies up to $2{\cdot}6 \times 10^6$ electron-volts (Anderson and Neddermeyer, 1934). In more accurate observations with lead, Chadwick, Blackett and Occhialini (1934) found a maximum positron energy of $1{\cdot}55 \pm 0{\cdot}03 \times 10^6$ electron-volts, and from this result, knowing the energy of the γ-ray photons, $2{\cdot}62 \times 10^6$ electron-volts, the ratio of the masses of the electron and positron were calculated in the following manner. Let m_1 and m_2 be the masses of the electron and positron respectively, then the energy required to produce simultaneously a pair of these particles is $(m_1 + m_2)c^2$, where c is the velocity of light (see p. 4). If $h\nu$ represents the energy of the γ-ray photon, which on absorption produced the electron–positron pair, then the excess energy remaining must be equal to $h\nu - (m_1 + m_2)c^2$; this will represent the maximum energy which can be acquired by any single positron or by any electron–positron pair, and is equal to $1{\cdot}55 \pm 0{\cdot}03 \times 10^6$ electron-volts. Since $h\nu$ is equal to $2{\cdot}62 \times 10^6$ electron-volts, it follows that

$$(1{\cdot}55 \pm 0{\cdot}03) \times 10^6 = 2{\cdot}62 \times 10^6 - (m_1 + m_2)c^2$$

$$\therefore (m_1 + m_2)c^2 = 1{\cdot}07 \pm 0{\cdot}03 \times 10^6 \text{ electron-volts.}$$

Taking the actual mass, m_1, of the electron as 9×10^{-28} gram, and the velocity of light as 3×10^{10} cm. per sec., it can be shown, by the method previously described, that

$$m_1c^2 = 0{\cdot}51 \times 10^6 \text{ electron-volts.}$$

It follows, therefore, that

$$m_2 = (1{\cdot}10 \pm 0{\cdot}06)m_1.$$

The mass of the positron is therefore equal to that of the electron, within less than 10 per cent., and the total energy required to produce a positron–electron pair is about $1{\cdot}07 \times 10^6$ electron-volts; more accurate work will probably show this value to be $1{\cdot}02 \times 10^6$, that is, $2 \times 0{\cdot}51 \times 10^6$ electron-volts.

Theory of Positron Production. Experiments on the maximum energy of positrons and of positron–electron pairs, produced by

means of γ-rays from thorium-C'', provides some confirmation for the view that pair-production results from the absorption of the γ-ray photon by matter in accordance with the mathematical theory of Dìrac. There does not appear to be room in the atomic theory for the *separate* existence of positrons, and consequently the formation of a positron must always be accompanied by that of an electron, the actual pair-production may even take place outside the atomic nucleus. High-energy electrons are apparently able to produce positron–electron pairs in their passage through matter, and in this connection it is of interest that there is now evidence that positron emission accompanies the β-rays of radon, radio-thorium, and thorium active-deposit. The fast electrons emitted from the radioactive nuclei are evidently capable of pair-formation, some of their energy being presumably lost in the process : it is not certain, however, if the pairs are formed within the radioactive nucleus or in the intense field immediately surrounding it.

The theory of pair-production encounters some difficulty in the observation, which will be discussed more fully below, that the impact of α-particles on certain elements, *e.g.*, boron, nitrogen and magnesium, results in the liberation of positrons without accompanying electrons (Curie and Joliot, 1934). The first stage in the process is the fusion of the two colliding nuclei and the disintegration of the resulting complex ; for example, the behaviour with magnesium may be represented as

$$^{24}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{27}_{14}\mathrm{Si} + {}^{1}_{0}n,$$

a neutron being ejected, and the nucleus of the unstable isotope ^{27}Si remaining. The latter then disintegrates spontaneously yielding a positron,* and the stable aluminium nucleus ; thus

$$^{27}_{14}\mathrm{Si} \rightarrow {}^{0}_{1}p + {}^{27}_{13}\mathrm{Al}.$$

It is not clear in this instance, whether pair-production has occurred : if it has, then the fate of the electron is by no means evident, unless it may be assumed that it has united with a proton in the nucleus of the ^{27}Si to form a neutron, thus yielding

* The symbol $^{0}_{1}p$ will be used to represent the positron, since it has a positive change of unity, and a mass of virtually zero.

^{27}Al. In view of the generally accepted primary nature of the neutron this explanation does not appear valid. It must be remembered that the whole subject is still in its infancy, and there is little doubt that many of the present difficulties will resolve themselves in due course.

The positron is believed to have a very short life, and when its energy has fallen to a low value it suffers annihilation as a result of an encounter with an electron. This destruction must, of course, be accompanied by the emission of energy, namely $1{\cdot}02 \times 10^6$ electron-volts, for each positron and electron annihilated, which would be expected to consist of two quanta, each of $0{\cdot}51 \times 10^6$ electron-volts energy, moving in opposite directions, so that momentum is conserved. Some evidence has been obtained that radiation of this type is actually produced.

THE NEUTRINO

Before proceeding to consider further types of artificial disintegration, mention may be made of another primary particle, the existence of which has been postulated but not yet proved. When electrons are emitted from a radioactive nucleus undergoing β-ray disintegration, the quantum theory requires that their energy should be constant provided the law of conservation of energy is obeyed. In actual practice there is a continuous distribution of energy amongst the electrons, sometimes known as the β-ray spectrum, and in order to overcome this difficulty the suggestion was made, originally by Pauli and developed by Fermi (1934), that a particle having a very small mass when at rest, probably less than that of an electron, with *no charge* accompanied the emission of the β-ray electrons. This new particle has been called a " neutrino," and it is supposed to share part of the energy and momentum of the electron emitted from the radioactive nucleus. By postulating the hypothetical neutrino, therefore, the β-ray spectrum can be explained. In view of its properties the neutrino, even if it exists, will certainly be difficult to detect, and experiments made so far have not been successful. Quite recently it has been stated that there is reason for believing

that the conservation of mass and energy does not apply exactly to small particles like electrons : if this view is correct then the immediate difficulty of the β-ray spectrum disappears, but many facts will still require explanation.

There is evidence of a continuous distribution of energy in the emission of positrons from certain unstable elements, and consequently a particle, analogous to the neutrino, called the " anti-neutrino " has been postulated by de Broglie. It is supposed to bear the same relationship to the neutrino as a positron does to an electron, but the physical significance of this idea is far from clear. It can only be said that just as a positron and an electron can annihilate one another with the emission of energy, so a neutrino and an anti-neutrino can disappear with liberation of one or more quanta of radiation.

THE NEGATIVE PROTON

The discovery of the positive electron and the development of the theory of the neutrino and anti-neutrino, has raised the question of the possible existence of the negative proton, that is of a particle of unit mass carrying a single negative charge. Gamow (1934, 1935) has considered this subject from the theoretical point of view, and concludes that the negative proton should exist, but that its relation to the ordinary proton would not be the same as that of the electron to the positron, in so far, at least, as they would not be mutually destructible. The postulation of the existence of the negative proton permits of the existence of " isomeric nuclei," that is of nuclei having the same atomic number and mass number yet differing in radioactive properties. Two examples of this remarkable phenomenon appear to be established : firstly, uranium-Z and uranium-X_2, both formed from uranium-X_1 by a branching β-ray process, and secondly radium-D and the inactive lead isotope ^{210}Pb, present to the extent of 0·08 per cent. in ordinary lead. If a pair of neutrons in one nucleus are replaced by a positive and a negative proton in the other, both the atomic mass and the nuclear charge will remain unchanged, thus giving isomeric nuclei which might well have different stabilities, and thus different radioactive properties.

DISINTEGRATION BY PROTONS

Production of α-Particles. A great advance in the subject of artificial disintegration was made by Cockroft and Walton (1932), who developed a technique for the production of streams of high-velocity protons; the protons were obtained from a discharge tube containing hydrogen and accelerated by falling through potentials up to 600,000 volts. When a layer of lithium oxide was bombarded by the swift protons scintillations were observed on a zinc sulphide screen, which could not have been due to scattered protons. The scintillations were first observed at potentials of 125,000 volts, and as the potential increased so the number increased; for example, at 250,000 volts there was one scintillation for about 10^9 protons, and at double this voltage the number was increased ten-fold. The range of the particles producing the scintillations was greater than that of the protons and remained independent of changes in the potential. From the brightness of the scintillations, and from the appearance of the tracks produced by the particles in an expansion chamber, it was evident that they were α-particles. The suggested explanation of their origin is that the lithium nucleus captures a proton and the resulting complex breaks up into two α-particles, thus

$$^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H} \rightarrow 2\ {}^{4}_{2}\mathrm{He}.$$

This interpretation of the observations is supported by Wilson cloud-chamber photographs (Dee and Walton; Kirchner, 1933) which show two tracks of equal length, evidently due to α-particles, emitted in opposite directions from the lithium-covered target. If momentum is to be conserved then each α-particle must take up an equal amount of energy, and from the observed range it is calculated that $17{\cdot}1 \times 10^6$ electron-volts of energy are liberated in the disintegration process. The masses of the lithium and the hydrogen atom are 7·0146 and 1·0078, respectively, and that of helium is 4·00216, consequently the loss of mass in the process depicted above is $(7{\cdot}0146 + 1{\cdot}0078) - 2(4{\cdot}00216) = 0{\cdot}0181$, which is equivalent to $17{\cdot}0 \times 10^6$ electron-volts of energy.* This energy, in addition to that of the bombarding proton, which

* See footnote, p. 3.

is no more than $0{\cdot}5 \times 10^6$ electron-volts, should thus appear on the α-particles produced: the observed value of $17{\cdot}1 \times 10^6$ electron-volts is in sufficiently close agreement with that calculated to confirm the view expressed as to the mechanism of the process occurring in the bombardment of lithium by protons.

Under certain conditions this bombardment has been found to result in the production of γ-rays of two types, having energies of 4 and 12×10^6 electron-volts, respectively (Crane, Lauritsen, *et al.*, 1934). Since the sum of these energies is almost equal to that which should theoretically be liberated in the formation of two α-particles (17×10^6 electron-volts), it is evident that in the complex nucleus resulting from the taking up of a proton by the lithium nucleus, the α-particles can be formed either in their ground state when the excess energy appears as kinetic energy, or else in an excited state which falls back to the ground level in two stages, the energy being emitted as photons of 4 and $12–13 \times 10^6$ electron-volts.

Bombardment of Separate Isotopes. Another proof of the supposition that the ^{7}Li isotope is involved in the disintegration being considered has been obtained by Oliphant, Shire and Crowther (1934), who passed a beam of positively charged lithium ions through crossed electrostatic and magnetic fields, as in the mass spectrograph, and collected the ^{6}Li and ^{7}Li isotopes separately on two small targets placed slightly apart. Quantities of the order of 5×10^{-8} gram of each isotope were obtained in the pure state in this manner. Each isotope was separately subjected to bombardment by rapid protons: the ^{7}Li isotope gave two α-particles, as found with the normal isotopic mixture generally employed, but ^{6}Li gave two different particles, having different ranges, although both were doubly charged. There is reason for believing that whereas one of these is an ordinary α-particle, $^4_2$He, the other is an isotopic form of mass 3, that is, $^3_2$He, formed thus

$$^6_3\text{Li} + {}^1_1\text{H} \rightarrow {}^4_2\text{He} + {}^3_2\text{He}.$$

The ranges of the two particles were 9·5 mm. and 12·0 mm., the former being evidently due to the heavier and the latter to the lighter helium isotope (Dee, 1935). An α-particle having the same

velocity as the ^{3}He nucleus of range 12 mm. would have a range 4/3 times as great, that is, 16·0 mm., because of its greater energy ; this would be equivalent to $2{\cdot}6 \times 10^6$ electron-volts energy. The actual energy of the ^{3}He particle may then be taken as three-quarters of this amount, namely $1{\cdot}95 \times 10^6$ electron-volts. The energy of the 9·5 mm. range ^{4}He particle produced at the same time is $1{\cdot}55 \times 10^6$ electron-volts, making a total of $3{\cdot}5 \times 10^6$ electron-volts, equivalent to the destruction of 0·0038 units of mass. It is now possible to determine the atomic weight of the new isotope ^{3}He : the isotopic masses of ^{6}Li, ^{4}He and ^{1}H are 6·0145, 4·0022 and 1·0078, respectively, from the older mass-spectroscopic data, and so it follows, neglecting the energy of the proton bringing about the disintegration, that the mass of ^{3}He is $(6{\cdot}0145 + 1{\cdot}0078) - (4{\cdot}0022 + 0{\cdot}0038) = 3{\cdot}0163$, with a possible error of 0·0004 (Dee, 1935). A similar result has been obtained from other disintegration processes, but the use of the new atomic weights (see p. 29) gives a value of 3·0174.

Further Instances of Proton Disintegration. Other elements besides lithium, particularly boron, were found by Cockroft and Walton (1933) to be disintegrated by fast protons with the emission of α-particles ; cloud-chamber photographs by Kirchner (1933) showed that three particles having the same range were emitted symmetrically from boron, so that the disintegration process is presumably

$$^{11}_{5}\mathrm{B} + {}^{1}_{1}\mathrm{H} \rightarrow 3\ {}^{4}_{2}\mathrm{He}.$$

On the other hand, Dee and Gilbert (1936) have observed that of the three tracks, two have a relatively long range and are formed at almost 180° to one another, whereas the third is much shorter ; it is suggested, therefore, that there are two stages in the disintegration, thus

$$^{11}_{5}\mathrm{B} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{8}_{4}\mathrm{Be},$$

followed by the spontaneous breakdown of the ^{8}Be nucleus into two α-particles, which should be emitted in opposite directions. Further work by Laurence, Livingston, *et al.*,* (1933) and by

* The American workers have used an ingenious device known as a " cyclatron," to obtain high-energy particles ; the latter are made to move in a spiral, acquiring 20,000 volts energy in each turn. With this relatively low

Oliphant and Rutherford (1933) showed that beryllium and fluorine could also be disintegrated by high-energy protons, although to a much smaller extent than lithium and boron; in each case α-particles were emitted, thus

$$^{9}_{4}\mathrm{Be} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{6}_{3}\mathrm{Li},$$

and

$$^{19}_{9}\mathrm{F} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{16}_{8}\mathrm{O}.$$

In the latter case disintegration is accompanied by the emission of γ-rays of high energy, namely, $5{\cdot}4 \times 10^{6}$ electron-volts (Crane, Lauritsen, *et al.*, 1934).

In order to bring about disintegration protons of higher energy are required as the atomic number of the bombarded nucleus is increased; with lithium, α-particle emission has been observed with 20,000-volt protons, but with boron only protons having energy greater than 60,000 volts are effective. It has been claimed that by the use of very high velocity protons, accelerated to an extent equivalent to a million volts or more, magnesium (^{26}Mg) and aluminium (^{27}Al) nuclei have been broken up in the normal manner, each giving an α-particle and leaving a nucleus with a mass of three units less, and an atomic number of one unit less, than that of the parent. The increased repulsion between the nucleus and the proton, the greater the charge on the former, that is to say, the increased height of the energy barrier, means that with elements of high atomic number only particles of high energy can penetrate into the nucleus. The phenomenon is somewhat similar to that already considered in connection with bombardment by α-particles (p. 5), and further disintegrations may be expected as more energetic protons become available. Mention will be made later of the production of unstable nuclei, definitely in the case of carbon and possibly with other light elements, as a result of proton bombardment.

DISINTEGRATION BY DEUTERONS

Production of α-Particles. It was quite reasonable that soon after the discovery of deuterium, experiments should be made on

voltage the particles can be accelerated to an extent equivalent to a fall of potential of several million volts, by arranging so that there should be two or three hundred turns in the spiral path.

the disintegration effects of fast deuterons, and Lewis, Lawrence and Livingston (1933) found that they were much more effective than protons of the same velocity. The technique for the production of high-speed deuterons is, of course, exactly similar to that employed for protons, except that deuterium gas replaces hydrogen in the discharge producing the ions. The impact of fast deuterons on lithium, for example, gave α-particles of higher

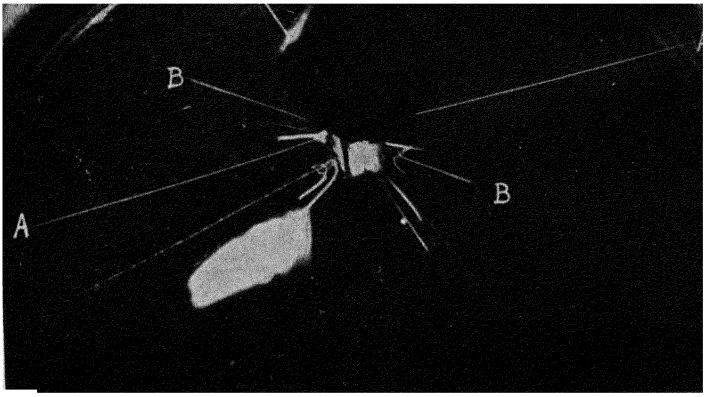


FIG. 3.—Cloud-track photographs obtained by the bombardment of lithium oxide by deuterons and protons of high velocity: the 13 cm. α-particles produced by the former are shown by AA, and the 8·4 cm. particles from the latter by BB. The shorter track is probably caused by the passage of the α-particle through the mica carrying the lithium oxide. (After Dee and Walton.)

energies than had been observed in ordinary radioactive disintegrations; the process may be formulated as

$$^{6}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{D} \rightarrow 2\,{}^{4}_{2}\mathrm{He}.$$

This interpretation was confirmed by Oliphant, Kinsey and Rutherford (1933), who measured the range of the α-particles and found it to be 13 cm., equivalent to a total energy of $11{\cdot}5 \times 10^{6}$ electron-volts, whereas the mass defect for the formation of two α-particles from a lithium nucleus and a deuteron, as indicated above, should result in the liberation of 11×10^{6} electron-volts. The cloud-track photographs of Dee and Walton (1933) also

showed two equal tracks, evidently caused by α-particles, emerging in opposite directions, as would be expected for this disintegration. The liberation of α-particles from nuclei by deuteron bombardment also occurs in a number of other instances; the following cases have been definitely established: ^{9}Be, ^{10}B, ^{11}B, ^{12}C, ^{14}N, ^{19}F, ^{23}Na and ^{27}Al. With the isotope ^{10}B complete disintegration into three α-particles, analogous to that observed when ^{11}B is bombarded with protons, may also occur (Cockroft and Lewis, 1936); thus

$$^{10}_{5}\mathrm{B} + {}^{2}_{1}\mathrm{D} \rightarrow 3\,{}^{4}_{2}\mathrm{He},$$

but it has not been established if this takes place in one or two steps. Since deuteron bombardment often results in the liberation of α-particles of high energy, the process has been employed for the production of α-particles which may be used for experimental work in place of those derived from radioactive sources.

Liberation of Protons. An unusual type of disintegration has been observed in the bombardment of lithium, and some other elements, by high-speed deuterons; the attacked nucleus is converted into an isotope with a mass number one unit higher, and at the same time high-velocity protons are ejected (Oliphant, Shire and Crowther, 1934; Cockroft and Walton, 1934); thus

$$^{6}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H}.*$$

With ^{7}Li an unstable isotope ^{8}Li, which is transformed into ^{8}Be with the emission of an electron, is said to be formed (Crane, Delsasso, Fowler and Lauritsen, 1935); similar results have been observed with ^{11}B, ^{14}N, ^{19}F, ^{23}Na, ^{26}Mg and ^{27}Al, unstable species being formed in every case (Henderson, 1935; Laurence, *et al.*, 1935). The common isotope of carbon ^{12}C gives the stable isotope ^{13}C, present to a small extent in ordinary carbon, and at the same time there is emission of energy in the

* Attention may be called to the fact that an alternative mode of disintegration of the ^{6}Li isotope on bombardment by deuterons has been already given. It is quite common, however, for two or more different nuclear disintegrations to occur simultaneously, and many examples will be evident in this chapter.

form of γ-rays of 3×10^6 electron-volts (Lauritsen and Crane, 1934). The data from the disintegration

$$^{12}_{6}\mathrm{C} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{13}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} + \gamma\text{-rays},$$

may be used to calculate the atomic weight of ^{13}C. The isotopic atomic weights of ^{12}C, ^{2}D and ^{1}H can be taken as 12·0036, 2·0136 and 1·0078, respectively, and the energy of the proton, after subtracting that of the bombarding deuteron, is $2{\cdot}6 \times 10^6$ electron-volts, which is equivalent to 0·0027 mass units (Cockroft and Walton, 1934). The mass equivalent of the 3×10^6 electron-volts photons constituting the γ-radiation is 0·0032 ; hence

$$\begin{aligned} {}^{13}\mathrm{C} &= 12{\cdot}0036 + 2{\cdot}0136 - 1{\cdot}0078 - 0{\cdot}0027 - 0{\cdot}0032 \\ &= 13{\cdot}0035. \end{aligned}$$

A somewhat higher value, namely, 13·0075, is obtained by the use of the revised atomic weights to be considered shortly. The ^{10}B isotope behaves in a manner similar to that of ^{12}C, the product being the stable isotope ^{11}B when a proton is emitted as a result of deuteron bombardment.

Formation of Neutrons. A third mode of disintegration brought about by deuterons results in the liberation of neutrons. When bombarding lithium, Oliphant, Kinsey and Rutherford (1934) observed that in addition to the 13 cm. group of α-particles there was a mixed group having ranges up to 7·8 cm. This was attributed to the process

$${}^{7}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{D} \rightarrow 2\,{}^{4}_{2}\mathrm{He} + {}^{1}_{0}n,$$

a neutron being emitted. Some evidence for this suggestion was obtained by Oliphant, Shire and Crowther (1934) employing the separate isotopes ^{6}Li and ^{7}Li, as already explained, but Lawrence and Livingston (1934) have expressed doubt as to its accuracy. On the other hand, Bonner and Brubaker (1935) consider that this disintegration does occur, as well as the interaction

$${}^{7}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{8}_{4}\mathrm{Be} + {}^{1}_{0}n,$$

which may be an intermediate stage. In other instances, however, there is no doubt concerning the formation of neutrons : for example, exposure of beryllium to high-speed deuterons gives one

of the most intense sources of neutrons yet obtained (Crane, Lauritsen and Soltan, 1934); the process may be written

$$^{9}_{4}\mathrm{Be} + ^{2}_{1}\mathrm{D} \rightarrow ^{10}_{5}\mathrm{B} + ^{1}_{0}n.$$

Other elements yielding neutrons, together with a stable nucleus, by impact with deuterons are ^{11}B, ^{19}F, ^{23}Na and ^{27}Al. The following isotopes, however, on collision with high-speed deuterons leave an unstable species, after emitting neutrons: ^{10}B, ^{12}C, ^{14}N and ^{16}O.

Simultaneous Disintegrations. It will be noted that in several cases the same isotope has been recorded as undergoing different disintegration processes: the ^{27}Al isotope forms an excellent illustration of this behaviour; thus

$$^{27}_{13}\mathrm{Al} + ^{2}_{1}\mathrm{D} \rightarrow ^{25}_{12}\mathrm{Mg} + ^{4}_{2}\mathrm{He},$$

$$^{27}_{13}\mathrm{Al} + ^{2}_{1}\mathrm{D} \rightarrow ^{28}_{13}\mathrm{Al}^{*} + ^{1}_{1}\mathrm{H},$$

and

$$^{27}_{13}\mathrm{Al} + ^{2}_{1}\mathrm{D} \rightarrow ^{28}_{14}\mathrm{Si} + ^{1}_{0}n,$$

in which $^{28}_{13}$Al* represents an unstable species. The common form of nitrogen ^{14}N undergoes three similar disintegrations; those leading to emission of a proton and a neutron leave an unstable nucleus. When an α-particle is emitted the remaining nucleus is generally stable, although there may be one or two exceptions to this rule.

Production of Tritium. A specially interesting example of deuteron disintegration is that brought about by the impact of one deuterium nucleus on another. When a target covered with a thin layer of either deuterammonium chloride or sulphate, that is, ND_4Cl or $(ND_4)_2SO_4$, or trideuterophosphoric acid, D_3PO_4, was exposed to fast deuterons (100,000 volts), two prominent groups of particles having ranges of about 15 cm. and 1·6 cm., respectively, were observed (Oliphant, Harteck and Rutherford, 1934). The particles were all singly charged and almost identical numbers were found to be present in each group; hence it is probable that each disintegration results in the emission of a pair of particles, one having a short, and the other a long, range. The only constituent the three target materials have in common is deuterium, and so the results suggest that the disintegration

$$^{2}_{1}\mathrm{D} + ^{2}_{1}\mathrm{D} \rightarrow ^{1}_{1}\mathrm{H} + ^{3}_{1}\mathrm{T}$$

has occurred. This means that two isotopic hydrogen nuclei of mass number 2 have disappeared, and two others, with mass numbers 1 and 3, respectively, have been formed. Wilson-chamber photographs (Dee, 1935) show distinctly two tracks, one definitely longer than the other, emerging from the target in opposite directions, as is to be expected from the type of disintegration proposed. A careful study of the ranges of the ^1H and ^3T particles indicates that their energy is $3{\cdot}97 \times 10^6$ electron-volts, equivalent to 0·0042 mass units, in excess of that of the deuterium used as the projectile (Oliphant, Kempton and Rutherford, 1935); the atomic weight of tritium can then be calculated as follows:

$$\begin{aligned} {}^3_1\mathrm{T} &= (2 \times 2{\cdot}0136) - 1{\cdot}0078 - 0{\cdot}0042 \\ &= 3{\cdot}0152. \end{aligned}$$

This figure, or the amended value based on the revised atomic weights (p. 29), namely, $3{\cdot}0163 \pm 0{\cdot}002$, is somewhat less than that calculated for the helium isotope of mass number 3, viz., 3·0163, or 3·0174 based on the newer atomic weights; the tritium nucleus is consequently somewhat more stable than that of ^3He, the binding energy, as determined by the loss of mass in the formation of the nuclei from protons and neutrons, being greater in the former case. It is interesting to note that by the mutual disintegration of deuterons the element tritium has been obtained in sufficient amount to be detected in the mass spectrograph (see p. 186).

Other Disintegrations. An alternative mode of disintegration is observed in the bombardment of deuterium compounds by deuterons, especially when high-energy deuterons are streamed into deuterium gas (Dee and Gilbert, 1935); this apparently involves emission of neutrons, thus

$$ {}^2_1\mathrm{D} + {}^2_1\mathrm{D} \rightarrow {}^3_2\mathrm{He} + {}^1_0n. $$

Support for this interpretation is obtained from a study of the energy liberated in the process, which was found to have a net value, after subtracting that of the deuteron projectiles, of $2{\cdot}6 \pm 0{\cdot}2 \times 10^6$ electron-volts, equivalent to $0{\cdot}0028 \pm 0{\cdot}002$ mass units. Using the older mass-spectroscopic data for the atomic

weight of deuterium, 2·0136, it follows that the total mass of the ^{3}He atom and the neutron is $(2 \times 2{\cdot}0136) - 0{\cdot}0028 = 4{\cdot}0244$. Taking the mass of ^{3}He as 3·0163 (p. 21), it is seen that the mass of the neutron should be 1·0081 ($\pm$ 0·0004); this result is in excellent agreement with the result of Chadwick and Goldhaber already reported (p. 9). The use of the modified atomic weights, given below, results in a somewhat larger value for the neutron mass, probably 1·0085.

Mention may be made here of the claim that disintegration of heavy elements has been brought about by means of deuteron bombardment; a similar claim had been made for the action of protons which was subsequently shown to be due to contamination by boron from the glass of the apparatus. In view of the very high energy barrier preventing the entry of a deuteron into a nucleus of high atomic number, it is probable that the results observed in deuteron bombardment may equally have been due to impurities.

REVISION OF ATOMIC WEIGHTS

One of the most surprising results of the study of the mass and energy changes involved in disintegration processes is the suggestion that the mass-spectroscopic atomic weights of the lighter elements hitherto in use are incorrect. This view has been expressed independently by Oliphant, Kinsey and Rutherford (1935) and by Bethe (1935). In the process

$$^9_4\mathrm{Be} + {}^2_1\mathrm{D} \rightarrow {}^7_3\mathrm{Li} + {}^4_2\mathrm{He}$$

the observed energy change is equivalent to a loss of mass of 0·0077 units, whereas the value calculated from the accepted isotopic atomic weights is 0·0123, a difference quite outside experimental error, as indicated by the examples already quoted. Similar discrepancies have been noted in other disintegrations involving protons and neutrons, as well as deuterons. Mass-spectroscopic atomic weights for the light elements depend ultimately on the value for the ^{4}He isotope of helium, as compared with that of the ^{16}O isotope, and if there were a small error in

this result then most atomic weights between hydrogen and oxygen would be affected. From a consideration of the probable extent of these errors and from the data obtained in various disintegrations, revised atomic weights have been computed, and the latest compilation made by Cockroft and Lewis (1936) is given in Table I. Similar results are recorded by H. A. Wilson (1935), based on the view that energies emitted from nuclei are multiples of $0{\cdot}385 \times 10^6$ electron-volts.

TABLE I

Revised Isotopic Atomic Weights from Disintegration Data, etc.

Isotope.	Mass Spectroscopic.	Revised Value.
^{1}H	1·0078	1·0082
^{2}D	2·0136	2·01445
^{3}T	—	3·0163
^{3}He	—	3·0174
^{4}He	4·0022	4·00377
^{6}Li	6·0145	6·0168
^{7}Li	7·0146	7·0176
^{9}Be	9·0155	9·0146
^{10}B	10·0135	10·0161
^{11}B	11·0110	11·0126
^{12}C	12·0036	12·0040

The revised atomic weights have generally little *net* effect on the calculations involving isotopic masses and energy changes, as already mentioned, but in the anomalous cases to which reference has been made the new values give results in agreement with those found by experiment. For example, in the case quoted above, involving ^{9}Be and a deuteron, the calculated loss of mass is now 0·0077, as compared with the almost identical observed value, equivalent to the energy liberated. Equally good agreement has been found in other instances which had previously presented anomalies. The doubt cast in this way on the mass-spectroscopic isotopic weights of light elements is of considerable importance, and new determinations will have to be made. In a preliminary announcement Aston (1935) has admitted the possibility of error

in the results obtained by the mass spectroscope, and has proposed (1936) the following new experimental values :

$$^{1}H = 1{\cdot}00812 \pm 0{\cdot}00004$$
$$^{2}D = 2{\cdot}01471 \pm 0{\cdot}00007$$
$$^{4}He = 4{\cdot}00391 \pm 0{\cdot}00016$$
$$^{12}C = 12{\cdot}00350 \pm 0{\cdot}00030.$$

The discrepancy between this new atomic weight for ^{1}H and the chemical value for normal hydrogen, consisting of a mixture of isotopes, is quite appreciable and will require investigation.

ARTIFICIAL RADIOACTIVITY

Unstable Species. Mention has already been made from time to time of the formation of unstable nuclei in certain disintegrations : in a sense every process in which the projectile is engulfed by the bombarded nucleus results in the formation of an unstable entity, but many of these break up *instantaneously* and so can be regarded as having no separate existence. The complex is generally in such a highly excited energy state that its life period is extremely short : for example, when a $^{12}_{6}C$ nucleus takes up a deuteron $^{2}_{1}D$ the product should be $^{14}_{7}N$, the stable isotope of nitrogen, but it is in such a high energy level that it disintegrates within an infinitesimally short period. There are formed in certain cases, on the other hand, nuclei which break up at a *definite measurable rate*, and often exist long enough for their isotopic identity to be ascertained by chemical tests. It is to these nuclei that the term " unstable species " has been applied, and their discovery marks one of the outstanding scientific events of modern times.

In the course of a study of the effect of α-particles from polonium on boron, magnesium and aluminium, Curie and Joliot (1934) found that both neutrons and positrons were emitted in addition to protons (p. 2) ; about 95 per cent. of the nuclei disintegrated gave protons, and only 5 per cent. neutrons and positrons. When the α-particle source was removed, however, the neutrons stopped, but positron emission still continued for

some time, the intensity falling off exponentially. Similarly, it was observed that when fresh material was exposed to α-particles the positron activity increased exponentially from zero to a constant value. It appears, therefore, that the production of the neutron and the positron cannot occur simultaneously, but must be involved in two steps differing in their essential nature. The suggestion was made that the process, alternative to the proton emission already considered, resulted in the α-particle being engulfed and a neutron being emitted; thus, with ^{27}Al, the first stage of the interaction may be represented as

$$^{27}_{13}Al + ^{4}_{2}He \rightarrow ^{1}_{0}n + ^{30}_{15}P,$$

leaving an isotope of phosphorus ^{30}P, which has certainly not been detected by the mass spectrograph. This new isotope is presumably unstable and disintegrates spontaneously, at a definite rate, in an exponential manner exactly analogous to that of an ordinary radioactive element, except that positrons are emitted instead of α-particles or electrons; thus,

$$^{30}_{15}P \rightarrow ^{0}_{1}p + ^{30}_{14}Si,$$

the final product being the known stable isotope of silicon. The element ^{30}P was called radio-phosphorus, and from a study of the rate of decay of the positron emission its half-life period was found to be $3{\cdot}2 \pm 0{\cdot}1$ min.

Chemical Identity of Unstable Isotopes. Some evidence that the artificial radioactive element was an isotope of phosphorus was obtained in the following manner: a piece of aluminium foil was irradiated with α-particles and dissolved immediately in hydrochloric acid, when the hydrogen evolved was found to carry with it the positron-emission activity, probably in the form of phosphine. Further, if the irradiated aluminium was dissolved in a mixture of hydrochloric and nitric acids, a little sodium phosphate added, and then a zirconium salt, the precipitate of zirconium phosphate carried all the activity with it. The active material thus appears whenever phosphorus or its compounds would normally be expected. The half-life period of the artificial radioactivity, as with the natural phenomenon, is independent of the state of combination of the active element, and so is presumably

a property of the nucleus. Curie and Joliot observed similar phenomena with boron (^{10}B) and magnesium (^{24}Mg); the expected products resulting from neutron emission should be ^{13}N and ^{27}Si, that is, radio-nitrogen and radio-silicon respectively, both of which emitted positrons and decayed at a definite rate. The half-life periods were found to be 14 min. (later corrected to 11 min.) and 2·5 min. respectively. Some chemical evidence for the formation of radio-nitrogen was obtained by exposing boron nitride to α-particles and then dissolving rapidly in hot alkali; the activity was found in the gas evolved, presumably in the form of ammonia.

Study of Artificial Radioactivity. The discovery of "artificial radioactivity," as the phenomenon of the production of unstable species with measurable rates of decay is called, caused by α-particles, has stimulated research in other directions, and at the present time more than thirty different artificial radio-elements are known, obtainable by bombardment with either α-particles, protons, deuterons or neutrons. Some emit positrons, others electrons, and one case of a somewhat unusual type has been reported of the emission of heavier, namely, α-particles (see p. 45). The chemical properties of the unstable elements are studied in various ways, as will be seen shortly, determined by their expected nature. The artificial radio-elements can often be concentrated, and separated from their sources by the use of an electrical field, such as is employed for collecting the "active deposits" obtained from naturally radioactive emanations (Paneth and Fay, 1936).

The rate of decay of the induced, or artificial, activity is generally measured by the Geiger-Müller counter. This consists of a small sealed cylinder, about 8 cm. long by 1·5 cm. diameter, made of thin metal, carrying a fine wire stretched along its axis. The wall of the cylinder is attached to a suitable high potential, *e.g.*, about 1,000 volts, and the wire is connected in an appropriate manner to the grid of an amplifying valve, coupled to a gas-filled "thyratron" relay, which operates a mechanical counter. The entry of a positron or an electron through the walls of the cylinder produces ionisation of the air, at low pressure, within it and a momentary discharge takes place between the cylinder walls and the central wire. The effect is transmitted through the

valve and relayed to the counter, and every particle entering is recorded automatically in this manner. The substance to be examined, packed into the space between two concentric cylindrical tubes, is exposed to suitable projectiles and then fitted round the cylindrical portion of the recorder; the rate of emission of particles is then measured over a period of time and the half-life period calculated in the manner employed with the natural radio-elements. Where a large amount of material of relatively high activity is available the familiar electroscope, or ionisation chamber and electrometer, methods may be applied. For purposes of convenience the results will be considered here under the headings of the various projectiles used, although it will be seen that the same radio-element can often be obtained in a number of different ways.

Alpha-Particles as Projectiles. The positron activity obtained by α-particle bombardment of boron, aluminium and magnesium was soon confirmed and extended to other elements, *e.g.*, nitrogen (^{14}N) giving radio-fluorine (^{17}F; half-life 1·1 min.); sodium (^{23}Na) giving radio-aluminium (^{26}Al; half-life 7 sec.); phosphorus (^{31}P) giving radio-chlorine (^{34}Cl; half-life 40 min.); and potassium (possibly ^{41}K) giving radio-scandium (possibly ^{44}Sc; half-life 180 min.). That the active product from phosphorus is probably an isotope of chlorine has been shown by exposing elementary red phosphorus to the α-rays from thorium-*B* and -*C*, and then burning in oxygen: the product was dissolved in sodium hydroxide, acidified with nitric acid, and a small quantity of ammonium chloride and finally an excess of silver nitrate were added. The silver chloride precipitated was filtered off, washed, and on examination shown to contain over 50 per cent. of the original activity, with the same rate of decay (Frisch, 1934).

The activity obtained from magnesium has been found to be complex and to consist both of electrons and positrons, their parents decaying at different rates. It appears that there are at least two different radio-elements produced from the two isotopes of magnesium, thus

$$^{24}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{0}n + {}^{27}_{14}\mathrm{Si}\,; \quad {}^{27}_{14}\mathrm{Si} \rightarrow {}^{0}_{1}p + {}^{27}_{13}\mathrm{Al}$$

and

$$^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{28}_{13}\mathrm{Al}\,; \quad {}^{28}_{13}\mathrm{Al} \rightarrow {}^{0}_{-1}e + {}^{28}_{14}\mathrm{Si}.$$

It is noteworthy that in this case the proton-emission process yields an unstable product which is radioactive, giving off electrons, the half-life period being 137 sec. The radio-silicon, which emits positrons, has a half-life of about 7 min. (Curie and Joliot, 1934; Alichanov *et al.*, 1934). A third disintegration process appears to occur with the ^{26}Mg isotope at the same time; thus

$$^{26}_{12}\mathrm{Mg} + ^{4}_{2}\mathrm{He} \rightarrow ^{1}_{1}\mathrm{H} + ^{29}_{13}\mathrm{Al}; \quad ^{29}_{13}\mathrm{Al} \rightarrow ^{0}_{-1}e + ^{29}_{14}\mathrm{Si},$$

a proton being given off in the first stage and another radio-aluminium, emitting electrons and having a half-life period of 11 min., being formed (Ellis and Henderson, 1935).

Protons and Deuterons as Projectiles. Soon after the discovery of the artificial radio-elements resulting from α-particle bombardment, Cockroft, Gilbert and Walton (1934) and Lauritsen, Crane and Harper (1934), obtained evidence that unstable nuclei, disintegrating at a measurable rate, can be formed by the use of high-velocity protons or deuterons as projectiles. Other workers have also carried out experiments of this type and interesting results have been obtained. The only element which definitely gives a radioactive product as a consequence of proton bombardment is carbon; it has been suggested that boron also does so, but there is apparently some uncertainty in this connection (Crane and Lauritsen, 1934). Cloud-track observations show that an effective collision between a carbon nucleus and a proton results in the capture of the latter without another particle being involved, so that the first stage is probably

$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \rightarrow ^{13}_{7}\mathrm{N}.$$

The unstable nitrogen isotope, ^{13}N, then disintegrates spontaneously with a half-life period of about 11 min., giving off positrons; thus

$$^{13}_{7}\mathrm{N} \rightarrow ^{0}_{1}p + ^{13}_{6}\mathrm{C}.$$

With an acceleration potential of 550,000 volts, only one proton in 5×10^9 is effective in the formation of a radio-nitrogen nucleus, and so it is evident that the extent of the effect is small; with deuterons, however, having the same velocity, the efficiency is ten times as great. In addition to the process involving the emis-

sion of protons (p. 25), the action of the fast deuterons on carbon results in the liberation of neutrons, to some extent, with the simultaneous formation of the unstable ^{13}N isotope, having a half-life period of 11 min. ; thus

$$^{12}_{6}C + {}^{2}_{1}D \rightarrow {}^{1}_{0}n + {}^{13}_{7}N.$$

The ^{13}N isotope is evidently formed from carbon as a result of bombardment either by protons or by deuterons, and, according to Curie and Joliot, ^{13}N should also be obtained in the neutron-emission process following the collision between ^{10}B and an α-particle, as already indicated (p. 32). The half-life period in the latter case was originally stated to be 14 min., and the discrepancy between this result and the 11 min. period reported for the product of proton or deuteron bombardment presented some difficulty ; careful repetition of the work with α-particles and boron (^{10}B) has shown, however, that the product has actually a half-life period of 11 min., and so the situation is now clear (Ellis and Henderson, 1935).

Chemical Identification of Radio-Nitrogen. Cockroft, Gilbert and Walton (1935) obtained some indication concerning the nature of the product resulting from the action of deuterons on carbon by exposing a disc covered with soot to the accelerated particles. The disc was then heated to drive off gases, which were passed through a tube cooled in liquid air : the positron-active material was found to be in the gas and was not condensed. Replacement of the liquid air by liquid nitrogen, however, resulted in the active material being almost entirely condensed in the tube, leaving none in the gas. On removing the liquid nitrogen the activity once more passed into the gas phase. These observations are in harmony with the view that the active material is an isotope of nitrogen.

A more comprehensive experimental investigation to prove its chemical identity has been reported by Yost, Ridenour and Shinohara (1935) ; the bombarded carbon was employed in the form of graphite, and after exposure to deuterons, accelerated by a potential of 800,000 volts, the surface layers were scraped off and burned in air. The resulting gases were first passed over heated

copper oxide and then through a train of absorption bulbs containing solid potassium hydroxide, or soda lime, 50 per cent. potassium hydroxide solution, calcium chloride and phosphorus pentoxide, respectively. The emergent gas was still active, but the solid potash and calcium chloride were not; this eliminates hydrogen, lithium, beryllium, boron and carbon as the source of the positron-activity, since the oxides of any of these elements, if originally present, would have been absorbed. The exit gases were then passed through alkaline pyrogallol which did not remove the activity; hence this could not have been due to oxygen. Another specimen of bombarded carbon was burnt in a helium–air mixture and the oxygen and carbon dioxide removed completely by means of alkaline pyrogallol; the remaining gas, which, of course, retained all the radioactivity, was passed into an evacuated tube containing shavings of metallic calcium. On heating, extensive absorption of the gas occurred, and the remainder, consisting mainly of helium, was pumped off. After cooling, the contents of the tube showed strong activity, and so helium is eliminated as a source of the radioactivity, since this would have been removed with the helium added to the air used for combustion. The calcium powder was allowed to interact with water and the evolved gas collected: it was found to be strongly radioactive. This result clearly supports the view that a nitrogen isotope is the source of the activity, since the calcium nitride formed by heating with calcium evolves ammonia when acted upon by water. It also eliminates the possibility of fluorine being the active substance in the form of unreactive CF_4 or C_2F_6; if they had been present and reacted with calcium to form calcium fluoride, no volatile product would have been obtained when water was added. This elaborate investigation has eliminated all the elements of the first group of the periodic classification, except nitrogen, as the positron-emitting substance, although from a consideration of the total charges involved in the original carbon–deuterium collision, namely seven, it is hardly likely that an element with atomic number greater than this, that is beyond nitrogen, could have resulted. It may be noted that measurements of the half-life of the active gas at various stages of the experi-

ments just described gave a consistent value of 10·5 min., showing the activity to be due to a single element.

Chemical Identification of Radio-Carbon. Bombardment of boron, in the form of boron trioxide, by high-energy deuterons results in the formation of a positron-emitting radio-element, accompanied by the liberation of neutrons; the active element is probably ^{11}C, formed in the following manner:

$$^{10}_{5}B + ^{2}_{1}D \rightarrow ^{11}_{6}C + ^{1}_{0}n.$$

It disintegrates with a half-life period of 20 ± 1 min., in accordance with the equation

$$^{11}_{6}C \rightarrow ^{11}_{5}B + ^{0}_{1}p.$$

After exposure to deuterons, a boron trioxide target was heated and the activity was found to be driven off in the gas evolved which could be condensed in liquid air (Cockroft, Gilbert and Walton, 1934); this observation agrees with the view that the active element is an isotope of carbon, and so would be present in these experiments as carbon monoxide or dioxide. Yost, *et al.* (1935), made a thorough examination of the active product driven off by heating the irradiated boron trioxide. A small amount of carbon dioxide was mixed with the gas, which was then passed repeatedly through potassium hydroxide solution: the residue had about one-third the activity of the original gas, after allowing for the natural decay during the period of the operations. Some of the active material is obviously absorbed by the alkali, but about one-third is evidently different in its chemical nature. To another sample of the active gas a small proportion of carbon monoxide was added, and the mixture passed over heated cupric oxide: the resulting gas was active, but the activity was now completely removed by potassium hydroxide solution. These results, so far, eliminate (*a*) lithium and beryllium, since their compounds are not easily volatile, (*b*) boron in the form of volatile hydrides, as their oxidation product, boron trioxide, would not be gaseous, and (*c*) nitrogen and oxygen, which could not be absorbed by the alkali. Helium clearly cannot be the active element, since it also would not be removed by the solution of potassium hydroxide. Finally, a sample of gas to which carbon monoxide and nitrogen dioxide had been added, was passed over hot cupric

oxide and then through a concentrated solution of permanganate in sulphuric acid : the residual gas was still active, with a half-life period identical with that of the original gas. The experiment was repeated, omitting the passage over cupric oxide, but the result was the same. These observations exclude hydrogen, nitrogen as nitric oxide or as nitrogen dioxide, and fluorine if present as boron trifluoride ; hydrogen would have been burned to water and would be retained, to some extent, by the permanganate solution ; the oxides of nitrogen would be oxidised and absorbed by this reagent, and boron trifluoride would be hydrolysed and also removed from the gas phase. The only element of the first period of the periodic classification not eliminated by the experiments described is carbon, and in fact the results are in accord with the supposition that the active gas is a mixture of the monoxide and the dioxide. It is of interest that both oxides always appear to be formed : this fact is not surprising when it is remembered that the boron bombarded by deuterons was in the form of B_2O_3, so that approximately equivalent amounts of carbon monoxide and dioxide might be expected.

Radio-Oxygen. When nitrogen is exposed to deuterons of energy exceeding a million electron-volts, several types of disintegration occur simultaneously ; one of these results in the formation of a radioactive substance, with a half-life period of 126 ± 5 sec., giving off positrons. The active substance is probably an isotope of oxygen, as the following experiments indicate. A sample of air activated by deuterons was mixed with hydrogen, passed over platinised asbestos at 500° C., and then through a calcium chloride tube. The positron activity was taken up completely by the drying agent. When the platinised asbestos was not heated, however, the activity passed right through in the form of gas. It is evident that the radio-element could not be carbon or nitrogen, in the form of oxide, since the products of the catalysed reaction with hydrogen would not have been absorbed by calcium chloride. From a consideration of the processes by which other radio-elements are produced by deuteron bombardment, the interaction with nitrogen is probably

$$^{14}_{7}\mathrm{N} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{1}_{0}n + {}^{15}_{8}\mathrm{O},$$

so that the active substance should be oxygen. The treatment described above would convert it into water, and this would, of course, be retained by the calcium chloride (MacMillan and Livingston, 1935). The positron emission results, as in the instances already quoted, in the formation of an isotope of the element originally bombarded but having a mass one unit greater ; thus

$$^{15}_{8}\mathrm{O} \rightarrow {}^{0}_{1}p + {}^{15}_{7}\mathrm{N}.$$

Radio-Fluorine. The bombardment of oxygen by deuterons gives results quite analogous to those obtained with nitrogen : these may be represented by :

$$^{16}_{8}\mathrm{O} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{1}_{0}n + {}^{17}_{9}\mathrm{F} \text{ and } {}^{17}_{9}\mathrm{F} \rightarrow {}^{0}_{1}p + {}^{17}_{8}\mathrm{O}.$$

The active element has a half-life period of 1·16 min., and is identical with that obtained by the action of α-particles on nitrogen (see p. 33). Oxygen, in the form of water, was exposed to deuterons, and rinsed into a boiling solution of potassium fluoride which also contained small amounts of aluminium chloride and nitric acid. Calcium chloride was then added and the precipitate of calcium fluoride filtered off : it was found to have a strong activity decaying with the original half-life period of 1·16 min. These results are in accord with the suggestion that the radio-element is an isotope of fluorine.

Radio-Sodium : γ-Ray Activity. Under the influence of deuteron bombardment sodium emits protons, neutrons, α-particles and an intense γ-ray activity of $5{\cdot}5 \pm 0{\cdot}5 \times 10^6$ electron-volts energy ; a radio-element with a half-life period of 15·5 hours, giving off electrons, is left. The amount of radioactive product obtained is almost identical with the number of protons ejected during the bombardment, and so it seems that the process leading to the formation of the radio-element is

$$^{23}_{11}\mathrm{Na} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{24}_{11}\mathrm{Na} + \gamma\text{-rays}.$$

The ^{24}Na emits electrons by the disintegration

$$^{24}_{11}\mathrm{Na} \rightarrow {}^{0}_{-1}e + {}^{24}_{12}\mathrm{Mg},$$

giving finally the common stable isotope of magnesium (Lawrence,

1935). By bombarding sodium chloride with 1 micro-amp. of deuterons, accelerated by a potential of $1{\cdot}7 \times 10^6$ volts, about four million atoms of radio-sodium (^{24}Na) have been produced per second, and much larger yields are expected when higher accelerating voltages become available. In this way quantities of a radio-element, with a relatively long life (15·5 hrs.), giving off powerful β- and γ-rays, have been obtained artificially in amounts of the same order as those in which the natural radioactive materials are available for experimental work. Such a remarkable result may well have important consequences in many directions.

Radio-Aluminium. An electron-emitting radioactive element is also obtained, amongst other products, when aluminium is exposed to high-speed deuterons (Henderson, Livingston and Lawrence, 1934) : by analogy it may be assumed that the active substance is probably either an isotope of aluminium itself or of one of the elements on either side of it in the periodic table, namely magnesium or silicon. A piece of aluminium foil after bombardment by deuterons was dissolved in hydrofluoric acid and the solution evaporated to dryness ; the activity remained in the residue, and so could not have been caused by silicon, which would have been evolved as silicon tetrafluoride. Magnesium was eliminated by dissolving another specimen of irradiated aluminium foil in hydrochloric acid and then adding magnesium chloride and excess of potassium hydroxide solution : the precipitate of magnesium hydroxide was inactive. It is evident that the new radio-element is an isotope of aluminium (MacMillan and Lawrence 1935), which must be formed and then disintegrates as follows :

$$^{27}_{13}\mathrm{Al} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{28}_{13}\mathrm{Al} \quad \text{and} \quad {}^{28}_{13}\mathrm{Al} \rightarrow {}^{0}_{-1}e + {}^{28}_{14}\mathrm{Si}.$$

Short-Life Radio-Elements. According to preliminary observations recently announced (Crane, Delsasso, Fowler and Lauritsen, 1935) both lithium and boron after bombardment with deuterons give active products emitting electrons, in addition to those giving the positron-emission already considered. The half-life periods of these elements is very short, being only $0{\cdot}02 \pm 0{\cdot}01$ sec. for the boron product and $0{\cdot}5 \pm 0{\cdot}1$ sec. for that obtained from lithium ; from a cloud-chamber study of the process resulting in the forma-

tion of the active elements it is considered that they result from proton emission ; thus

$$^{11}_{5}\mathrm{B} + ^{2}_{1}\mathrm{D} \rightarrow ^{1}_{1}\mathrm{H} + ^{12}_{5}\mathrm{B}$$

and

$$^{7}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{D} \rightarrow ^{1}_{1}\mathrm{H} + ^{8}_{3}\mathrm{Li}.$$

Neither of the resulting isotopes, ^{12}B and ^{8}Li, has been reported previously ; this may be explained by their very short life period.

Neutrons as Projectiles. It has been already seen that because of the repulsion between atomic nuclei and the positively charged protons, deuterons or α-particles, only elements of low atomic number can be disintegrated by these projectiles, and in fact potassium, atomic number 19, is the heaviest element to be capable, with certainty, of undergoing interaction with a positively charged particle under the conditions at present available. Calcium, copper, silver, platinum and gold have been reported as being disintegrated by high-velocity deuterons, but this claim has not yet been confirmed (see p. 28). With neutrons, however, it is reasonable to expect nuclear reactions to occur with heavy elements, and this has been verified in a comprehensive series of experiments by Fermi and his collaborators (1934, 1935), in which a considerable number of new radio-elements have been obtained. It is on account of its having no charge that the neutron is proving such a valuable projectile in the study of nuclear disintegrations. Whereas with the positively charged particles the effectiveness generally increases with their speed, with neutrons the reverse is frequently the case, and in fact Fermi, *et al.*, have found that if the neutrons are slowed down by interposing water or paraffin wax, or other hydrogen-containing substance, between the neutron source and the bombarded material, the disintegration effects are often increased to a marked extent. The heavy isotope of hydrogen, deuterium, in the form of "heavy water" (Chapter IV.), is much less effective in this respect than is ordinary hydrogen as water. The source of neutrons generally employed in connection with the study of artificial radioactivity consists of powdered beryllium and radon sealed together into a thin glass tube through which the neutrons are able to penetrate.

Types of Disintegration by Neutrons. In the course of their

work, Fermi and his collaborators exposed sixty elements to the action of neutrons and in forty cases reported the detection of artificial radioactivity; the work has been extended by others, and in general it has been confirmed and additional examples of neutron-induced activity have been recorded. In all instances the radio-elements resulting from bombardment by neutrons emit negatively charged electrons on disintegration; quite frequently the additional energy appears in the form of γ-rays. The unstable species can result in at least three different ways; probably the most common is that in which the neutron is taken into the bombarded nucleus to form a radio-active isotope of the latter without the simultaneous emission of any particles. An example of this type of behaviour, which occurs almost exclusively with elements of high atomic number, is shown by sodium; thus,

$$\checkmark {}^{23}_{11}\mathrm{Na} + {}^{1}_{0}n \rightarrow {}^{24}_{11}\mathrm{Na}.$$

The second mode of formation of radio-elements involves emission of a proton as the immediate result of neutron bombardment as, for example, with magnesium:

$${}^{24}_{12}\mathrm{Mg} + {}^{1}_{0}n \rightarrow {}^{1}_{1}\mathrm{H} + {}^{24}_{11}\mathrm{Na}.$$

A less common type of interaction between neutrons and atomic nuclei leading to the production of artificial radioactive elements, is accompanied by the liberation of α-particles, as is the case with aluminium:

$${}^{27}_{13}\mathrm{Al} + {}^{1}_{0}n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{24}_{11}\mathrm{Na}.$$

It will be observed that in each of the examples quoted, the same isotope, ^{24}Na, is formed: these illustrations were definitely chosen so as to bring out the point. This type of result occurs in other instances, the products being identical both in chemical properties and in their half-life periods, 15 hours in the case quoted. After bombarding aluminium or magnesium metals, or a sodium salt, with neutrons the material was dissolved either in acid or in water, and then small quantities of the salts of the other two elements added in each case, so that there was present in every instance a mixture of aluminium, magnesium and sodium salts

The magnesium and aluminium were precipitated by ammonia or by ammonium phosphate, but the precipitate was inactive: the residue obtained after evaporating to resulting filtrate contained all the electron-activity, and hence the radio-element is probably sodium in all three cases. It may be noted that the same isotope, ^{24}Na, is obtained when sodium is bombarded by deuterons with the simultaneous emission of a proton (p. 39).

With certain elements the three different types of neutron interaction leading to the formation of artificial radio-elements take place with the same isotope: one of the best examples of this behaviour is found with sodium, ^{23}Na. In addition to the process already mentioned above, in which ^{24}Na is formed, there also occur

$$^{23}_{11}\mathrm{Na} + {}^{1}_{0}n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{20}_{9}\mathrm{F}$$

and

$$^{23}_{11}\mathrm{Na} + {}^{1}_{0}n \rightarrow {}^{1}_{1}\mathrm{H} + {}^{23}_{10}\mathrm{Ne}.$$

With other elements only two of the three types occur; this branched disintegration is made manifest by apparently complicated rates of radioactive decay. On analysis of the decay curves it is evident that two or three periods are superimposed. In still other instances the different isotopes of a given element interact in a different manner when bombarded with neutrons, thus with magnesium the ^{26}Mg isotope undergoes the change

$$^{26}_{12}\mathrm{Mg} + {}^{1}_{0}n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{23}_{10}\mathrm{Ne},$$

and in addition the ^{24}Mg isotope gives ^{24}Na and a proton, as shown above. When different products are obtained in neutron bombardment, it is sometimes possible to separate them by making use of their chemical and physical properties; an inert gas, such as neon, remains gaseous, and other elements may be separated by addition of, and subsequent separation with, an appreciable amount of a stable isotope.

Extraction of Radioactive Isotopes. The identity of many of the isotopes obtained by means of neutron action has been confirmed by the type of chemical separation already described; in addition an interesting method has been suggested by Szilard

and Chalmers (1934), which is applicable when the radio-element is isotopic with its parent. The procedure may be illustrated by reference to iodine, which undergoes the process

$$^{127}_{53}\mathrm{I} + ^{1}_{0}n \longrightarrow ^{128}_{53}\mathrm{I}.$$

If ethyl iodide, to which a small amount of elementary iodine has been added, is exposed to neutrons, the free iodine is found to contain nearly the whole of the activity. The explanation of this behaviour is that the γ-ray recoil accompanying the disintegration produced by the neutrons disrupts the molecule of ethyl iodide, producing ethyl radicals and radioactive iodine. The iodine atoms combine to form molecules, and the ethyl radicals react amongst themselves, or with the ethyl iodide or free iodine, more readily than re-combination between the radicals and the atoms with which they were originally united. Most of the radioactivity is thus found in the elementary iodine and, after reduction to iodide ions, can be separated as silver iodide by adding silver nitrate. The same principle has been used to identify the unstable species resulting from the action of neutrons on chlorine in chloroform, carbon tetrachloride and sodium chlorate, on bromine in bromoform and sodium bromate, on manganese in potassium permanganate, and on arsenic in cacodylic acid (Fermi *et al.*).

A modification of the procedure of Szilard and Chalmers, which involves an analogous principle, has been described by Glückauf and Fay (1936) for obtaining organic compounds containing radioactive halogen atoms. The method can also be employed for concentrating the active element. For example, when methyl iodide is exposed to neutrons a large proportion of the resulting radioactive iodine is extracted together with methylene iodide; ethylene dibromide gives active bromoform, and bromoform yields carbon tetrabromide with active bromine. If a mixture of two substances, one containing a halogen, is irradiated by neutrons the halogen atoms liberated by γ-ray recoil are often able to enter the second compound, and the activity can be separated with a new organic halogen derivative. Some of the results obtained in this way are recorded in Table II.

TABLE II

Products of Neutron Bombardment of Mixtures.

Mixture Exposed to Neutrons.	Radioactive Products.
Ethyl alcohol and iodine.	Methyl and ethyl iodides.
Acetic acid and iodine.	Methyl iodide.
Benzene and carbon tetrachloride.	Chlorobenzene.
Phenol and methyl bromide.	Bromobenzene and bromophenol.
Aniline hydrobromide.	Bromobenzene and bromaniline

By suitable experimental arrangements it is possible to obtain continuous supplies of a radioactive organic halide, *e.g.*, methyl iodide from acetic acid and iodine.

Disintegration in Stages. An unusual type of artificial radioactivity produced by neutrons has been reported by Libby, Peterson and Latimer (1935); silver chloride after bombardment by neutrons gave, in addition to electrons, an α-particle activity with a half-life period of $1{\cdot}9 \pm 0{\cdot}3$ min. If this claim is substantiated it will represent the first example of two-stage disintegration and the emission of α-particles by an element of low atomic number. The changes occurring are stated to be

$$^{37}_{17}\mathrm{Cl} + {}^{1}_{0}n \rightarrow {}^{38}_{17}\mathrm{Cl} \text{ and } {}^{38}_{17}\mathrm{Cl} \rightarrow {}^{0}_{-1}e + {}^{38}_{18}\mathrm{A},$$

the ^{38}A, radio-argon, then disintegrating, thus

$$^{38}_{18}\mathrm{A} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{34}_{16}\mathrm{S}.$$

The suggestion that argon is the active element is supported by the observation that the activity cannot be condensed out by liquid air.

The Trans-Uranium Elements. One of the most remarkable claims connected with the many remarkable phenomena of artificial radioactivity is the report of Fermi and his collaborators (1934, 1935) that neutron bombardment of uranium gives elements of atomic numbers greater than 92, that is to say, beyond uranium in the periodic classification. It appears as a definite fact that the nuclei of the heavy elements take up a neutron without simultaneous emission of another particle; hence, with uranium, the interaction

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\mathrm{U}$$

is to be expected. The product definitely emits electrons, so that the disintegration process is

$$^{239}_{92}\mathrm{U} \rightarrow {}^{0}_{-1}e + {}^{239}_{93}\mathrm{X}$$

where ^{239}X should be a homologue of rhenium, and has consequently been called "eka-rhenium." The product of neutron action on uranium actually exhibits four types of activity, with half-life periods of 15 sec., 40 sec., 13 min., and 100 min. If the neutrons are slowed down by water, the second period is not affected, and so probably belongs to a different process, but the activity of the others is increased. An analysis of the decay curves indicates that the 13 min. and 100 min. processes occur to equal extents, and so it is probable that they result from consecutive disintegration stages. If one of these represents that shown above, namely, $^{239}_{92}$U to $^{239}_{93}$X, then since the latter might naturally be expected to be radioactive, the second period gives the rate of decay of the element of mass 239 and atomic number 93. The product should have an atomic number of 94. It is possible that the 15 sec. activity belongs to the same series, in which case elements of still higher atomic number must be present.

According to Fermi the radio-elements produced from uranium are not identical chemically with any known element; a large proportion of the activity can, however, be precipitated together with rhenium sulphide, but not with zirconium phosphate, suggesting that one of the active elements is related to, presumably as a homologue of, rhenium. This property might be anticipated for element number 93. Grosse and Agruss (1935) are, nevertheless, of the opinion that the active substance is an isotope of atomic number 91, that is of proto-actinium, since as far as precipitation with manganese dioxide or with rhenium sulphide is concerned the properties are supposed to be identical. As a result of a more complete investigation Hahn and Meitner (1935) have concluded that neither the 13 min. nor the 90 min. substances have atomic numbers of 91, since they are not precipitated with uranium-Z, an isotope of proto-actinium, although both may be separated with rhenium or platinum. The substance with half-life period of 13 min. has properties similar to rhenium; the oxides of both are soluble

in sodium hydroxide, both sulphides are readily precipitated by hydrogen sulphide from 20 per cent. hydrochloric acid solution; and like rhenium the active substance can be converted into the septavalent form and then precipitated from acetic acid solution by means of nitron. The active substance may, therefore, well be an isotope of eka-rhenium.

The 100 min. half-life period element differs from the one just considered in giving an oxide insoluble in sodium hydroxide and in being precipitated as sulphide from more strongly acid solutions. It may possibly be an element of atomic number 94, although unlike osmium it does not give a volatile product on distillation with nitric acid. This difference from osmium is not surprising when it is remembered that the filling up of the fifth quantum level of electrons may well introduce new properties at this stage. Although there is yet no general agreement as to the interpretation of the results, the observations on the production of artificial radioactivity in uranium certainly opens up interesting possibilities.

Nuclear Stability. If atomic nuclei may be regarded as made up fundamentally of protons and neutrons, and if Z is the atomic number of an element and A its isotopic mass number, then Z gives the number of protons and $A - Z$ the number of neutrons in the nucleus. As the atomic number of the element increases so the number of neutrons accumulate, with the result that the mass number becomes greater than twice the atomic number, that is $A > 2Z$. If the difference $A - 2Z$ for every known stable and unstable isotope is plotted against the corresponding atomic number Z certain striking regularities become evident: all unstable nuclei which emit positrons contain a smaller number of neutrons than the stable isotope of the same atomic number, whereas when electrons are emitted the unstable isotope contains the greater number of neutrons. The process giving rise to positron emission may be represented formally * as

$$^{1}_{1}\mathrm{H} \rightarrow {}^{1}_{0}n + {}^{0}_{1}p,$$

so that when the unstable nucleus gives up a positron its

* This must not be taken to imply that the proton is necessarily made up of a neutron and positron.

neutron/proton ratio is increased, thus tending towards stability. Similarly, the emission of an electron can be written formally as

$$^{1}_{0}n \rightarrow {}^{1}_{1}\mathrm{H} + {}^{0}_{-1}e,$$

so that the result is a decrease in the ratio of neutrons to protons, as required for greater stability of this type of nucleus which contains an excess of neutrons. Nuclei containing equal numbers of protons and neutrons are stable up to an atomic number of 10 ; for elements between 11 and 20, inclusive, such nuclei are only stable for elements having *even* atomic numbers, but are unstable, emitting positrons, if the atomic numbers are odd. All nuclei, up to atomic number 20, are stable if there is one neutron in excess of the number of protons, and when the atomic number is even an excess of two neutrons also confers stability ; if it is odd, however, the nucleus is unstable and emits electrons. Similar, but less completely recognised, regularities apparently hold for elements of higher atomic number.

These empirical facts permit of predictions to be made concerning the stability of known isotopes, and account for many of the observations made in the study of artificial radioactivity. When this is excited by neutrons, the first stage either involves no emission of particles, or else a proton or an α-particle is liberated ; in any case the effect will be to increase the neutron/proton ratio in the resulting nucleus. If this is unstable it will obviously tend to acquire stability by the emission of an electron, as is actually the case in every instance so far studied. Bombardment by α-particles may result in the emission of neutrons or protons in the first stage : if the resulting nucleus is unstable it will be because it contains too few neutrons in the former case and too many in the latter. When the radio-element is formed as a result of neutron emission, it will itself give off a positron, whereas if its formation is accompanied by proton emission, electrons will be liberated during its disintegration : this may be seen in the examples

$$^{24}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{0}n + {}^{27}_{14}\mathrm{Si}\,; \quad {}^{27}_{14}\mathrm{Si} \rightarrow {}^{0}_{1}p + {}^{27}_{13}\mathrm{Al}$$

and

$$^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{28}_{13}\mathrm{Al}\,; \quad {}^{28}_{13}\mathrm{Al} \rightarrow {}^{0}_{-1}e + {}^{28}_{14}\mathrm{Si}.$$

The production of an active species by deuteron bombardment may be accompanied either by emission of neutrons or of protons ;

the results in each case will be similar to those with α-particles, as for example

$$^{14}_{7}N + ^{2}_{1}D \rightarrow ^{1}_{0}n + ^{15}_{8}O\,; \qquad ^{15}_{8}O \rightarrow ^{0}_{1}p + ^{15}_{7}N$$

and $$^{23}_{11}Na + ^{2}_{1}D \rightarrow ^{1}_{1}H + ^{24}_{11}Na\,; \quad ^{24}_{11}Na \rightarrow ^{0}_{-1}e + ^{24}_{12}Mg.$$

Since elements of high atomic number, greater than 20, interact, as far as is known at present, only with neutrons, and not with positively charged particles, it is evident that any unstable species formed will emit only electrons. The observations recorded here may eventually prove of value in the elucidation of the structures of atomic nuclei.

Applications of Artificial Radioactivity. The possibility of conferring radioactivity upon common elements by means of neutron bombardment, often without altering their chemical nature, is already providing a weapon for experimental investigations, in connection with which important developments may be expected. The radioactive property permits of the identification of a particular atom during a chemical reaction, and consequently its *rôle* in the process can be studied. For example, a solution of sodium bromide was exposed to neutron bombardment, so as to produce the radio-bromide, and divided into two equal parts; to one part was added free bromine and then both solutions were evaporated to dryness, and their radioactivities compared. The activity of the residue from the untreated solution was found to be 2·5 times as great as that from the other, showing that exchange had taken place between the inactive elementary bromine and the active bromide ions, with the result that some of the latter, after conversion into bromine, had passed off during evaporation (Grosse and Agruss, 1935). It has been suggested that in aqueous solution the elementary bromine sets up the equilibrium

$$Br_2 + H_2O \rightleftharpoons Br' + H^{\bullet} + HOBr,$$

and interchange takes place between the active and inactive bromide ions. Iodine and sodium iodide exchange in a similar manner in aqueous solution, and so also does iodine with methyl and allyl iodides; ethyl, *n*-propyl, *iso*-propyl and methylene iodides, and iodoform, on the other hand, exchange very slowly if at all (Juliusburger, Topley and Weiss, 1935). An exchange does

take place, however, when active sodium iodide and inactive ethyl iodide are dissolved together in alcohol and heated at 100° C. for five minutes (Hull, Shiflett and Lind, 1936). Organic bromine linked to carbon is said to show little tendency to interchange with free bromine, with hydrobromic acid, or with potassium or cupric bromide, as is to be expected. Cupric bromide containing radio-bromine, as a result of neutron bombardment, on heating to cuprous bromide and reconversion to the cupric form by inactive bromine shows less than the theoretical loss of activity. In fact, after five cycles of the decomposition of cupric bromide and its re-formation by ordinary bromine, the cupric compound still contains about one-half of its original activity. This result suggests that the two atoms of bromine in cupric bromide are joined in different ways to the copper atom, a possible explanation being that in the solid state the structure is somewhat analogous to $(CuBr)^{+}Br^{-}$ (Roginsky and Gopstein, 1935).

The Walden Inversion. An interesting application of artificially radioactive indicators is to throw some light on the problem of the Walden inversion. It is generally accepted that the stereochemical inversion occurs when substitution takes place within the optically active molecule, and direct proof of this view has been obtained for the special case in which interchange occurs between an iodine ion and the iodine atom of an optically active alkyl iodide, resulting in the racemisation of the latter. Sodium iodide was exposed to neutron action, so as to activate the iodine, and then dissolved in acetone together with *dl-sec.*-octyl iodide ; after a definite time had elapsed the reaction was stopped by the addition of crushed ice, and the organic iodide extracted by means of carbon tetrachloride. The organic and the inorganic iodine were both separately precipitated as silver iodide, dried, powdered, and the radioactivity of known weights determined in the usual way with a Geiger-Müller counter. The measurements were repeated, allowing different times of reaction, and from the results the rate of exchange between the octyl iodide and the iodine ion was determined. In another series of experiments the rate of racemisation of *d-sec.*-octyl iodide by sodium iodide in acetone solution was determined polarimetrically. When reduced to the same units the

two different processes were found to have velocity constants agreeing to within 10 per cent. The inversion reaction, in this instance, clearly involves exchange between the iodine atom attached to carbon in the *sec*-octyl iodide and the iodine ions in solution (Hughes, Topley *et al.*, 1935).

Other Applications. In conclusion, mention may be made of the use of radioactive phosphorus, ^{32}P, with a half-life period of 13 days, in the study of the fate of phosphorus in metabolic processes; the radio-phosphorus can be obtained by neutron bombardment of sulphur or chlorine compounds (Chiewitz and Hevesy, 1935). Other elements which play a part in the living organism may be applied in an analogous manner for the solution of biological problems.

REFERENCES

ANDERSON *et al.*, *Physical Rev.*, 1933, **43**, 491, 1034; 1934, **45**, 352; *Nature*, 1934, **133**, 313.*

BETHE. *Physical Rev.*, 1935, **47**, 633.

BLACKETT. *Nature*, 1933, **132**, 917.*

BLACKETT and OCCHIALINI. *Proc. Roy. Soc.*, 1933, [*A*], **139**, 699.

BLEAKNEY *et al.* *Physical Rev.*, 1934, **46**, 81.

BRADDICK. *Ann. Reports Chem. Soc.*, 1935, **33**, 15.*

CHADWICK *et al.* *Proc. Roy. Soc.*, 1931, [*A*], **130**, 463; 1932, [*A*], **136**, 692; 1933, [*A*], **142**, 1*; 1934, [*A*], **144**, 235; 1935, [*A*], **151**, 479; *Nature*, 1935, **135**, 65.

COCKROFT *et al.* *Proc. Roy. Soc.*, 1932, [*A*], **137**, 229; 1934, [*A*], **144**, 704; 1935, [*A*], **148**, 225; 1936, [*A*], **154**, 246, 261.

CRANE, LAURITSEN *et al.* *Physical Rev.*, 1934, **45**, 63, 345, 430, 493, 497, 507, 531; 1935, **47**, 420; **48**, 484.

CURIE and JOLIOT. *Comptes rend.*, 1932, **194**, 273, 708, 876; 1933, **196**, 1105; 1934, **198**, 254, 559, 2089; *J. Chem. physique*, 1934, **31**, 611.

DEE *et al.* *Nature*, 1933, **133**, 564; *Proc. Roy. Soc.*, 1933, [*A*], **141**, 733; 1935, [*A*], **148**, 623; **149**, 200; 1936, [*A*], **154**, 279.

ELLIS and HENDERSON. *Ibid.* 1934, [*A*], **146**, 206; *Nature*, 1934, **133**, 530; 1935, **135**, 429.

FEATHER. *Proc. Roy. Soc.*, 1932, [*A*], **136**, 709; 1933, [*A*], **141**,, 194; **142**, 689; *Ann. Reports Chem. Soc.*, 1934, **31**, 368.*

FERMI *et al.* *Proc. Roy. Soc.*, 1934, [*A*], **146**, 483; 1935, [*A*], **149**, 522.

FLÜGGE and KREBS. *Physikal Z.*, 1935, **36**, 466.*

FRISCH. *Nature*, 1934, **133**, 721; 1935, **136**, 220.

GAMOW. *Ibid.*, 1935, **135**, 858.

GLÜCKAUF and FAY. *J. Chem. Soc.*, 1936, 390.

GROSSE and AGRUSS. *J. Amer. Chem. Soc.*, 1935, **57**, 438, 440, 591.

HAFSTAD and TUVE. *Physical Rev.*, 1934, **45**, 902; 1935, **48**, 306.

HAHN *et al.* *Naturwiss*, 1935, **23**, 37, 230, 544.

HARKINS, GANS and NEWSON. *Physical Rev.*, 1933, **44**, 529.

HUGHES, TOPLEY *et al.* *J. Chem. Soc.*, 1935, 1525.

HULL, SHIFLETT and LIND. *J. Amer. Chem. Soc.*, 1936, **58**, 535.
JULIUSBURGER, TOPLEY and WEISS. *J. Chem. Physics*, 1935, **3**, 437; *J. Chem. Soc.*, 1935, 1295.
KIRCHNER. *Physikal Z.*, 1933, **34**, 777.
KURIE. *Physical Rev.*, 1934, **45**, 904; 1935, **47**, 97.
LAWRENCE, LIVINGSTON *et al.* *Ibid.*, 1932, **40**,19; 1934, **45**, 220, 346, 428, 608; **46**, 437; 1935, **47**, 17, 273, 343, 452.
LIBBY, PETERSON and LATIMER. *Ibid.*, 1935, **48**, 571.
LIVINGOOD and SNELL. *Ibid.*, 1934, **46**, 437.
LOZIER *et al.* *Ibid.*, p. 81.
MEITNER and PHILIPP. *Naturwiss.*, 1933, **21**, 268, 468.
MILLIKAN. "Electrons," 1935.*
NEWSON. *Physical Rev.*, 1935, **48**, 790.
OLIPHANT, RUTHERFORD *et al.* *Proc. Roy. Soc.*, 1933, [*A*], **141**, 259, 722; **144**, 692; 1934, [*A*], **146**, 922; 1935, [*A*], **149**, 406; **150**, 241.
PANETH and FAY. *J. Chem. Soc.*, 1936, 384.
PANETH and LOLEIT. *Nature*, 1935, **136**, 950.
RUPP. *Physikal. Z.*, 1934, **35**, 999; *Z. Physik.*, 1934, **92**, 485.
RUSSELL, *Ann. Reports Chem. Soc.*, 1933, **30**, 344.*
RUTHERFORD and CHADWICK. *Phil. Mag.*, 1921, **42**, 809; 1922, **44**, 417.
SUGDEN. *Science Progress*, 1935, **30**, 16.*
SZILARD and CHALMERS. *Nature*, 1934, **134**, 462, 494.
TUVE, HAFSTAD and DAHL. *Physical Rev.*, 1935, **48**, 315.
WILSON. *Proc. Roy. Soc.*, 1935, [*A*], **152**, 497.
YOST, RIDENOUR and SHINOHARA. *J. Chem. Physics*, 1935, **3**, 133.

* Review papers and books, wherein further references can be found, are marked with an asterisk.

CHAPTER II

STATISTICAL METHODS

THE principles involved in the statistical methods for calculating thermodynamic quantities, based on the concept of probability as used by Boltzmann and by Planck, have been clearly understood for some time, but only in recent years has it been possible to apply them for the determination of quantities of direct value to the chemist. The fundamental basis of the statistical treatment is very elegant, and although the derivation of some of the quantities involved requires a mathematical knowledge beyond the average, the results are relatively simple to understand and their application in many instances presents no serious difficulty. As a result of developments in the study of band spectra the energies of the various possible states of a given molecular species can now be calculated, provided its spectrum has been analysed, and the probability of the occurrence of each of these states is given in a simple manner by the results of wave mechanics. It is the combination of these two factors, that is, the energy of a given level and its probability, only available with certainty during the past few years, which has permitted the satisfactory application of statistical methods to the calculation of equilibrium constants and of free energy and entropy changes for gaseous reactions involving simple molecules. It is already well known ("Recent Advances in Physical Chemistry," Chapter IV.) that spectroscopic data can be used to determine heats of dissociation, and consequently of other thermochemical quantities, with an accuracy as great as, if not greater than, that possible by means of the best direct chemical measurements; the situation is rapidly being attained when the same can be said for the thermodynamic quantities already mentioned. Further, the methods to be described in this chapter are unique in the respect that they can

frequently be applied to reactions involving molecular fragments and unstable free radicals which are not capable of direct chemical investigation, provided, as is often the case, the particles give definite band spectra. The whole subject represents one of the most remarkable advances in theoretical chemistry of recent times and is worthy of consideration.

Translational Entropy. The energy of a molecule may be considered as divided into two independent parts : one is concerned with translational motion only, whereas the other involves all forms of internal energy. The portion due to translation of a thermodynamic quantity, for example, entropy, total energy or heat capacity, of any molecule, no matter how complex, in the ideal gaseous state, may be taken as being equal to the total value for a monatomic gas, since molecules of the latter have no internal energy. It is known from the kinetic theory that the total energy and heat capacity of a monatomic gas are $3RT/2$ and $3R/2$ per gm.-mol., and consequently these quantities must represent the *translational* energy and heat capacity of any molecular species. The entropy (S) of a monatomic gas has been calculated in a number of different ways and the result may be expressed in the form of the well-known Sackur-Tetrode equation, thus

$$S = R[\ln(2\pi kmT)^{3/2}V/h^3N + \tfrac{5}{2}] \quad . \; . \; . \; . \; . \; \text{(i)}$$

where R is the ordinary gas constant per gm.-mol., and k is the value per single molecule, $1{\cdot}37 \times 10^{-16}$ ergs per degree (Boltzmann constant), m is the weight of a single molecule, T the absolute temperature, V the volume of 1 gm.-mol. in cubic centimetres, h the Planck constant ($6{\cdot}547 \times 10^{-27}$ erg-secs.), and N the Avogadro number. The same expression will represent the translational entropy of any ideal gas : for convenience it may be written in the form

$$S_{\text{tr.}} = R\ln(mT)^{3/2}V + R\ln(2\pi k/h^2)^{3/2}/N + \tfrac{5}{2}R \quad . \; . \; \text{(ii)}$$

in which the variable factors are all contained in the first term. For a perfect gas $PV = R'T$ per gm.-mol., where the constant R' depends on the units used to express pressure and volume ; if P is expressed in atmospheres and V in c.c., as in equations (i) and

(ii), R' is equal to kN/a, where k has its usual value in ergs, and a is the equivalent of the normal atmosphere (760 mm. of mercury) in dynes per sq. cm., that is, $1{\cdot}0132 \times 10^6$. Substituting the term kNT/aP for V in equation (ii) and M/N for m, M being the ordinary molecular weight, it follows directly that

$$S_{\text{tr.}} = \tfrac{3}{2}R\ln M + \tfrac{5}{2}R\ln T - R\ln P + R\ln(2\pi k/h^2N)^{3/2}k/a + \tfrac{5}{2}R \quad \text{(iii)}$$

$$= \tfrac{3}{2}R\ln M + \tfrac{5}{2}R\ln T - R\ln P - 7{\cdot}267 + 4{\cdot}967 \quad \text{(iv)}$$

the latter equation being obtained by taking R as equal to $1{\cdot}985$ calories per gm.-mol., and using the recognised values for the constants k, h, N and a. The entropy, as obtained from equation (iv), is now expressed in calories per gram-molecule. The standard state of a gas is generally chosen as the ideal gas at a pressure of one atmosphere, and consequently if P is put equal to unity, the translational entropy becomes

$$S^{\circ}_{\text{tr.}} = \tfrac{3}{2}R\ln M + \tfrac{5}{2}R\ln T - 2{\cdot}300 \quad \text{(v)}$$

the usual superscript being used to indicate the standard state.

Internal Energy Functions. For polyatomic molecules it is now necessary to consider the portion of the various thermodynamic functions due to the different forms of internal energy, and the requisite equations can be obtained in several ways: one of the methods given by Giauque (1930) will be described here. According to the Maxwell-Boltzmann distribution law the ratio of the number of molecules (n') in one state possessing energy ε', to the number (n) in another state having energy ε is given by the expression

$$n'/n = e^{-\Delta\varepsilon/kT} \quad \text{(vi)}$$

where e is the base of natural logarithms, $\Delta\varepsilon$ is equal to $\varepsilon' - \varepsilon$, and k and T have their usual significance. If A is the number of molecules of a given gas in the lowest internal energy, *i.e.*, zero, state, then the number in any other, say the ith, state will be given by $Ae^{-\varepsilon_i/kT}$ where ε_i is the actual internal energy per molecule in this state, with reference to the zero state, *i.e.*, in excess of the zero-point energy.

Every state corresponds to a definite number of quantum specifications not possessed in every particular by any other

state, and each state may be assumed to have equal probability: that is to say, given equal opportunity to possess the energy necessary for their separate existence, all states are equally probable. A number of states, however, may possess energies which are so close to one another that they are almost indistinguishable: it is then convenient for purposes of calculation to group these together and to describe to the combined state an "*a priori* probability" or "statistical weight," representing the number of individual states included. The probability or weight-factor may be regarded as the degeneracy of a particular energy level, or alternatively as the multiplicity of that level; in the absence of a perturbing field these multiplets would coincide, but as some perturbing field is always present, *e.g.*, due to adjacent molecules or to the earth's magnetic field, there are very small energy differences between them. In terms of wave mechanics the statistical weight is the number of "proper values" (eigenvalues) which satisfy the wave equation for the molecule in any definite quantum state. If p_i is the statistical weight of the ith state, then the actual number of molecules in this state is $p_i Ae^{-\varepsilon_i/kT}$, the slight difference in energy of the multiplet levels being neglected. When one gram-molecule of a gas is considered the total number of molecules is the Avogadro number (N), and this must be equal to the sum of the molecules in the various states, characterised by 0, 1, 2, . . . etc.; hence

$$N = p_0 A + p_1 Ae^{-\varepsilon_1/kT} + p_2 Ae^{-\varepsilon_2/kT} + p_3 Ae^{-\varepsilon_3/kT} + \quad \text{(vii.)}$$

$$= A\Sigma pe^{-\varepsilon/kT} \quad \text{(viii.)}$$

The internal energy, in excess of the zero-point energy, of the molecular species in any state, is obtained by multiplying the energy of each molecule by the number in that state, and so this is given by $\varepsilon_i p_i Ae^{-\varepsilon_i/kT}$. The total internal energy of 1 gm.-mol. of the given substance, referred to the value at the absolute zero, *i.e.*, the zero-point, is the sum of all such terms, and so

$$E^\circ_{\text{int.}} = 0p_0 A + \varepsilon_1 p_1 Ae^{-\varepsilon_1/kT} + \varepsilon_2 p_2 Ae^{-\varepsilon_2/kT} + \quad \text{(ix.)}$$

$$= A\Sigma\varepsilon pe^{-\varepsilon/kT} \quad \text{(x.)}$$

the superscript in $E^\circ_{\text{int.}}$ referring to the standard state, in this

case that of a hypothetical ideal gas at one atmosphere pressure. From equations (viii.) and (x.) it is seen that

$$E^\circ_{\text{int.}} = \frac{N\Sigma\varepsilon p e^{-\varepsilon/kT}}{\Sigma p e^{-\varepsilon/kT}} = RT^2\frac{d\ln Q}{dT} \quad . \quad . \quad . \quad . \quad \text{(xi.)}$$

where Q is equal to $\Sigma p e^{-\varepsilon/kT}$, and is known as the "partition function," or sometimes as the "summation of state" or "state sum" ("zustandsumme," Planck). Strictly speaking this equation for the internal energy applies only if the Maxwell-Boltzmann distribution holds, and this is certainly not the case for real gases, especially at low temperatures; the assumption of an ideal gas, however, permits the use of the classical law, and in any case at appreciable temperatures both the alternative Bose-Einstein and Fermi-Dirac statistics lead to the same result. For the standard state, therefore, equation (xi.) may be taken as exact, and as a reasonable approximation for other conditions provided the temperature is not low.

If $E^\circ_{\text{int.}}$ is differentiated with respect to temperature an expression for the heat capacity due to the internal degrees of freedom, $C_{\text{int.}}$, is obtained; thus from equation (xi.) it follows that

$$\frac{dE^\circ_{\text{int.}}}{dT} = C_{\text{int.}} = \left(\frac{R}{T^2}\right)\frac{d^2\ln Q}{d(1/T)^2} \quad . \quad . \quad . \quad \text{(xii.)}$$

This is identical in form with an equation deduced by Reiche in 1919, but it can also be written in other forms which are often more convenient; thus

$$C_{\text{int}} = \frac{N^2}{RT^2}\left[\frac{\Sigma\varepsilon^2 p e^{-\varepsilon/kT}}{\Sigma p e^{-\varepsilon/kT}} - \left(\frac{\Sigma\varepsilon p e^{-\varepsilon/kT}}{\Sigma p e^{-\varepsilon/kT}}\right)^2\right] \quad . \quad . \quad \text{(xiii.)}$$

$$= \frac{N^2}{RT^2}\left[\frac{\Sigma C}{\Sigma A} - \left(\frac{\Sigma B}{\Sigma A}\right)^2\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv.)}$$

where $\Sigma A = Q = \Sigma p e^{-\varepsilon/kT}$; $\Sigma B = \Sigma\varepsilon p e^{-\varepsilon/kT} = kT^2(dQ/dT)$; and $\Sigma C = \Sigma\varepsilon^2 p e^{-\varepsilon/kT} = 2k^2T^3(dQ/dT) + k^2T^4(d^2Q/dT^2)$.

By making use of the definition of entropy change, $dS = Cd\ln T$, it is possible to write

$$dS^\circ_{\text{int.}} = \frac{dE^\circ_{\text{int.}}}{dT}\, d\ln T \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xv.)}$$

and $$S^\circ_{\text{int.}} - S_0^\circ = \int_0^T \frac{dE^\circ_{\text{int.}}}{dT} d\ln T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xvi.)}$$

The value of $E^\circ_{\text{int.}}$ given by equation (xi.) may be written in the alternative form

$$E^\circ_{\text{int.}} = -R\frac{d\ln Q}{d(1/T)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xi}a\text{.)}$$

and hence

$$S^\circ_{\text{int.}} - S_0^\circ = -R\int_0^T \frac{d}{dT}\left[\frac{d\ln Q}{d(1/T)}\right] d\ln T \quad . \quad . \quad . \quad \text{(xvii.)}$$

$$= R\left[\ln Q - \ln Q_0 + T\frac{d\ln Q}{dT}\right] \quad . \quad . \quad \text{(xviii.)}$$

The term $R\ln Q_0$ is equal to S_0°, the standard entropy at the absolute zero, and so it follows that

$$S^\circ_{\text{int.}} = R\left[\ln Q + T\frac{d\ln Q}{dT}\right] . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xix.)}$$

or in the alternative form,

$$S^\circ_{\text{int.}} = R\left[\ln A + \frac{1}{kT}\frac{\Sigma B}{\Sigma A}\right] \quad . \quad . \quad . \quad . \quad . \quad \text{(xx.)}$$

$$= R\left[\ln \Sigma p e^{-\epsilon/kT} + \frac{\Sigma \epsilon p e^{-\epsilon/kT}}{kT\Sigma p e^{-\epsilon/kT}}\right] . \quad . \quad \text{(xxi.)}$$

where A and B have the same significance as given above. From any of these equations it is possible to calculate the internal entropy of an ideal gas, and the addition of the translational entropy, as obtained from equation (v.), gives the value of S°, the total entropy in the standard state ; that is,

$$S^\circ = S^\circ_{\text{tr.}} + S^\circ_{\text{int.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxii.)}$$

If necessary, a correction can be applied for deviation of an actual gas from the standard state, that is, from ideal behaviour, but this is generally quite small for appreciable temperatures.

For chemical purposes the free energy of a substance is of more direct interest, since by means of such data it is possible to

calculate the equilibrium constants of gaseous reactions. Utilising the familiar equations

$$F = H - TS$$

and

$$H = E + PV$$

where F is the free energy, H the heat content and E the total energy, it is possible to write for a gas in its standard (ideal) state, for which $PV = RT$, the relationships

$$H^\circ = E^\circ + RT$$

and

$$F^\circ = E^\circ + RT - TS^\circ \quad . \; . \; . \quad \text{(xxiii.)}$$

where E° and S° refer to the *total* energy and entropy, respectively, including both translational and internal degrees of freedom. The total energy E° must also include the energy of the gas in its lowest energy state, that is, the zero-point energy (E_0°), in addition to the translational energy ($3RT/2$) and the internal energy ($E^\circ_{\text{int.}}$) obtained from equation (xi.); thus

$$E^\circ = E_0^\circ + \tfrac{3}{2}RT + RT^2(d\ln Q/dT) \quad . \; . \; . \quad \text{(xxiv.)}$$

From equations (xxiii.) and (xxiv.) it follows that

$$F^\circ - E_0^\circ = \tfrac{3}{2}RT + RT^2(d\ln Q/dT) + RT - TS^\circ \quad \text{(xxv.)}$$

and substituting the value for S° as given by equations (v.), (xix.) and (xxii.), it can be readily shown that

$$F^\circ - E_0^\circ = -\tfrac{3}{2}RT\ln M - \tfrac{5}{2}RT\ln T - RT\ln Q + 7{\cdot}267T \quad \text{(xxvi.)}$$

and

$$F^\circ = E_0^\circ - \tfrac{3}{2}RT\ln M - \tfrac{5}{2}RT\ln T - RT\ln Q + 7{\cdot}267T \quad \text{(xxvi}a\text{.)}$$

From equation (xxvi.) it is possible, provided Q is known, to determine the $F^\circ - E_0^\circ$ values for resultants and reactants, and consequently $\Delta(F^\circ - E_0^\circ)$ for a chemical reaction can be computed; this is related to the thermodynamic equilibrium constant in the following manner. By definition, for the standard state,

$$\frac{\Delta F^\circ}{T} = -R\ln K_p \quad . \; . \; . \; . \; \text{r} \quad \text{(xxvii.)}$$

and since

$$\Delta F^\circ = \Delta(F^\circ - E_0^\circ) + \Delta E_0^\circ,$$

it follows that

$$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right) - \frac{\Delta E_0^\circ}{T} = R\ln K_p \quad . \; . \quad \text{(xxvii}a\text{.)}$$

The determination of K_p for a reaction involves a knowledge of

$-(F^\circ - E_0^\circ)/T$ for the substances concerned in the process, and these "free energy functions" have been calculated for many elements and compounds with the aid of equation (xxvi.), in the manner to be described below, and the results tabulated in the literature of the subject (see p. 91). Alternatively, K_p can be expressed by combining equations (xxvi*a*.) and (xxvii.), giving

$$-\ln K_p = \frac{\Delta E_0^\circ}{RT} - \tfrac{3}{2}\Sigma\nu\ln M - \tfrac{5}{2}\Sigma\nu\ln T - \Sigma\nu\ln Q + \Sigma\nu\frac{7{\cdot}267}{R} \quad \text{(xxviii.)}$$

from which K_p may be evaluated; ν represents the number of molecules of each of the species involved in the reaction.

In addition to a knowledge of the partition function Q it is always necessary to know the value of ΔE_0° for the reaction as a whole: this may be determined by combining appropriate spectroscopic data for heats of dissociation, since these are the values for the lowest (zero) energy levels. Alternatively ΔE_0° may be obtained from the zero-point energies of the reactants and resultants calculated, for each substance, from the equation

$$E_0^\circ = (\tfrac{1}{2}\omega_e - \tfrac{1}{4}x\omega_e)Nhc \quad . \quad . \quad . \quad . \quad \text{(xxix.)}$$

in which ω_e (cm.$^{-1}$) is the equilibrium vibration frequency, x the anharmonicity constant, c the velocity of light, and N and h are the Avogadro and Planck constants, as usual ("Recent Advances in Physical Chemistry," Chapter IV.). If there are several modes of vibration in a molecule, *e.g.*, one containing three or more atoms, then E_0° is the sum of the zero-point energies, as calculated by equation (xxix.), for each vibrational mode. Another method for obtaining ΔE_0° is available if ΔH° the heat of reaction at constant pressure is known: since $H^\circ = E^\circ + RT$ it can be deduced from equations (xxiii.) and (xxiv.) that

$$\Delta E_0^\circ = \Delta H^\circ - \Delta[\tfrac{5}{2}RT + RT^2(d\ln Q/dT)] \quad . \quad . \quad \text{(xxx.)}$$

and consequently ΔE_0° can be determined provided $d\ln Q/dT$ is available.

The equations for the free energy and the equilibrium constant may be written in other ways which are of both practical and theoretical interest. The factor 7·267 in equation (xxvi.) arises

from the term $-R\ln(2\pi k/h^2N)^{3/2}k/a$, as may be seen by comparing equations (iii.) and (iv.), and so equation (xxvi.) may be written as

$$F^\circ - E_0^\circ = -RT\ln[Q(2\pi mkT/h^2)^{3/2}kT/a] \quad \text{(xxxi.)}$$

and a further modification, in which E_0° is replaced by $\ln e^{E_0^\circ}$, leads to the expression

$$F^\circ = -RT\ln\{[e^{-E_0^\circ/RT}Q(2\pi mkT/h^2)^{3/2}](kT/a)\} \quad \text{(xxxii.)}$$

$$= -RT\ln G(kT/a) \quad \text{(xxxiii.)}$$

where G is used to represent the term within the square brackets. For any reversible chemical reaction

$$aA + bB \ldots \rightleftharpoons mM + nN \ldots$$

it follows, since $\Delta F^\circ = -RT\ln K_p'$ (equation xxvii.), that

$$K_p = \frac{G_M^m \times G_N^n \times \ldots}{G_A^a \times G_B^b \times \ldots} \times (kT/a)^{\Delta\nu} \quad \text{(xxxiv.)}$$

where $\Delta\nu = (m + n + \ldots) - (a + b + \ldots)$, that is, the increase in the number of molecules in the reaction as written. The equation (xxxiv.) gives K_p with pressures, expressed in atmospheres, but if $a^{\Delta\nu}$ is omitted the constant is then given in dynes per sq. cm. as the pressure unit; if the factor $(kT/a)^{\Delta\nu}$ is left out the equilibrium constant is obtained with concentrations of reactants and resultants in molecules per cubic centimetre.

The quantity G, which may be regarded as the *complete* partition function of any molecular species under given conditions, is made up of three separate terms. The first of these, $e^{-E_0^\circ/RT}$, is called the "zero-point" or "structural" factor, and the second, Q, is the partition function for internal energy, that is, for vibration and rotation, including nuclear-spin effects (*vide infra*). The third portion $(2\pi mkT/h^2)^{3/2}$ is effectively the partition function for translatory motion with three degrees of freedom; the cube-root of this quantity, namely $(2\pi mkT/h^2)^{1/2}$, is the function for each translational degree of freedom. This quantity is of importance in connection with modern theories of reaction velocity and reference to it will be made in another chapter (p. 309).

EVALUATION OF PARTITION FUNCTIONS

In order to apply the equations which have been deduced here, the essential point remaining is the determination of the state sum or partition function Q for internal degrees of freedom: to calculate this quantity it is necessary to evaluate the $pe^{-\epsilon/kT}$ terms and to sum them over *all possible* energy states of the molecule. The energy of each state can be obtained from spectroscopic data with the aid of the fundamental equation of the quantum theory, $\Delta\epsilon = hc\nu$, where ν cm.$^{-1}$ is the frequency of the spectral line, but there is sometimes an uncertainty concerning the correct statistical weight (p) to be assigned to any given energy state. The use of incorrect values of p invalidated the earlier applications of some of the equations given above, but developments in wave mechanics have helped very considerably to clarify the position. The principles involved in the determination of the partition function may be conveniently considered under three headings: (*a*) atoms and monatomic molecules, (*b*) diatomic, and (*c*) more complex molecules.

Atoms and Monatomic Molecules. The partition function (Q) for an atom or a monatomic molecule is given by the product of the function for nuclear-spin orientation and that for every possible electronic configuration. The nuclear-spin function is equal to the corresponding statistical weight, since ϵ is zero, and is given by $2i + 1$, where i is the number of units of nuclear-spin momentum; this quantity represents the total number of possible orientations, having nearly the same energy, of the nucleus in a perturbing field. The weight-factor (p) for each electronic configuration is $2j_s + 1$, where j_s, which has only positive values given by the term $l \pm s$, results from the combination of the orbital quantum number (l) and the resultant spin (s) of the electrons. To obtain the complete electronic partition function the statistical weight must be multiplied by $e^{-\epsilon/kT}$ for the appropriate state, ϵ being the energy in excess of the ground state, and summed over all possible configurations indicated by spectroscopic data. This apparently stupendous task is simplified by the fact that the quantity $e^{-\epsilon/kT}$ has an appreciable value only when the temperature exceeds $hc\nu/4k$, where ν in cm.$^{-1}$ is the frequency

separation of the given energy level above the ground level. It is only at high temperatures, therefore, that any level other than the ground state, for which $\varepsilon = 0$, need be considered. With atomic hydrogen, for example, $i = \frac{1}{2}$ (see Chapter III.), and so the nuclear-spin partition function is 2; the electronic ground level ($n = 1$) is a singlet state with $j_s = \frac{1}{2}$, l being 0 and s is $\frac{1}{2}$, and since $\varepsilon = 0$, the electronic function is also 2. Since no higher level need be considered, the complete partition function is 4, there being no vibrational or rotational energy for an atom.

The nuclear spin of the chlorine atom is $\frac{5}{2}$, and so the nuclear-spin function is 6; spectroscopic evidence indicates the ground state to be an inverted ^2P doublet, with j_s values of $\frac{3}{2}$ for the lower and $\frac{1}{2}$ for the upper level, the frequency separation being 881 cm.$^{-1}$ The statistical weights for the two levels, that is $2j_s + 1$, are 4 and 2, respectively, and so the electronic partition function is $4 + 2e^{-881hc/kT}$; the complete function for the atom is then obtained by multiplying by 6, the nuclear-spin factor. No other energy levels need be considered at any reasonable temperature.

Oxygen Atoms. The ground level of normal atomic oxygen is an inverted triplet (^3P) term, the j_s values being 2, 1 and 0, respectively, with frequency separations of 157·4 cm.$^{-1}$ and 226·1 cm.$^{-1}$ above the lowest level; the corresponding statistical weights are 5, 3 and 1, respectively. At high temperatures it is also necessary to include the contributions for two metastable levels consisting of $^1D_2$ and $^1S_0$ terms, the complete data being given in Table III.

TABLE III.—*Energy Levels and Statistical Weights of Atomic Oxygen.*

Term.	Frequency Separation.	j_s	p
$^3P_2$	—	2	5
$^3P_1$	157·4	1	3
$^3P_0$	226·1	0	1
$^1D_2$	15807	2	5
$^1S_0$	33662	0	1

The electronic partition function is obtained by summing the five $pe^{-hcv/kT}$ terms, provided the temperature is high enough to make this necessary; at low temperatures only the first three levels need be included. Since the oxygen nucleus has no spin, that is $i = 0$, the complete partition function is the same as the electronic contribution.

Diatomic Molecules. The internal energy of a diatomic molecule may be divided into three parts, namely, electronic, vibrational and rotational ("Recent Advances in Physical Chemistry," Chapter IV.), and the partition function must be summed over every one of the corresponding energy levels which contributes appreciably towards the total. In the first place each electronic level should be considered separately, and all the vibrational levels within it must be taken individually and the $pe^{-\epsilon/kT}$ terms, where ϵ is the sum of the appropriate electronic, vibrational and rotational energies, for all the rotational states within each must then be summed. In general, electronic levels above the ground state can be neglected, since the energy of an excited state is usually so high as to contribute to an inappreciable extent to the complete partition function, except at elevated temperatures. Oxygen, for example, has excited states at 0·97 and 1·62 electron-volts, respectively, above the ground level; such separations are unusually small, nevertheless it has been shown that the effect of the excited levels on the partition function becomes noticeable only at 1000° K. and 2500° K., respectively. Although, as a general rule, excited levels can be ignored, it is essential to allow for the multiplicity, if any, of the ground state. Most diatomic molecules have $^1\Sigma$ ground terms, and so there are no multiplet levels, but nitric oxide, oxygen, hydroxyl, and the cyanide radical are the chief exceptions, to some of which reference will be made shortly.

Nitric Oxide. The energy separations of successive vibrational levels are smaller than for electronic levels, and so it is often necessary to sum the $pe^{-\epsilon/kT}$ terms over a number of levels, but only a few of the lowest states need actually be included, especially if the temperature is not very high. The point may be illustrated by the data in Table IV., taken from the calculations of Johnston

and Chapman (1933), for nitric oxide at 2000° K. The rotational sums ($Q_{rot.}$) are given for the first twelve vibrational levels, *i.e.*, $v = 0, 1, 2, \ldots 11$, where v is the vibrational quantum number; it is evident that the contribution to the partition function falls off rapidly in the higher vibrational levels, and that for most purposes the neglect of levels above the eighth will introduce no serious error.

TABLE IV.—*Rotational Sums for Nitric Oxide at 2000° K. in Twelve Vibrational Levels*

v	$Q_{rot.}$	v	$Q_{rot.}$	v	$Q_{rot.}$
0	1582·80	4	8·64	8	0·07
1	417·20	5	2·47	9	0·02
2	112·26	6	0·72	10	0·01
3	30·84	7	0·22	11	0·00

Similar results have been obtained for oxygen, but with hydrogen the contribution to the partition function is appreciable at 2000° K. only for the first four vibrational levels ($v = 0$, 1, 2 and 3). At lower temperatures the rotational sums are smaller and the values fall off to negligible amounts more rapidly: thus for oxygen and nitric oxide only five levels need be considered at 900° K., whereas at this temperature only the lowest level ($v = 0$) contributes appreciably to the partition function for hydrogen.

The rotational levels of a molecule are generally close together, that is, the energy separations are small, and so a large number must be included when summing the $pe^{-\epsilon/kT}$ terms; with nitric oxide, for example, 81, 168 and 200 levels, respectively, contribute to the rotational sum at temperatures of 1000°, 2000° and 3000° K., for the lowest vibrational level. In the higher vibrational states the total number of rotational levels to be included is, however, much smaller. It is evident that the process of summation may become very tedious, but it will be seen later that various means have been devised for simplifying the procedure.

Rotational Statistical Weights. Whereas each electronic level, apart from multiplets, and each vibrational level, provided it is not

degenerate, has a statistical weight of unity, this is not the case for the rotational states. As well as the rotational degeneracy resulting from nuclear spin, each rotational level has a statistical weight of $2J + 1$, where J is the quantum number of the level. When the molecule has two similar nuclei with spin i, the total statistical weight of each rotational level in a Σ^+ state* is obtained by multiplying the $2J + 1$ value by the nuclear-spin factor $(i + 1)(2i + 1)$, for even values of J, including zero, and by $i(2i + 1)$ for odd values of J, if the nuclei follow the Bose-Einstein statistics, but the factors are reversed if the Fermi-Dirac statistics are followed. Ordinary molecular hydrogen obeys the latter statistics, and since the nuclei have one-half unit of spin momentum, *i.e.*, $i = \frac{1}{2}$, the statistical weights of even rotational levels are $2J + 1$ and those of the odd levels are $3(2J + 1)$. Deuterium molecules, on the other hand, have nuclei with unit spin, *i.e.*, $i = 1$, which follow the Bose-Einstein statistics; hence the statistical weight for even and odd levels are $2(2J + 1)$ and $2J + 1$, respectively. The rotational partition functions ($Q_{\text{rot.}}$), including spin factors, may thus be written:

for hydrogen $$Q_{\text{rot.}} = \sum_{J = 0, 2, 4, 6 \ldots}(2J + 1)e^{-\varepsilon_J/kT} + 3\sum_{J = 1, 3, 5, 7 \ldots}(2J + 1)e^{-\varepsilon_J/kT}$$

and for deuterium $$Q_{\text{rot.}} = 2\sum_{J = 0, 2, 4, 6 \ldots}(2J + 1)e^{-\varepsilon_J/kT} + \sum_{J = 1,3,5,7 \ldots}(2J + 1)e^{-\varepsilon_J/kT}$$

where ε_J represents the rotational energy for the particular level having the quantum number J.

Molecular Oxygen. For a molecule in a Σ^- state the statistical weights are the reverse of those for the corresponding conditions with a Σ^+ state (see p. 133); this may best be illustrated by a consideration of the symmetrical $^{16}O^{16}O$ molecule. The ^{16}O nucleus obeys the Bose-Einstein statistics, and since it has no spin momentum, *i.e.*, $i = 0$, the statistical weights are zero for even rotational levels and $2J + 1$ for the odd levels. It is evident that alternate rotational levels are missing for the molecule $^{16}O^{16}O$, which is the main constituent of ordinary oxygen gas. The ground level of these molecules is a triplet state, and since the

* For an explanation of the term symbols, see p. 132, and "Recent Advances in Physical Chemistry," Chapter I.

energy separations are very small, of the order of 2 cm.$^{-1}$, the three levels may be regarded as having the energy of the lowest level, that is, $\varepsilon = 0$. The value of J used in calculating the statistical weight is determined by the rotational quantum numbers, which are $K + 1$, K, and $K - 1$, respectively, for the three constituent levels, only odd values of K being permitted. The corresponding p values are, therefore, $2K + 3$, $2K + 1$ and $2K - 1$, where K has a series of values 1, 3, 5, etc., and the rotational contribution to the partition function for the symmetrical oxygen molecules may be written thus:

$$Q_{\text{rot.}} = \underset{K = 1, 3, 5 \ldots}{\Sigma}(2K+3)e^{-\varepsilon_K/kT} + \underset{K = 1, 3, 5 \ldots}{\Sigma}(2K + 1)e^{-\varepsilon_K/kT} + \underset{K = 1, 3, 5 \ldots}{\Sigma}(2K - 1)e^{-\varepsilon_K/kT}.$$

It has been already mentioned (p. 64) that at high temperatures two excited states of molecular oxygen must be taken into consideration in computing the total state sum.

Hetero-nuclear Molecules. If a diatomic molecule has two dissimilar nuclei, having spins i and i', the nuclear-spin factor, by which the $2J + 1$ value for the statistical weight of *every* level is to be multiplied, is then $(2i + 1)(2i' + 1)$ to obtain the complete rotational statistical weight. For a $^1\Sigma$ molecule the determination of the partition function involves no complications, but where other types of ground terms have to be considered there are additional factors to be taken into consideration. The cyanide radical, for example, has a $^2\Sigma$ ground term, that is to say every rotational level is a doublet. The value of J for one set is $K + \frac{1}{2}$, and for the other it is $K - \frac{1}{2}$, where K, the rotational quantum number, can have any integral value, including zero, provided J is not negative. The statistical weights for the two sets of levels are thus $2K + 2$ and $2K$, respectively, which must still be multiplied by the nuclear-spin factor. The spins of carbon (^{12}C) and nitrogen (^{14}N) nuclei are 0 and 1, respectively; hence the nuclear-spin factor for every rotational level is 3. The complete rotational partition function for the cyanide radical is, therefore, given by the expression

$$Q_{\text{rot.}} = \underset{K = 0, 1, 2, 3 \ldots}{3\Sigma}(2K + 2)e^{-\varepsilon_K/kT} + \underset{K = 1, 2, 3, 4 \ldots}{3\Sigma 2K}e^{-\varepsilon_K/kT}.$$

For molecules having other than Σ ground terms, the phenomenon

known as Λ-type doubling must be taken into consideration: this results in the splitting of every rotational level into two slightly separated sub-levels. Nitric oxide, for example, in its ground state is represented by the term $^2\Pi$, the normal doublets having a frequency separation of 120 cm.$^{-1}$, which is too large to be ignored; for the lower constituent of the doublet the smallest value of J, here also the effective rotational quantum number is $\frac{1}{2}$, whereas for the upper constituent it is $\frac{3}{2}$, subsequent values increasing by steps of unity. In addition to this doubling the Λ-type doubling results in a further splitting of each constituent into two sub-levels: the frequency separation of these sub-levels is generally so small that the energies may be regarded as identical, so that the effect is merely to double the statistical weights. Finally, the nuclear-spin factor must be included: since the nuclear spins of nitrogen (^{14}N) and oxygen (^{16}O) are 1 and 0, respectively, this factor, by which the weight of every level must be multiplied, is 3, so that the complete rotational partition function may be written:

$$Q_{\text{rot.}} = 2 \times \underset{J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \ldots}{3\Sigma(2J + 1)e^{-\epsilon_J/kT}} + 2 \times \underset{J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2} \ldots}{3\Sigma(2J+1)e^{-\epsilon' J/kT}},$$

where 2 and 3 are the Λ-type doubling and nuclear-spin factors, respectively. The energies of the two main constituents of the doublet are represented by ε_J (lower) and ε'_J (upper), the corresponding values differing by the equivalent of approximately 120 cm.$^{-1}$. The hydroxyl radical is similar to nitric oxide in the respect that it has a $^2\Pi$ ground term, although it is "inverted," so that the smallest values of J are $\frac{3}{2}$ and $\frac{1}{2}$, respectively, for the lower and upper constituents. In this case, however, the separation of the Λ-type doublets is unusually large, so that it is not sufficient merely to double the statistical weights, as is done with nitric oxide. The complete rotational partition function is therefore obtained as the sum of four $2\Sigma(2J + 1)e^{-\epsilon_J/kT}$ terms, with different sets of ε_J values for each series. The factor 2 is the nuclear-spin contribution, since the spins of the hydrogen and oxygen nuclei are $\frac{1}{2}$ and 0, respectively.

Energy Values. In the early applications of the partition

'unction for the determination of thermodynamic constants, the :nergies of the rotational levels were calculated from the actual)bserved frequencies of the spectral lines of the molecules con-:erned, the lowest rotational level in the lowest vibrational band, $v = 0$), being taken as the zero point. More recently, however, ıse has been made of formulæ by means of which the frequencies)f the lines in the band spectrum of a molecule can be expressed ; .hus, for a diatomic molecule, equations of the type

$$\nu = \nu_0 + \omega_e(v + \tfrac{1}{2}) - x\omega_e(v + \tfrac{1}{2})^2 \ . \ . \ .$$
$$+ B_vJ(J + 1) + D_vJ^2(J + 1)^2 + F_vJ^3(J + 1)^3 \quad . \quad \text{(xxxv.)}$$

ıave been employed, where ν_0 is the electronic frequency-separation, vhich is zero for the ground state, ω_e is the equilibrium vibration 'requency, x the anharmonicity constant, and v and J (sometimes K) are the vibrational and rotational quantum numbers, respec-:ively. The factors B_v and D_v vary with the vibrational level ıccording to the relationships.

$$B_v = B_e - \alpha(v + \tfrac{1}{2}) + \gamma(v + \tfrac{1}{2}^2 - \ . \ . \ . \text{ etc.}$$
$$D_v = D_e + \beta(v + \tfrac{1}{2})^2 + \delta(v + \tfrac{1}{2})^4 + \ . \ . \ . \text{ etc.}$$

B_e, D_e and α, β, γ and δ being constants for the given electronic .evel, which are determined from the observed frequencies of the ines constituting the band spectrum of the molecule. The ıuantity F_v also depends on v, but as it is in any case very small .he variation may be neglected. The purpose of the correction 'actors, α, β, γ and δ, is to allow for changes in the moment of nertia of the molecule in the different vibrational levels, and also 'or interaction of vibrational and rotational energies. For a rigid nolecule in which there is also no interaction, D_v and F_v would)e zero, and B_v would be constant and equal to $h^2/8\pi^2Ic$, where I s the moment of inertia. By means of the equations given above :he frequencies of all the rotational lines can be calculated, and hence the total internal energy, that is the sum of the electronic, vibrational and rotational terms, of the corresponding levels :an be evaluated by the aid of the fundamental equation of the ıuantum theory (p. 62). The value of ε to be used in the determination of the partition function is then obtained by sub-tracting the energy for the lowest level ($v = 0$, and $J = 0$) in the

ground state, that is, the zero-point energy $(\frac{1}{2}\omega_e - \frac{1}{4}x\omega_e)hc$. It is obviously possible, as an alternative, to multiply equation (xxxv.) by hc and then subtract the expression for the zero-point energy, thus leaving an equation from which the ε values may be obtained directly by inserting the appropriate v and J values. When spectroscopic measurements are relatively limited, it is often possible by means of such an equation to determine, with fair accuracy, the energies of levels giving rise to bands beyond the limit of actual experimental observation; such energies have frequently to be included in the evaluation of the partition function.

Summation Procedure. It is clear from what has been already said that a tedious process of summation is necessary for obtaining the complete partition function of a molecule, especially at high temperatures, where the $pe^{-\varepsilon/kT}$ terms for a large number of rotational levels in each of several vibrational, and possibly electronic, states must be included. Various methods have been suggested for simplifying the labour involved. The most important of these employs the device of expressing the total internal energy in the form of an equation, as already indicated; this is then arranged as an asymptotic series of exponential terms and summation is replaced by integration. Provided the temperature is not too low this approximation involves no appreciable error. The method in its simplest form was first used for rigid diatomic molecules (Mulholland, 1928) and was later extended (Giauque and Overstreet, 1932) to allow for non-rigidity in molecules having $^1\Sigma$ ground terms. By summing a small number of terms in a series it was possible to determine the rotational partition function for a given vibrational state, and the calculation had to be repeated for each vibrational level contributing appreciably to the total sum. Since the evaluation of entropy and heat capacity require a knowledge of the first and second derivatives of Q, as well as of Q itself (see equations (xiv.) and (xx.)), these have also been expressed in the form of a series which can be readily summed. If many vibrational levels have to be taken into account, the summation may still be laborious, although the work can be simplified by utilising the observation that the rotational function

$Q_{\text{rot.}}$ and its derivatives, $dQ_{\text{rot.}}/dT$ and $d^2Q_{\text{rot.}}/dT^2$, for one vibrational level v bear a constant ratio to the values for the $v + 1$ level. Further mathematical developments have eliminated even this summation, and have permitted the application of the methods described to determine complete partition functions of $^2\Pi$ and $^3\Sigma$ diatomic molecules, and even of polyatomic molecules. By means of suitable tables, based on the formulæ derived, the labour involved in the calculation of partition functions has been considerably diminished (Gordon and Barnes, 1933, 1934). These tables and equations apply only to unsymmetrical molecules in which there is no alternation in the statistical weights of odd and even levels, and no allowance is made for nuclear-spin degeneracy : appropriate corrections for both these factors can, however, readily be made, as will be seen later (p. 72).

Approximation Methods. In addition to the method already outlined others of a definitely simpler and more approximate nature have been applied, and at relatively high temperatures they give results which compare quite favourably with those obtained by the accurate procedure (*vide infra*). If the different forms of internal energy can be regarded as being independent of one another, just as they are independent of the translational energy, then the complete partition function could be taken as equal to the product of electronic, vibrational and rotational functions, $Q_{\text{el.}}$, $Q_{\text{vib.}}$, and $Q_{\text{rot.}}$, respectively, where

$$Q_{\text{el.}} = \Sigma p_{\text{el.}} e^{-\epsilon_{\text{el.}}/kT}\ ;\ Q_{\text{vib.}} = \Sigma p_{\text{vib.}} e^{-\epsilon_{\text{vib.}}/kT}\ ;\ Q_{\text{rot.}} = \Sigma p_{\text{rot.}} e^{-\epsilon_{\text{rot.}}/kT}.$$

This is, of course, not actually the case, since a change in the vibrational energy affects the spacing of the rotational levels, and similarly vibrational and rotational levels are both affected by the electronic state of the molecule ; it is only possible, therefore, as a first approximation to assume complete independence of the different forms of energy and to write :

$$Q = Q_{\text{el.}} \times Q_{\text{vib.}} \times Q_{\text{rot.}} \quad . \ . \ . \ . \quad \text{(xxxvi.)}$$

In evaluating the separate terms $p_{\text{el.}}$ may be taken as equal to the multiplicity of the particular electronic state being considered, provided the energy of separation of these multiplets is not large, and $\epsilon_{\text{el.}}$, the corresponding energy of the level above the ground

state, is determined from the value of ν_0 in equation (xxxv.). In the $Q_{\text{vib.}}$ term, $p_{\text{vib.}}$ is always unity for a diatomic molecule, and $\varepsilon_{\text{vib.}}$ may be taken to be the same in all electronic levels and equal to $hc\omega_0 v$ in excess of the zero-point energy, where ω_0 is the fundamental frequency in the ground state, the anharmonicity constant being neglected.* The vibrational partition function is thus given by the expression

$$Q_{\text{vib.}} = \sum_{v=0}^{\infty} e^{-hc\omega_0 v/kT} = (1 - e^{-hc\omega_0/kT})^{-1} \quad . \quad . \quad \text{(xxxvii.)}$$

Since the rotational and vibrational energies are assumed independent, the molecule may be regarded as being rigid, so that the moment of inertia is constant; the rotational energy of such a $^1\Sigma$ diatomic molecule is then $J(J+1)h^2/8\pi^2 I$, and consequently

$$Q_{\text{rot.}} = \sum_{J=0}^{\infty} (2J+1)e^{-\sigma J(J+1)} \quad . \quad . \quad . \quad \text{(xxxviii.)}$$

where

$$\sigma = h^2/8\pi^2 IkT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxix.)}$$

If σ is small, that is, at relatively high temperatures, especially for molecules having large moments of inertia, the summation may be replaced by integration, with the result that

$$Q_{\text{rot.}} = 1/\sigma = 8\pi^2 IkT/h^2. \quad . \quad . \quad . \quad . \quad . \quad \text{(xl.)}$$

For molecules in other than $^1\Sigma$ states, analogous approximate expressions for the rotational function, applicable at appreciable temperatures, can be deduced; if necessary, the effect of Λ-type doubling must be included by means of a factor 2, the frequency separation of the sub-levels being ignored.

Nuclear-Spin Factor. It is important to note that in the deduction of equation (xl.) the nuclear-spin factor has not been taken into consideration, and no allowance has been made for the possibility of alternations in the statistical weights of successive rotational levels, such as would arise in a homonuclear, *i.e.*, symmetrical, molecule. If the molecule is heteronuclear both odd and even levels have a weight of $2J+1$, and there is no alterna-

* If the vibration is harmonic, the energy is equal to $hc\omega_0(v+\frac{1}{2})$, and the zero-point energy, for $v=0$, is $\frac{1}{2}hc\omega_0$; consequently the vibrational energy in excess of the zero-point value is $hc\omega_0 v$.

tion : the effect of nuclear spin on the particular function is then obtained by multiplying the value of $Q_{\text{rot.}}$ given by equation (xl.) by the $(2i + 1)(2i' + 1)$ factor (see p. 67). For a homonuclear molecule, however, the allowance for nuclear-spin multiplicity should be obtained by multiplying the odd and even terms by $(i2i + 1)$ and $(i + 1)(2i + 1)$, as already explained (p. 66). In the summation of the $(2J + 1)e^{-\sigma J(J+1)}$ terms over all values of J from 0 to ∞, it can be shown that, provided σ is small, *i.e.*, when equation (xl.) is applicable, the sum of the terms for which J is even is equal to that for the terms with odd J values : that is to say,

$$\sum_{J=0,2,4,6\ldots}^{\infty}(2J + 1)e^{-\sigma J(J+1)} = \sum_{J=1,3,5,7\ldots}^{\infty}(2J + 1)e^{-\sigma J(J+1)} = 1/2\sigma \quad . \quad \text{(xli.)}$$

Allowance for the nuclear-spin factor thus gives the complete rotational function as

$$\begin{aligned} Q_{\text{rot.}} &= i(2i + 1)/2\sigma + (i + 1)(2i + 1)/2\sigma \\ &= (2i + 1)^2/2\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xlii.)} \end{aligned}$$

so that the inclusion of the effect due to nuclear spin is obtained by multiplying the value of $Q_{\text{rot.}}$ given by equation (xl.) by $(2i + 1)^2/2$. For hydrogen this correction factor is 2, for deuterium it is $\frac{9}{2}$, and for oxygen $\frac{1}{2}$: this last result is clearly in agreement with the fact that the alternate rotational levels of oxygen are missing and the others show no nuclear-spin degeneracy (p. 66). For molecules of this (oxygen) type the approximate value of $Q_{\text{rot.}}$ becomes $1/2\sigma$, a result which had been previously deduced by classical mechanics (Ehrenfest and Trkal, 1920); the factor 2, called the " symmetry number," is then supposed to represent the number of equivalent orientations in space which the molecule is able to occupy as a result of simple rotation.

The equality of odd and even terms in the $Q_{\text{rot.}}$ summation (equation xli.) is only approached when σ is small; for most molecules the temperature at which this occurs is quite low, but with *equilibrium* hydrogen and deuterium (see pp. 107, 159) it is not the case. For these substances the equality only applies when the ratio of ortho- to para-forms has attained the values of 3 to 1, and 1 to 2, respectively, and this is only so at above 273° K. for

hydrogen and 200° K. for deuterium. For " normal " hydrogen and deuterium, in which the ortho–para ratio is supposed to remain constant at all temperatures at the values just quoted, the approximations are, of course, always applicable. With other homopolar molecules possessing nuclear spin, the " normal " ratio of ortho- and para-states is reached at such low temperatures that under all reasonable conditions the summation and the nuclear-spin correction factor described above may be taken as being adequate. Further reference to this subject will be made in Chapter III.

Omission of Nuclear-Spin Factor. If the partition functions are required for the purpose of calculating equilibrium constants, then provided the temperatures are such that the approximations discussed above are valid, it is permissible to omit the nuclear-spin factor, both from atoms and molecules, although the " symmetry number " must be included (Gibson and Heitler, 1928). Consider, for example, the reaction

$$A_2 + B_2 = 2AB,$$

and suppose the partition functions, ignoring the nuclear-spin effect, are Q_A, Q_B and Q_{AB}, respectively : the complete functions, including this factor, will then be $Q_A(2i_A + 1)^2/2$, $Q_B(2i_B + 1)^2/2$, and $Q_{AB}(2i_A + 1)(2i_B + 1)$, remembering that A_2 and B_2 are homonuclear whereas AB is heteronuclear, where i_A and i_B are the respective spins of the A and B nuclei. From equations (xxxii.), (xxxiii.) and (xxxiv.) it is evident that the equilibrium constant of the reaction under consideration will be related to the quantity

$$\frac{[Q_{AB}(2i_A + 1)(2i_B + 1)]^2}{[Q_A(2i_A + 1)^2/2]\,[Q_B(2i_B + 1)^2/2]},$$

which is equal to $4Q_{AB}^2/Q_AQ_B$. If the nuclear-spin effect had been completely disregarded, but the symmetry number, which is 2 for both A_2 and B_2 and unity for AB, introduced, the partition functions would have been $Q_A/2$, $Q_B/2$ and Q_{AB}, respectively. The equilibrium constant obtained from these functions is identical with that obtained by including the complete nuclear-spin factors. The same conclusion is reached by considering any other reaction,

whether it involves symmetrical or unsymmetrical molecules, or even atoms.

Since nuclear spins are not always known, it has become customary to quote entropy and $F^\circ - E_0^\circ$ values determined from partition functions with the spin-multiplicity effect omitted, *but with due allowance for symmetry.* It is in fact accepted that if entropies calculated from spectroscopic data, by the methods described in this chapter, are to be used in conjunction with others obtained from thermal measurements the spin effect must be omitted. These entropies have been called " virtual," as distinct from " absolute," entropies and given the symbol S^*. In order to obtain the absolute entropies the factor $R\ln(2i + 1)$ must be added to the virtual entropy for every atom of spin i in the molecule ; this correction arises from the fact that the expression for entropy involves $R\ln Q$ (equation xix.), and the spin factor, apart from symmetry, is $2i + 1$ for each atom (see p. 73).

Isotope Effect. For substances containing two or more isotopic atoms, accurate band-spectroscopic data are generally available only for the species with the predominant isotope. The corresponding values for other isotopic forms can be readily calculated, however, by assuming the binding forces between atoms to be independent of their isotopic nature. In the determination of the entropy of the normal mixture of isotopic compounds, the entropies of the separate forms from spectral data are multiplied by their respective molar fractions, determined from isotopic and chemical atomic weights, and the results are added, the entropy of mixing being included (see p. 112). Entropies obtained from thermal measurements do not involve the last quantity, and for use in conjunction with them, *e.g.*, in the calculation of equilibrium constants, the entropy of mixing must be omitted. If this is done, then it is also necessary to neglect the fact that the statistical weight of a heteronuclear molecule, *e.g.*, $^{35}Cl^{37}Cl$, is double that of the symmetrical molecules, $^{35}Cl^{35}Cl$ and $^{37}Cl^{37}Cl$. The same result, at least for chlorine, may be obtained in a simpler manner by treating the substance as a homonuclear molecule, each atom having an atomic weight 35·46, the average energy at each level being obtained by giving the appropriate proportional weights to

the energies at the corresponding level for the three types of isotopic molecules. This effect is believed to be general and to apply to all analogous cases (Giauque and Overstreet, 1932). Hydrogen chloride may be treated as a mixture of definite amounts of $H^{35}Cl$ and $H^{37}Cl$, although the entropy of mixing and the nuclear-spin factor must not be included if the values are to be used in conjunction with entropies obtained from thermal measurements.

POLYATOMIC MOLECULES

With polyatomic molecules the precise calculation of thermodynamic constants from spectroscopic data is very difficult, partly because the spectra are complex and not analysable with certainty, and partly because of the labour involved in the evaluation of the partition functions when three, or more, moments of inertia and several types of vibration have to be taken into consideration. By replacing summation with integration and using the method of asymptotic expansion already mentioned (p. 70), it has been possible to diminish the labour involved in obtaining the partition functions for relatively simple polyatomic molecules, *e.g.*, hydrogen cyanide, carbon dioxide, nitrous oxide, acetylene, water, sulphur dioxide, methane and tetradeuteromethane, due allowance being made for anharmonicity and for stretching and interaction terms. In most cases, however, the simplification is made of treating the molecule as rigid and of assuming the different forms of energy to be independent of one another. The complete partition function is then obtained as the product of the separate electronic, vibrational and rotational functions. At relatively high temperatures the errors involved in using this approximate method are generally quite small.

The classification of polyatomic molecules according to the electronic configuration of the ground state is possible only for the relatively small number of linear molecules which behave as quasi-diatomic. In other cases it is assumed that there is only one electronic ground level and that excited levels do not contribute to the total state sum at temperatures which are not excessively high. The electronic factor in the partition function is thus

generally assumed, unless there is direct evidence to the contrary, to be equal to unity.

Vibrational Partition Function. A molecule containing n atoms has, in general, $3n-6$ normal modes of vibration: for a linear molecule this is increased to $3n-5$, and is decreased to $3n-7$ for a molecule of the ethane type having one degree of freedom of internal rotation. Of this total, $n-1$ are stretching (valency), and the others are bending (deformation) vibrations. If the energy of the vibrational levels can be expressed in terms of a formula similar to the one used for diatomic molecules (cf. equation xxxv.), it is sometimes possible to make a reasonably accurate estimate of the vibrational partition function (Kassel, 1934; Blue and Giauque, 1935). For a complex molecule, however, it is generally the practice to employ for each mode of vibration the approximate relationship obtained for a diatomic molecule, (equation xxxvii.); thus

$$Q_{\text{vib.}} = (1 - e^{-hc\omega_i/kT})^{-1} \quad . \quad . \quad . \quad \text{(xxxvii}a\text{.)}$$

where ω_i represents the fundamental vibration frequency of the mode under consideration. The vibrational function for the whole molecule is given by the *product* of these terms, one for every possible vibrational mode. If any of the frequencies are degenerate, due allowance must be made in the product, the corresponding term being included for each component of the degenerate frequency. The vibrational contribution to the complete partition function is relatively small, except perhaps at very high temperatures. At 298° K., for example, the vibrational contribution to the partition function of nitrous oxide is only 1·1, compared with the rotational contribution of 496. It is obvious, therefore, that the use of uncertain frequencies and of approximation methods will result only in the introduction of relatively small errors. The rotational function is much more important, and it is necessary to obtain as accurate a value as is possible with the limited methods and data available. The subject may best be considered under the headings of different types of molecule.

Rotational Functions—Linear Molecules. The rotational energy of a linear molecule, at least in the lower vibrational states, may be expressed by the same formula as for a diatomic molecule

(p. 69), although this is not strictly accurate. Since the moment of inertia will be relatively large, because of the increased dimensions as compared with a diatomic molecule, the $\bar{\sigma}$ term will be small, and it is permissible to replace summation by integration in the determination of the partition function. The statistical weight of each level, apart from the nuclear-spin factor, is $2J + 1$, so the rotational partition function is, as for a diatomic molecule, given by $Q_{\text{rot.}} = 1/\sigma$, where σ has the same significance as before, since a linear molecule has only one moment of inertia. Allowance for symmetry is made by introducing the symmetry number s, thus giving

$$Q_{\text{rot.}} = \frac{1}{s\sigma} = \frac{8\pi^2 IkT}{sh^2} \quad \ldots\ldots \text{(xliii.)}$$

This result does not include the whole nuclear-spin factor, but, as already explained, allowance for this need only be made if absolute entropies are required ; it is then necessary to multiply the value for $Q_{\text{rot.}}$ given by equation (xliii.) by $2i + 1$ for each atom, possessing i units of nuclear spin, in the molecule. Examples of linear substances to which the equations given apply are hydrogen cyanide, nitrous oxide, carbon dioxide and acetylene. For hydrogen cyanide and nitrous oxide the symmetry number is unity, and for the other compounds it is 2 : the nuclear-spin factors are 6, 9, 1 and 4, respectively, since the spins involved are hydrogen $= \frac{1}{2}$, carbon and oxygen $= 0$, and nitrogen $= 1$. The calculation of the partition function still involves a knowledge of the moment of inertia of the molecule, and this is generally obtained from the separation of the rotational lines in the band spectrum ; it may also be evaluated from the interatomic dimensions of the molecule if they are known.

Spherical Rotator. Next in order of complexity come the molecules such as methane and the tetrahalogeno-methanes, which possess tetrahedral symmetry and may be treated as spherical rotators having three equal moments of inertia. It should be noted that substances like tetramethylmethane are not included in this category, as they have an additional moment of inertia due to the free rotation of the methyl groups about the central carbon atom. Since the spherical rotator has effectively one moment of

inertia it may be treated as a diatomic molecule, and the rotational energy expressed, for a rigid molecule, by the simple relationship $\varepsilon_{\text{rot.}} = J(J+1)h^2/8\pi^2 I$. Some complication arises, however, in connection with the statistical weights required for the calculation of the partition function. From quantum mechanical considerations it is occasionally possible to allow for the different weights to be ascribed to different rotational levels, but, as a general rule, if missing levels and nuclear-spin effects are ignored, each level has a statistical weight of $(2J+1)^2$, instead of the usual value of $2J+1$ for a diatomic molecule. It follows, therefore, that

$$Q_{\text{rot.}} = \sum_{J=0}^{\infty} (2J+1)^2 e^{-\sigma J(J+1)} \quad . \quad . \quad . \quad \text{(xliv.)}$$

where σ has the same significance as previously (equation xxxix.). If summation is replaced by integration, then provided σ is small, as it invariably is at appreciable temperatures, it follows that

$$Q_{\text{rot.}} = \frac{\pi^{1/2}}{\sigma^{3/2}} = \pi^{1/2} \left(\frac{8\pi^2 IkT}{h^2}\right)^{3/2} . \quad . \quad . \quad . \quad \text{(xlv.)}$$

This value of $Q_{\text{rot.}}$ should be divided by the symmetry number (s), to give the rotational partition function, not allowing for the whole nuclear-spin effect, correction for which may be made in the usual manner; thus $Q_{\text{rot.}} = \pi^{1/2}/s\sigma^{3/2}$. For a spherical rotator of the type under consideration the symmetry number is equal to 12.

Symmetrical Top. Under this heading may be considered two types of molecule: either single-pyramidal, such as ammonia and chloroform, or double-pyramidal, as, for example, ethane. In molecules of this nature two of the three moments of inertia are identical, thus $I_A = I_B > I_C$, so that there are effectively two different moments. For the single-pyramid type the rotational energy, assuming a rigid molecule, may be written:

$$\varepsilon_{\text{rot.}} = \frac{h^2}{8\pi^2 I_A}\left[J(J+1) + \left(\frac{I_A}{I_C} - 1\right)K^2\right] . \quad . \quad \text{(xlvi.)}$$

where the subsidiary rotational quantum number K can have a series of $2J+1$ values, viz., J, $J-1$, $J-2$, . . . , 0, . . . $-J+2$, $-J+1$, $-J$, for every value of J. The multiplicity

of each rotational level is, as usual, $2J + 1$, but the introduction of the additional quantum number K makes each sub-level $2J + 1$-fold degenerate. The application of the approximation methods, in which integration is employed, leads to the expression

$$Q_{\text{rot.}} = \frac{\pi^{1/2}}{s\sigma_A\sigma_C^{1/2}} \quad . \quad . \quad . \quad . \quad . \quad \text{(xlvii.)}$$

including the effect of symmetry ; the terms σ_A and σ_C are defined as follows :

$$\sigma_A = h^2/8\pi^2 I_A kT \quad \text{and} \quad \sigma_C = h^2/8\pi^2 I_C kT.$$

The symmetry number for the ammonia molecule is taken as **3**.

For a double-pyramidal molecule, that is an ethane-like top, the expression for the rotational energy is similar to equation (xlvi.), but another term involving K', equal to $K \pm 2n$, where n is an integer, is included. The approximate method of summation then leads to the result that $Q_{\text{rot.}} = \pi/s\sigma_A\sigma_C$.

Asymmetrical Top. For the general case in which the molecule is non-linear and has three different moments of inertia, the rotational energy cannot be expressed by a simple equation, even for a rigid molecule. The energies of the lower levels have been expressed by a complex formula (Kramers and Ittmann, 1930), which has been actually used by Gordon and Barnes (1932) to calculate the partition function for the water molecule ; the procedure is, however, tedious and of limited applicability. It is more usual, therefore, to adopt an approximate empirical method, which appears to be quite satisfactory at appreciable temperatures ; this involves the assumption that $Q_{\text{rot.}}$ for a rigid non-linear molecule may be obtained by replacing I_A in the equation for a pyramidal molecule by $(I_A I_B)^{1/2}$. The result is that

$$Q_{\text{rot.}} = \frac{\pi^{1/2}}{s(\sigma_A\sigma_B\sigma_C)^{1/2}} \quad . \quad . \quad . \quad . \quad . \quad \text{(xlviii.)}$$

the term σ_B being expressed in an analogous manner to that for σ_A and σ_C, given above. For a planar molecule, *e.g.*, water or benzene, there is some simplification in so far as $I_A + I_B$ is equal to I_C. It may be mentioned that the symmetry number (s) for the water molecule is 2, whereas it is 12 for benzene.

APPLICATIONS

The methods described above have been used to determine the heat capacities, entropies and free energies of a considerable number of simple molecules, and a large number of equilibrium constants have been calculated. Reference to some of the more important results, dealing with ortho- and para-hydrogen and with deuterium, will be considered in Chapters III. and IV. : a few examples of general interest, to show the applicability of the statistical methods, will be considered here.

Heat Capacity. The total heat capacity, at constant volume, is obtained by adding $3R/2$, the translational heat capacity per gm.-mol., to the value for the internal degrees of freedom computed by some form of equation (xii.). Wherever reliable experimental data are available, *e.g.*, for hydrogen, the agreement between observed and calculated values is excellent (cf. p. 110), and in many instances, when the experimental results are uncertain, there is little doubt that the statistical method gives heat capacities which may be taken as being the more accurate. The calculations can also be extended to temperatures below those on which direct determinations are normally possible, and a number of interesting results have been brought to light in this way.

Nitric Oxide. The total heat capacities at constant pressure of nitric oxide, for example, for temperatures up to 400° K. are shown in Fig. 4 (Johnston and Chapman, 1933), wherein a striking maximum is observed at about 75° K. Such a phenomenon, which in fact occurs with all molecules possessing multiplet levels in the electronic ground state, is of course inexplicable on the basis of classical theories of specific heat, but is in harmony with modern quantum concepts. As already seen (p. 68), nitric oxide in its ground state is a doublet, generally represented by the terms $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$, the former having the lower energy. At the absolute zero all the molecules exist in the lowest energy state, that is, the vibrational quantum number (v) is zero, and the rotational number (J) is $\frac{1}{2}$, in the lowest electronic, *i.e.*, $^2\Pi_{\frac{1}{2}}$, state, and there is no translational energy : the heat capacity is then zero. On raising the temperature the molecules rapidly acquire

kinetic energy, associated with translatory motion, and the heat capacity, which is determined by dE/dT, soon rises to the value $3R/2$, that is, about 2·98 cals. per gm.-mol. At the same time rotational energy is acquired and the molecules pass, to some extent, into levels with J values of $\frac{3}{2}$, $\frac{5}{2}$, etc., still in the $^2\Pi_{\frac{1}{2}}$ state: the heat capacity thus increases regularly in excess of the translational contribution. At about 30° K. an appreciable number of molecules acquire sufficient coupling energy, 350 cals. per gm.-

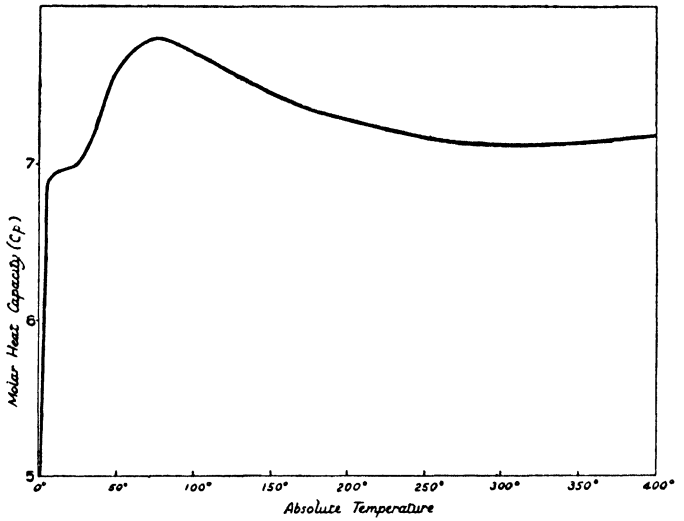


FIG. 4.—Calculated Heat Capacity of Nitric Oxide. (After Johnston and Chapman.)

mol., to bring them into the $^2\Pi_{\frac{3}{2}}$ electronic state, and this means a further increase of heat capacity, not to be anticipated from the classical theory of the equipartition of energy. At 75° K. the *rate* at which the molecules in various rotational levels in the $^2\Pi_{\frac{1}{2}}$ state pass over into the $^2\Pi_{\frac{3}{2}}$ state is greatest, so that at this temperature the heat capacity shows a maximum. It falls off above 75° K., but after passing through a minimum, at about 325° K., the heat capacity once more increases regularly as the higher vibrational levels steadily become excited. At 298° K. only 0·01 per cent. of the total number of molecules are in vibrational levels

above the lowest ($v = 0$); at 400° K. this has risen to 0·12 per cent., and subsequently it increases regularly, with consequent increase in the heat capacity.

Oxygen. The coupling energy for the electronic sub-levels of the ground state of oxygen is very much smaller than for nitric oxide, namely about 6 cals. per gm.-mol., so that the higher energy states become appreciably excited at very low temperatures. The maximum in the heat capacity curve is reached, according to the calculations of Johnston and Walker (1933), at 0·120° K., when the value, excluding the translational contribution, is as high as 2·866 cals. per gm.-mol. The rate of formation of the higher sub-levels has then attained its greatest value As the temperature of 0·12° K. is exceeded the heat capacity decreases rapidly, but it soon commences to rise again as the rotational levels above the lowest, for which $J = 1$, and vibrational levels above $v = 0$, become excited. There are two subsidiary, less sharp, maxima at 1·2° K. and at 12° K., and then the heat capacity increases regularly as the temperature is raised to high values. It is of interest to note that according to the calculations, based on spectroscopic data, the heat capacities at constant volume of both oxygen and nitric oxide, at temperatures above 2000° and 3000° K., respectively, exceed the maximum value, $7R/2$, permitted for a diatomic molecule by the concept of the equipartition of energy.

Ortho- and Para-States. Symmetrical molecules, such as nitrogen, deuterium and hydrogen, the nuclei of which possess spin momentum, also have maxima in their heat capacities: this effect is due to the existence of the molecules in ortho- and para-states, one form being exclusively present at the absolute zero, and the other being gradually produced as the temperature is raised. This aspect of the subject, for hydrogen and deuterium, will be considered more fully in later chapters. It is the necessity for the establishment of the ortho–para equilibrium which is responsible for the difference in the heat capacities of carbon monoxide and nitrogen at temperatures below 10° K.; the former being unsymmetrical does not exist in ortho- and para-states.

ENTROPY

Hydrogen. The entropy of hydrogen has been determined by he method of summation of the rotational terms, $pe^{-\epsilon/kT}$, in order o evaluate the partition function, only the lowest vibrational evel, and the electronic ground state, contributing appreciably o the total at ordinary temperatures. According to the calculations of Giauque (1930), based on the spectroscopic data of Birge, Lyman and Jeppesen (1930), the value of $\Sigma pe^{-\epsilon/kT}$, including the uclear-spin multiplicity, for hydrogen at 298·1° K., *i.e.*, 25° C., s 7·7533, and $(\Sigma\epsilon pe^{-\epsilon/kT})/kT$ at the same temperature is 7·1002, nd so by equation (xix.) it follows that

$$S^\circ_{\text{int.}} = R\left[\ln 7{\cdot}7533 + \frac{7{\cdot}1002}{7{\cdot}7533}\right]$$

$$= 5{\cdot}889 \text{ cals./degree per gm.-mol.}$$

The entropy due to translation is obtained by substituting the ppropriate values of the molecular weight M, that is, 2·0156, and he temperature (T) in equation (v.); it is found to be 28·09 units, hus giving a total (absolute) entropy of 33·98 units for molecular ydrogen, assumed to be an ideal gas, at 298·1° K.

Approximation Method. It may be of interest at this point o compare the accurate entropy value obtained above with that esulting from the approximate treatment already described p. 71). Assuming, as is actually the case for hydrogen at 5° C., that rotational degrees of freedom only are involved * in he entropy, then the approximate form of the partition function, or a rigid diatomic molecule, including the nuclear-spin contribuion, is given by equation (xlii.), p. 73; thus

$$Q = (2i + 1)^2/2\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xlii.)}$$

where $\sigma = h^2/8\pi^2 IkT$. Inserting the value for σ in the equation, nd differentiating with respect to T, it is seen that

$$\frac{d\ln Q}{dT} = \frac{1}{T},$$

* The allowance for vibrational degrees of freedom is considered later, . 86.

so that the quantity $T(d\ln Q/dT)$, required for the determination of entropy by equation (xix.) is unity ; it follows, therefore, that

$$S^\circ_{\text{rot.}} = R(\ln Q + 1) \quad . \quad . \quad . \quad . \quad . \quad \text{(xlix.)}$$

The expression for Q, from equation (xlii.), consists of universal constants, apart from I, T and i, and inserting the appropriate valves of π, k (ergs) and h (erg-secs.), equation (xlix.) takes the form

$$S^\circ_{\text{rot.}} = R\ln IT + 177{\cdot}68 + R\ln(2i + 1)^2/2 \quad . \quad . \quad \text{(l.)}$$

This expression gives the whole of the internal entropy, when the vibrational degrees of freedom do not contribute to the total, the nuclear-spin effect being included. If it is desired to neglect the latter except for the symmetry factor, then the (virtual) entropy is given by the equation

$$S^*_{\text{rot.}} = R\ln IT + 177{\cdot}68 - \ln s \quad . \quad . \quad . \quad . \quad \text{(l}a\text{.)}$$

where s is the symmetry number of the molecule, which is unity for a heteronuclear and 2 for a homonuclear diatomic compound.

These results may now be applied to the case of hydrogen ; taking the moment of inertia as $0{\cdot}47 \times 10^{-40}$ c.g.s. units, obtained from spectroscopic measurements, the value of $S^\circ_{\text{int.}}$ may be calculated as 6·00 cals./degree per gm.-mol., i being $\frac{1}{2}$. Adding the translational entropy obtained above (28·09), the total (absolute) entropy is given as 34·09 ; this is in remarkably good agreement with the accurate value of 33·98, when it is remembered that the approximate equation employed is more accurate for molecules possessing large moments of inertia. The virtual entropy is derived by subtracting $R\ln(2i + 1)^2$, *i.e.*, $R\ln 4$, from the total value.

The entropy of hydrogen from thermal data, corrected by means of the van der Waals equation for deviation from ideal behaviour, has been estimated as 29·64 (Giauque, 1930), a result which is probably 4·39 units too low, because of the persistence of rotation in the solid state (see p. 112). Making this allowance the absolute entropy would be 34·03, a value approximating closely to that calculated by the method of partition functions.

Hydrogen Chloride. This substance provides another example

where the summation method has been employed, in this instance both the detailed addition and integration procedures (p. 70) giving almost identical results. The value for a normal mixture of the two isotopic forms of hydrogen chloride was calculated to be 44·66 entropy units (Giauque and Overstreet) at 298·1° K., as compared with 44·5 units for the virtual entropy obtained from heat-capacity measurements. The calculated (virtual) entropies of the two forms $H^{35}Cl$ and $H^{37}Cl$ are 44·62 and 44·78, respectively, excluding the nuclear-spin effect. At ordinary temperatures only rotational states in the lowest vibrational level of the electronic ground state contribute to the partition function, and the approximate formula, based on the assumption of a rigid molecule, for the virtual internal entropy becomes

$$S^* = R\ln IT + 177{\cdot}68 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (lb.)$$

The moment of inertia of hydrogen chloride is $2{\cdot}66 \times 10^{-40}$ c.g.s. units, so that $S^*_{\text{int.}}$ at 298·1° K. is found to be 8·1 units; to this must be added the translational entropy, obtained from equation (v.), giving a total (virtual) entropy of 44·8, which compares favourably with the result obtained by the more complicated summation process.

Vibrational Entropy : Approximation Method. The calculation of the entropy of nitrous oxide raises a matter of some importance, namely, the contribution of the vibrational degrees of freedom, which was of negligible importance in the instances already considered. The vibrational partition function is never large, in comparison with the value for rotation, and so approximation methods are even more justifiable for the former than for the latter. According to equation (xxxvii*a*.) the approximate partition function for each vibrational mode (see p. 72) is given by

$$Q_{\text{vib.}} = (1 - e^{-hc\omega i/kT})^{-1} \quad . \quad . \quad . \quad . \quad (\text{xxxvii}a.)$$

so that,

$$T\frac{d\ln Q_{\text{vib.}}}{dT} = \frac{hc\omega_i/kT}{e^{hc\omega_i/kT} - 1},$$

and so from equation (xix.) it follows that the entropy contribution of each mode of vibration can be represented by

$$S_{\text{vib.}} = R\left[\frac{hc\omega_i/kT}{e^{hc\omega_i/kT} - 1} - \ln(1 - e^{-hc\omega_i/kT})\right] \quad . \quad . \quad . \quad (li.)$$

By inserting the appropriate values for ω_i the vibrational entropies can be determined and added for the several types of vibration in the molecule.

Calculated and Thermal Entropies. As instances of agreement between entropies calculated statistically and those obtained from thermal measurements, in addition to those already recorded, mention may be made of the following : oxygen, nitrogen, chlorine, bromine, iodine, hydrogen bromide and iodide, iodine monochloride, and ammonia. It is unnecessary to give further examples, for it is sufficient to state that whenever reasonably accurate spectroscopic measurements are available, so that the energy levels of the molecule can be calculated, the entropies obtained by the method of partition functions will be as reliable as the best results from heat capacity data. In some cases, as with hydrogen and deuterium, there are definite discrepancies between the entropies obtained in the two ways (pp. 112, 161), and in such instances it is probable that the thermal value is incorrect because of the failure to take into consideration some factor or other generally connected with the solid state. Nitrous oxide, carbon monoxide and nitric oxide are examples of substances for which the entropy obtained from partition functions is greater than the thermal value, and it is of interest to discuss briefly the cause of this difference.

Nitrous Oxide. The fundamental vibration frequencies for nitrous oxide are given as 1285·4, 589·1 (doubly degenerate) and 2224·1 cm.$^{-1}$, and from these values the total vibrational entropy may be calculated as approximately 1·0 units at 298·1° K. The moment of inertia is 66×10^{-40} c.g.s. units, and substituting in equation (*la.*), which is applicable, with $s = 1$, to nitrous oxide (see p. 76), the rotational entropy is found to be 14·32, apart from the effect due to nuclear spin. The translational contribution is 37·27, so that the total (virtual) entropy of nitrous oxide at 298·1° K. is 52·6 units.

Orientation in the Solid State. The thermally determined entropy of nitrous oxide, corrected for deviation from ideal gas behaviour, is 51·44 units, and the discrepancy of 1·16 between this and the calculated value is beyond the limit of experimental error,

and consequently must have some significance. The most reasonable explanation is that the entropy of nitrous oxide in the solid state does not approach zero at low temperatures, as required by the third law of thermodynamics, on which the thermal method of obtaining entropies is based. Because of the similarity of the two ends, *i.e.*, nitrogen and oxygen atoms, of nitrous oxide, NNO, it is probable that the molecules in the crystal lattice are unable to distinguish between one and the other, so that at appreciable temperatures they are oriented in a random manner, either as NNO or as ONN, instead of all being directed one way. As the temperature is lowered towards the absolute zero perfect order, requisite for zero entropy, should be established with the molecules all oriented in the same direction. If the readjustment to an ordered arrangement is very slow, however, the random orientation will be retained in the solid at low temperatures; the heat capacity of the solid will then be less than it should be theoretically, and the entropy will be lower than is to be expected if the entropy of the solid approached zero as the temperature is lowered towards the absolute zero. If the molecular arrangement were to remain completely random at the lowest experimental temperatures, so that each molecule can occupy two possible positions in the solid state, the entropy would be $R\ln 2$, that is, 1·38, instead of zero: the thermal entropy would thus be 1·38 units less than the total (virtual) value given by the statistical method. Any tendency towards a definite ordered arrangement would diminish the discrepancy, and the observed difference of 1·16 units between the thermal and statistical values for the entropy of nitrous oxide may be attributed to the fact that the orientation of the molecules in the solid state is not completely random at low temperatures.

Carbon Monoxide and Nitric Oxide. It is of interest that carbon monoxide exhibits a similar discrepancy of about 1·1 units between the entropy values determined by the two methods; the molecule of CO is clearly another case where the lattice might fail to discriminate between the two ends, so that at appreciable temperatures the random arrangement in the crystal lattice, either as CO or as OC, might be anticipated. If this randomness is not com-

pletely adjusted to a regular arrangement in the crystal at low temperature, then an error, up to $R\ln 2$ units, is to be expected in the thermally determined entropy. The same type of behaviour is also to be anticipated with nitric oxide : the discrepancy is here only 0·75 entropy units, so that a partially ordered arrangement appears to have existed in the crystals used in the actual experimental determination of heat capacity. It is quite possible that different results might be obtained with different specimens, since the extent of the random distribution may vary with the time at which they are kept at a low temperature.

EQUILIBRIUM CONSTANTS

Dissociation of Hydrogen Molecules. As an illustration of the calculation of equilibrium constants by the method of partition functions there may be taken the case of the reaction

$$H_2 \rightleftharpoons 2H,$$

for which the dissociation constant $K_p = p_H{}^2/p_{H2}$, with pressures in atmospheres, may be obtained by the application of equations (xxvi.) to (xxviii.). The partition functions for molecular hydrogen at various temperatures have been obtained by the summation process, the higher vibrational levels being taken into account, as required, at the higher temperatures : the values quoted in Table V. have been computed by subtracting $R\ln 4$, the nuclear-spin effect, from the total internal partition functions (cf. p. 73). For atomic hydrogen the partition function for the ground level, viz., 2 (see p. 63), neglecting nuclear spin, may be taken as being applicable over the whole range of temperature under consideration, since the excitation energy is so large. In order to calculate equilibrium constants it is still necessary to know $\Delta E_0°$ for the process being discussed. According to the convention adopted here the zero of energy, from which energies used in the calculations are reckoned, is that of the *molecule* in the lowest rotational and vibrational levels of its ground state, that is to say, at its zero-point. On this basis $E_0°$, the zero-point energy, for the hydrogen molecule is obviously zero, but on the same scale of reference $E_0°$

for the two hydrogen atoms, which result on dissociation, must be equal to the energy evolved in the reaction

$$2H \rightarrow H_2$$

at the absolute zero. The spectroscopically determined value of the energy of dissociation of molecular hydrogen ("Recent Advances in Physical Chemistry," Chapter IV.) is 102,800 cals. per gm.-mol., and this may be taken as equal to $E_0°$ for the two atoms; hence $\Delta E_0°$ for the hydrogen dissociation process is 102,800 cals. All the data necessary for the calculation of K_p are now available, and the results are given in Table V., which is adapted from the work of Giauque (1930). For the purpose of comparing the calculated constants with experimental values, which are only of limited accuracy, the results obtained by Langmuir (1915) are given in the last column.

TABLE V

Equilibrium Constants for the Dissociation of Hydrogen.

Temp.	Partition Function (Q).		Equilibrium Const. (K_p).	
	H_2	2H	Calc.	Obs.
1000° K.	6·262	4·00	—	—
2000°	13·274	4·00	$3·0 \times 10^{-6}$	$0·12 \times 10^{-6}$
2500°	17·424	4·00	$7·0 \times 10^{-4}$	$10·2 \times 10^{-4}$
3000°	22·648	4·00	$2·7 \times 10^{-2}$	$2·1 \times 10^{-2}$
3500°	28·262	4·00	$3·7 \times 10^{-1}$	$1·8 \times 10^{-1}$

Taking into consideration the difficulties involved in the experimental determination of the equilibrium constant for the dissociation of hydrogen, the agreement between the observed and calculated figures is quite satisfactory: the latter are probably the more reliable, since the partition functions and heat of dissociation employed in the calculation are known to be accurate.

Nitrogen–Oxygen–Nitric Oxide Equilibrium. In order to simplify the evaluation of equilibrium constants from partition functions it has become customary in the literature to tabulate the free energy function $-(F° - E_0°)/T$ derived from these functions by means of equation (xxvi.); thus,

$$-\frac{F^\circ - E_0^\circ}{T} = \tfrac{3}{2} R\ln M + \tfrac{5}{2} R\ln T + R\ln Q - 7{\cdot}267T \quad \text{(xxvi}b\text{.)}$$

To determine the equilibrium constant, use is then made of equation (xxvii*a*.),

$$-\Delta\left(\frac{F^\circ - E_0^\circ}{T}\right) - \frac{\Delta E_0^\circ}{T} = R\ln K_p \quad \text{(xxvii}a\text{.)}$$

so that by subtracting the free energy functions of the reactants from the resultants, and knowing ΔE_0°, the constant K_p can be obtained at any temperature. The reaction

$$\tfrac{1}{2}\,N_2 + \tfrac{1}{2}\,O_2 \rightleftharpoons NO$$

may be taken as an example to illustrate the procedure involved. The free energy functions recorded in Table VI. have been taken from accurate values in the literature, for oxygen, nitrogen and nitric oxide molecules, and to determine the equilibrium constant it is only necessary to know ΔE_0° for the reaction under consideration. This is not available with certainty, but Giauque and Clayton (1933) have assumed it to be 21,400 cals., based on the thermo-chemical measurements of Thomsen and Berthelot and the known heat capacities of the molecules involved. The equilibrium constants, with pressures in atmospheres, have been calculated at a number of temperatures, in the manner already described, and the results are compared in Table VI. with those obtained by interpolation from the experimental data of Nernst and his collaborators.

TABLE VI

Equilibrium Constants for the Reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$.

Temp.	$-(F_0 - E_0^\circ)/T$			$-\Delta[(F_0 - E_0^\circ)/T]$	Equilibrium Constant.	
	NO	N_2	O_2	$NO - \frac{1}{2}N_2 - \frac{1}{2}O_2$	Calc.	Obs.
1000° K.	51·878	47·322	50·715	2·859	$8{\cdot}8 \times 10^{-5}$	—
1500°	54·979	50·301	53·826	2·915	$3{\cdot}3 \times 10^{-3}$	$2{\cdot}4 \times 10^{-3}$
2000°	57·255	52·497	56·122	2·945	$2{\cdot}0 \times 10^{-2}$	$1{\cdot}5 \times 10^{-2}$
2500°	59·063	54·246	57·955	2·962	$6{\cdot}0 \times 10^{-2}$	$4{\cdot}5 \times 10^{-2}$
3000°	60·567	55·706	59·489	2·970	$1{\cdot}2 \times 10^{-1}$	$0{\cdot}9 \times 10^{-1}$

There is here an almost constant ratio between observed and calculated equilibrium constants which may well be due to the use of an incorrect value of ΔE_0° in the calculations; it is, of course, essential that this should be known accurately, otherwise even the most exact partition functions cannot give reliable results.

Approximation Methods. It has been seen that the approximate methods often give entropy values in good agreement with those obtained by laborious summation and equivalent methods; hence it is important to show that the same simplified methods can be applied to calculate equilibrium constants. In the case of a diatomic molecule the value of the internal partition function, that is, for rotation and vibration, excluding the nuclear-spin but including the symmetry term, can be written

$$Q = (8\pi^2 IkT/h^2)(1 - e^{-hc\omega/kT})/s \quad . \quad . \quad . \quad . \quad \text{(lii.)}$$

the first term on the right-hand side representing the rotational contribution, the second the vibrational function, and the third the symmetry number. After evaluating Q for the reactants and resultants from a knowledge of the moments of inertia and the vibration frequencies, the subsequent treatment is the same as that already described in connection with the dissociation of hydrogen (p. 89). If any of the reactants or resultants is an atom then the appropriate partition function, assuming the ground state only to be involved, is given by $2j_s + 1$, the electronic contribution (p. 62), since the nuclear-spin effect is not taken into consideration. The simplified approach described has been applied by Gibson and Heitler (1928) to calculate the equilibrium constant at several temperatures of the dissociation of molecular iodine into atoms; taking the moment of inertia of the iodine molecule to be $742{\cdot}6 \times 10^{-40}$ c.g.s. units, the fundamental vibration frequency as $213{\cdot}67$ cm.$^{-1}$, and the dissociation energy, which gives ΔE_0°, as $1{\cdot}544$ electron-volts, that is, 35,590 cals., the results in Table VII. were calculated. The only value of j_s for iodine atoms which need be considered is $\frac{3}{2}$, and so the partition function is 4, per gm.-atom. The calculated dissociation constants are compared with those taken from the experimental

determinations of Starck and Bodenstein (1910); the agreement is seen to be remarkably good.

TABLE VII

Equilibrium Constants for Dissociation of Molecular Iodine

Temp.	Equilibrium Constant.	
	Calculated.	Observed.
800° C.	$1{\cdot}13 \times 10^{-2}$	$1{\cdot}14 \times 10^{-2}$
900°	$4{\cdot}79 \times 10^{-2}$	$4{\cdot}74 \times 10^{-2}$
1000°	$1{\cdot}65 \times 10^{-1}$	$1{\cdot}65 \times 10^{-1}$
1100°	$4{\cdot}94 \times 10^{-1}$	$4{\cdot}92 \times 10^{-1}$
1200°	1·22	1·23

Iso-molecular Reactions. When there is no change in the number of molecules as a result of a reaction, that is, for processes of the type :

$$A_2 + B_2 \rightleftharpoons 2AB$$

and

$$AB + CD \rightleftharpoons AC + BD,$$

a further simplification is possible in the expression for the equilibrium constant; since $\Delta\nu$ is zero, the lnT and numerical terms disappear from equation (xxviii.), leaving the expression, which is the same for K_p and K_c,

$$-\ln K = \frac{\Delta E_0^\circ}{RT} - \tfrac{3}{2}\,\Sigma\nu \ln M - \Sigma\nu \ln Q \quad . \; . \quad \text{(liii.)}$$

For the second type of reaction quoted above, this becomes :

$$-\ln K = \frac{\Delta E_0^\circ}{RT} - \tfrac{3}{2}\ln\frac{M_{AC}\times M_{BD}}{M_{AB}\times M_{CD}} - \ln\frac{Q_{AC}\times Q_{BD}}{Q_{AB}\times Q_{CD}} \quad \text{(liv.)}$$

The values of Q may now be replaced by the expression from equation (lii.), and if the reasonable approximation be made that the vibrational terms, which in any case are close to unity, cancel out, the equation for the equilibrium constant becomes :

$$-\ln K = \frac{\Delta E_0^\circ}{RT} - \tfrac{3}{2}\ln\frac{M_{AC}\times M_{BD}}{M_{AB}\times M_{CD}} - \ln\frac{I_{AC}\times I_{BD}}{I_{AB}\times I_{CD}} + \ln\frac{s_{AC}\times s_{BD}}{s_{AB}\times s_{CD}} \quad \text{(lv.)}$$

The value of K may thus be determined from a knowledge of ΔE_0° for the reaction, and of the molecular weights, moments of inertia and symmetry numbers of reactants and resultants. In the special case under consideration AB, CD, AC and BD are written as being heteronuclear, and so the s terms are all equal to unity, and the last term in equation (lv.) is zero. If, however, A and B were identical, and so also were C and D, the reaction would correspond to the first of the two types mentioned at the commencement of this section, and the values of the symmetry number would be 2 for AB and CD, and 1 for AC and BD; the last term in equation (lv.) would then be ln 4. Equations of this type have been frequently employed in recent years in connection with the study of isotopic exchange reactions. Some of these, involving deuterium, will be discussed in Chapter IV., but a few examples may be considered here.

Isotopic Exchange Equilibrium. Oxygen contains appreciable amounts of the ^{18}O isotope in addition to the common ^{16}O form, and consequently there should always be an exchange equilibrium between two oxygen-containing molecules, *e.g.*, carbon dioxide and water, thus,

$$C^{16}O_2 + 2H_2{}^{18}O \rightleftharpoons C^{18}O_2 + 2H_2{}^{16}O.$$

The equilibrium constants for this and similar exchange reactions can be evaluated by the partition function method, provided sufficient spectroscopic data are available for the moments of inertia and the vibrational frequencies of the predominant isotopic forms, *e.g.*, $C^{16}O_2$ and $H_2{}^{18}O$ to be known. By assuming the force constants between two given atoms to be the same irrespective of their isotopic nature, it is possible to calculate (see p. 156) the corresponding values for the less common isotopic molecules, viz., $C^{18}O_2$ and $H_2{}^{18}O$. These being known, it is a relatively simple matter, with the aid of equations (lii.) and (xxviii.) or (xxxiv.), to evaluate the equilibrium constant for the isotopic exchange process. This has been done by Urey and Greiff (1935) for a number of cases involving the isotopes of oxygen, chiefly, and in some instances for lithium, carbon, nitrogen, chlorine and bromine. Some of the values obtained, at 0° and 25° C., are given in Table VIII.

TABLE VIII

Isotopic Exchange Equilibrium Constants.

Reaction.	K_c	
	0°C.	25°C.
$^{16}O_2 + 2H_2{}^{18}O(l) \rightleftharpoons C^{18}O_2 + 2H_2{}^{16}O(l)$	1·097	1·080
$O_2 + 2H_2{}^{18}O(l) \rightleftharpoons {}^{18}O_2 + 2H_2{}^{16}O(l)$.	1·020	1·012
$N_2 + 2^{15}NO \rightleftharpoons {}^{15}N_2 + 2^{14}NO$ . . .	1·033	1·030
$Cl_2 + 2H^{37}Cl \rightleftharpoons {}^{37}Cl_2 + 2H^{35}Cl$ . .	1·007	1·006

esults such as these are not only of great importance in showing, r example, that when carbon dioxide is in isotopic equilibrium th water that there is relatively more ^{18}O in the gas than in the uid, but they also account partly for the remarkable observation ole, 1935, 1936) that atmospheric oxygen is heavier than that tained from liquid water.

HEAT OF REACTION

In an early section of this chapter, see equation (xxx.), it was own that the value of $\Delta E_0°$ could be determined from a know- lge of $\Delta H°$, the change in the heat content of the process, that if the heat of reaction at constant pressure is known : the proce- ure can, in some instances, be reversed in order to give an accurate lue of $\Delta H°$, provided the zero-point energy change, $\Delta E_0°$, and rtition function data are available. The equation (xxx.) may written

$$\Delta H° = \Delta E_0° + \Delta [\tfrac{5}{2} RT + RT^2(d\ln Q/dT)] \quad . \quad . \quad \text{(xxx}a\text{.)}$$

$$= \Delta E_0° + \Delta \left[\tfrac{5}{2} RT + N \frac{\Sigma \varepsilon p e^{-\epsilon/kT}}{\Sigma p e^{-\epsilon/kT}} \right] \quad . \quad . \quad . \quad \text{(xxx}b\text{.)}$$

d the two summations may be evaluated in the manner already scribed. As an example of the application of the method the action

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl$$

may be considered. At 298·1° K. the expression in the square brackets for hydrogen, consisting of the normal ortho–para equilibrium, and for chlorine and hydrogen chloride, in which the isotopic molecules have been given their appropriate weights according to their proportions in the ordinary gases, has the values given below (Giauque and Overstreet, 1932).

Hydrogen . .	2023·20 cals. per gm.-mol.	
Chlorine . . .	2193·69	,, ,,
Hydrogen chloride .	2064·30	,, ,,

$$\therefore \quad HCl - \tfrac{1}{2} H_2 - \tfrac{1}{2} Cl_2 = -44{\cdot}1 \text{ cals.}$$

and so

$$\Delta H^\circ = \Delta E_0^\circ - 44 \text{ cals.}$$

The value of ΔE_0° is known, with some accuracy, to be − 21,984 calories, so that ΔH° at 298·1° K. is − 22,028 cals.; the heat evolved in the reaction at constant pressure is thus 22,028 cals., which is in excellent harmony with the thermochemical value of 22,000 cals., obtained both by Thomsen and by Berthelot.

The examples chosen to illustrate the applications of partition functions have mostly involved diatomic molecules and atoms, but the principles are the same when more complex substances are concerned. In these instances the only difficulty that may arise is the evaluation of the partition function, but there is little doubt that the approximate formulæ already given may be employed to obtain results of reasonable accuracy, especially as they are more accurate for large molecules. The methods can equally well be applied to unstable radicals, provided they yield definite spectra, and in this way information will be obtained of equilibria existing under abnormal conditions incapable of direct chemical investigation.

REFERENCES

BADGER and WOO. *J. Amer. Chem. Soc.*, 1932, **54**, 3523.
BRYANT. *Ibid.*, 1931, **53**, 3014.
CLUSIUS and BARTHOLOMÉ. *Z. Elektrochem.*, 1934, **40**, 524 *Z. physikal. Chem.*, 1935, [*B*], **30**, 258.
CRIST and DALIN. *J. Chem. Physics*, 1934, **2**, 442, 548, 735.
CROSS. *Ibid.* 1935, **3**, 168.
DAVIS and JOHNSTON. *J. Amer. Chem. Soc.*, 1934, **56**, 1045.
DOLE. *Ibid.*, 1935, **57**, 2731; *J. Chem. Physics.*, 1936, **4**, 268.
EIDINOFF and ASTON. *Ibid.*, 1935, **3**, 379.

EUCKEN. *Physikal. Z.*, 1929, **30**, 818.
FARKAS and FARKAS. *Trans. Faraday Soc.*, 1934, **30**, 1071.
FOWLER. "Statistical Mechanics"; *Proc. Roy. Soc.*, 1935, [*A*], **151**, 1.*
FOWLER and STERNE. *Rev. Mod. Physics.*, 1932, **4**, 635.*
GIAUQUE *et al.* *J. Amer. Chem. Soc.*, 1928, **50**, 101; 1929, **51**, 2300, 3194; 1930, **52**, 4808, 4816; 1932, **54**, 1731; 1933, **55**, 4875; 1935, **56**, 991; *Physical Rev.*, 1931, **38**, 196.
GIBSON and HEITLER. *Z. Physik.*, 1928, **49**, 465.
GLASSTONE. *Ann. Reports Chem. Soc.*, 1935, **32**, 66.*
GORDON *et al.* *J. Physical Chem.*, 1932, **36**, 1143, 2292, 2601; *J. Chem. Physics*, 1933, **1**, 297, 308; 1934, **2**, 65; 1935, **3**, 259, 336, 367; 1936, **4**, 100.
HALFORD. *Ibid.*, 1934, **2**, 694.
HUTCHISSON. *J. Amer. Chem. Soc.*, 1928, **50**, 1895.
JOHNSTON *et al.* *Ibid.*, 1929, **51**, 3194; 1933, **55**, 153, 172, 187, 2744, 3073; 1934, **56**, 271; 1935, **57**, 682; *J. Chem. Physics*, 1934, **2**, 389.
KASSEL. *Ibid.* 1933 **1**, 576; 1936, **4**, 276; *J. Amer. Chem. Soc.*, 1933, **55**, 1351; 1934, **56**, 1838; *Physical Rev.*, 1933, **43**, 364; *Chem. Reviews*, 1936, **18**, 277.*
LEWIS and VON ELBE. *J. Amer. Chem. Soc.*, 1933, **55**, 507, 511; 1935, **57**, 1399.
MACDOUGALL. *Physical Rev.*, 1931, **38**, 2074.
MACGILLAVRY. *Ibid.*, 1930, **36**, 1398.
MAYER, BRUNAUER and MAYER. *J. Amer. Chem. Soc.*, 1933, **55**, 37.*
MONTGOMERY and KASSEL. *J. Chem. Physics.*, 1934, **2**, 417.
PAULING. *Physical Rev.*, 1930, **36**, 43; *J. Amer. Chem. Soc.*, 1935, **57**, 2680.
RODEBUSH. *Chem. Reviews*, 1931, **9**, 319.*
SMITH and VAUGHAN. *J. Chem. Physics*, 1935, **3**, 341.
TELLER and TOPLEY. *J. Chem. Soc.*, 1935, 876.
TOPLEY and EYRING. *J. Chem. Physics*, 1934, **2**, 217.
UREY *et al.* *Ibid.*, 1933, **1**, 137; *J. Amer. Chem. Soc.*, 1935, **57**, 321; *Rev. Mod. Physics*, 1935, **7**, 34.
VILLARS. *Physical Rev.*, 1931, **38**, 998, 1552.
ZEISE. *Z. Elektrochem.*, 1933, **39**, 758,* 895*; 1934, **40**, 662,* 885*; 1935, **41**, 267.

* Review papers and books, wherein further references can be found, are marked with an asterisk.

CHAPTER III

ORTHO- AND PARA-HYDROGEN

Introduction : Nuclear Spins. Before the year 1927 hydrogen gas was generally believed to contain molecules of one type only : at present it is known that at least five, and probably more, kinds of molecules, all of them hydrogen in the sense that they possess an atomic number of unity, are present in the normal gas. The discovery of the forms of hydrogen, which has resulted from an exceptional combination of circumstances, represents one of the most remarkable chemical achievements of recent years. In 1924, Mecke observed a marked alternation in the intensities of successive rotational lines in the band spectrum of molecular hydrogen, the odd levels for the initial state being three times as intense as the even levels (Hori, 1927). Three years later, Heisenberg (1927) and Hund (1928) showed that the results were in harmony with the conclusion, arrived at from quantum mechanical considerations, that two different types of hydrogen molecules can exist. If a hydrogen nucleus has a spin of $\frac{1}{2}$, expressed in $h/2\pi$ units of angular momentum, then two nuclei can combine in a molecule of hydrogen either with their spins opposed, that is, antisymmetrical, so that the resultant spin of the molecule is zero or the combination may be such as to make the angular momentum additive, that is to say the spins are symmetrical, when the total nuclear spin is unity. Thus, ordinary hydrogen may be regarded as a mixture of the symmetrical and antisymmetrical forms.

Two Forms of Hydrogen. It can be shown (see p. 107) that at ordinary temperatures, that is, above 273° K., the proportion of the two forms reaches a limiting value of one part of the former to three parts of the latter, a ratio in agreement with the relative intensities of the spectral lines. It has been demonstrated theoretically (Wigner, 1929) that there is very considerable

reluctance to the reversal of spin of a nucleus, and consequently it is reasonable to suppose that as a result of the absorption of radiation by the hydrogen molecule, leading to the production of the spectrum under consideration, there will be no change in the nuclear spins. It may be deduced, therefore, that the more intense spectral lines, the odd levels, are produced by the symmetrical molecules, which in the ground state occupy only the rotational levels with odd quantum numbers, whereas the weaker lines are given by the antisymmetrical molecules, which have only even rotational quantum numbers. This conclusion is in harmony with expectations from quantum mechanics for a molecule obeying the Fermi-Dirac statistics : such a molecule is said to be antisymmetrical in its total eigenfunction (see p. 132).

Effect of Temperature. As the temperature of a gas is lowered and the energy content of the molecules decreases, the higher rotational levels become less common, and at low temperatures the molecules tend to accumulate in the lower rotational levels ; eventually, in the vicinity of the absolute zero, nearly all the molecules will occupy the lowest, that is, $J = 0$, rotational level, where J is the rotational quantum number. Since zero is to be regarded as an even number, it follows that at very low temperatures all the hydrogen molecules will be of the type which are symmetrical in their nuclear spins, there being a gradual change in the proportion of the two forms as the hydrogen is cooled.

At each temperature there should be a definite equilibrium ratio of the two kinds of hydrogen, and the application of the accurate statistical equations for heat capacity, etc., given in Chapter II., involves the implicit assumption that this equilibrium is always readily attained. The rotational heat capacities calculated from these equations were not in agreement with those determined experimentally at low temperatures by Eucken (1912), and in seeking for an explanation of the anomaly, Dennison (1927) suggested that the hydrogen gas used in this work did not contain the equilibrium proportions of the two forms. Decrease of temperature, as already indicated, should result in the conversion of a three to one mixture containing excess of the symmetrical form at ordinary temperatures, to a system consisting mainly of

the antisymmetrical form of hydrogen molecules. If equilibrium is to be maintained, therefore, the spins of many of the nuclei must undergo reversal, since this is the only way in which a molecule of one type can be converted into one of the other kind, as the gas is cooled. It has been already stated that this reversal does not occur at all readily, and consequently on lowering the temperature the " normal " ratio, namely 3 to 1, of the two forms is retained, instead of the equilibrium proportions to be expected theoretically. Making this assumption as to the composition of hydrogen gas, as a metastable mixture of three parts of symmetrical to one of antisymmetrical molecules, even at low temperatures, Dennison was able to calculate values for the molecular heat of hydrogen (see p. 108) in excellent agreement with the observed values (see Fig. 6, p. 110). This suggestion, that the rate of change of one form of hydrogen to the other is slow, is in agreement with the observation made later (McLennan and McLeod, 1929) that successive lines in the Raman spectrum of liquid hydrogen had the same ratio of intensities as with the gas, whereas attainment of equilibrium in the former case would have meant almost complete absence of the lines corresponding to odd rotational levels.

Attainment of Equilibrium in Hydrogen. Soon after the publication of Dennison's calculations, Condon suggested that if hydrogen were kept at liquid-air temperatures for some time, a change in the nature of the gas might be observed as a consequence of the tendency towards the attainment of equilibrium. Acting on this suggestion, Giauque and Johnston (1928) found, in fact, that after being kept for 197 days at a temperature of 85° K. the triple-point pressure of hydrogen was decreased from 5·38 to 5·34 cm. of mercury. This difference, although small, was considered to be outside the range of experimental error, and the result indicated, therefore, that a change had occurred in the hydrogen as a result of being kept at a low temperature. More striking confirmation of the correctness of the views already outlined was obtained by Bonhoeffer and Harteck (1929), who made the important discovery that the attainment of equilibrium between the symmetrical and the antisymmetrical forms of hydrogen at

low temperatures could be accelerated by means of charcoal. The normal gas was adsorbed on charcoal which had been baked out in a vacuum : the temperature was kept at that of liquid air, and was subsequently lowered to that of liquid hydrogen, when a large quantity of gas was taken up by the catalyst. After a short time the hydrogen was desorbed, by reducing the pressure, and the heat conductivity, which is directly related to the heat capacity, of the resulting gas was found to correspond to that to be expected from almost pure symmetrical hydrogen.

Ortho- and Para-Hydrogen. Almost simultaneously with the announcement of these results, Eucken and Hiller (1929) reported the results of direct measurement of the specific heat of hydrogen gas which had been kept at 90° K. for some weeks : a definite change was observed in accordance with that to be expected from a tendency towards the attainment of equilibrium proportions of the two types of molecules. Further work with hydrogen, to be described in detail later, has shown with certainty that two forms of this substance can exist : since their interconversion is generally slow, in the absence of a catalyst, there is some justification for ascribing individual names to the two forms, and the suggestion of Bonhoeffer and Harteck that the symmetrical and antisymmetrical kinds of hydrogen be designated by the prefixes " ortho " and " para," respectively, because of their analogy with the two spectroscopic forms of helium, has been generally adopted. It is realised that this nomenclature is not very satisfactory, for several reasons, particularly because the ortho- and para-states of helium are due to differences in the coupling of *electron* spins, as distinct from the *nuclear* spin configurations in hydrogen ; nevertheless, an attempt to introduce alternative names, as, for example, α- and β-hydrogen, has not been successful.

Preparation of Pure Para-Hydrogen. The best method for obtaining para-hydrogen in an almost pure form is the same in principle as that originally used by Bonhoeffer and Harteck. Active charcoal is placed in a quartz or pyrex-glass vessel and baked out under vacuum ; ordinary hydrogen gas is then allowed to enter and the temperature is gradually lowered to 20° K., the temperature of normal liquid hydrogen. After the elapse of a

short period, varying from a few minutes to some hours, depending on the activity of the charcoal catalyst, the gas is pumped off and consists, if sufficient time has been allowed, of 99·7 per cent. of para-hydrogen. If liquid air only is available the same principle may be used to yield a gas containing a little less than 50 per cent. of the para-form : under these conditions finely divided nickel, deposited on kieselguhr, is a very effective catalyst (Taylor and Sherman, 1932). By suitable arrangement of the apparatus it is possible to devise a continuous process for obtaining para-hydrogen from the ordinary gas.

At normal temperatures para-hydrogen can be stored in glass vessels for several weeks without appreciable change taking place ; oxygen must be rigorously excluded (see p. 122), and the gas should be kept over mercury, not water. The presence of metal catalysts, such as platinised asbestos or a synthetic ammonia catalyst, *i.e.*, finely divided iron together with small amounts of potassium and aluminium oxides, brings about relatively rapid restoration of equilibrium, even at ordinary room temperatures : the pure para-form is partly converted into the ortho-form so as to yield the normal mixture of one part of para- to three parts of ortho-hydrogen. Under the influence of an electrical discharge, or if the temperature is raised to 800° C., or more, the para to ortho conversion occurs, and equilibrium is restored (*vide infra*).

Hitherto no enrichment of the ortho-form of hydrogen gas has been reported. Since there is no temperature at which there is present at equilibrium relatively more of the ortho-form that in the normal gas, it is obvious that it is not a simple matter to obtain hydrogen in this state. Since para-hydrogen has a greater vapour pressure than the ortho-form (p. 105), it should be possible to obtain a partial concentration of the latter by a process of fractional distillation. The differences of vapour pressure are, however, so small that the separation is not likely to prove very effective.

PHYSICAL PROPERTIES

Spectra. The characteristic feature of the alternation in the intensities of the rotational lines in the band spectrum of molecular

hydrogen observed by Mecke, is to be attributed to the fact that there is no reversal of nuclear spin as a result of the absorption of radiation. That is to say, an ortho-molecule remains in the ortho-state even when its energy level is changed and it produces spectral lines; similarly, a para-molecule remains in the para-state. This fact is sometimes expressed by the statement that ortho-states combine only with ortho, and para-states only with para, in the production of molecular spectra. The formation of the so-called Lyman bands of hydrogen provides a simple illustration of this behaviour: the first excited electronic state of the hydrogen molecule is known as the Lyman level, but in this state, in contrast to the conditions in the ground level, ortho-states occupy the even, whereas the para-states occupy the odd rotational levels (see p. 133). The condition of affairs may be represented, thus:

	Ground Level (Σ_g^+).	Lyman Level (Σ_u^+).
Para-hydrogen . .	$J = 0, 2, 4, 6 \ldots$	$J = 1, 3, 5, 7 \ldots$
Ortho-hydrogen. .	$J = 1, 3, 5, 7 \ldots$	$J = 0, 2, 4, 6 \ldots$

When the hydrogen molecules receive enough energy to raise them to the Lyman level the para-molecules will undergo rotational transitions, J changing $0 \rightarrow 1$; $2 \rightarrow 3$ and 1; $4 \rightarrow 5$ and 3, etc., the values of J altering by ± 1, as is usual in such transitions ("Recent Advances in Physical Chemistry," Chapter IV.); similarly the ortho-molecules will undergo the transitions in which J changes $1 \rightarrow 0$ and 2; $3 \rightarrow 2$ and 4; $5 \rightarrow 4$ and 6, etc. (see Fig. 5). The transitions for which ΔJ is $+1$, *e.g.*, $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$, etc., constitute the so-called R-branch of the rotational band, and those for which ΔJ is -1, *i.e.*, $1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 2$, etc., make up the P-branch. It is evident, therefore, that alternate lines in each branch of the spectral band will result from combinations between ortho-states only, or from para-states only. Since in normal hydrogen the ortho-molecules are three times as numerous as those in the para-states, there will be

a 3 to 1 ratio in the intensities of successive lines; those corresponding to the odd values of J in the initial state will be three times as strong as those for which J has initially an even value. If the proportion of para-hydrogen in the gas is increased, for example by the use of a catalyst at low temperature, the intensities of the lines corresponding to para-transitions are correspondingly enhanced.

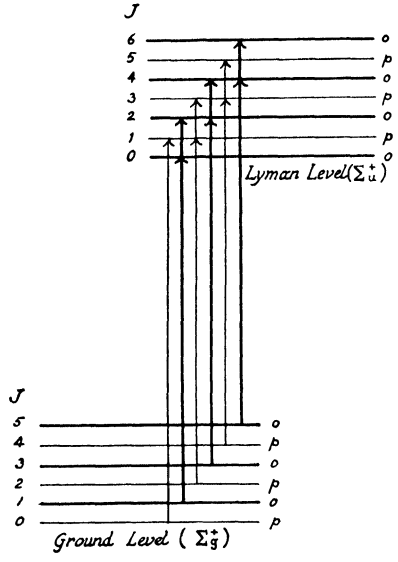


FIG. 5.—Diagrammatic representation of the formation of a band in the Lyman spectrum of molecular hydrogen.

The same alternation of intensities of successive lines has been observed in other electronic spectra of hydrogen, *e.g.*, in the Fulcher bands, and also in the Raman spectrum of both the liquid (McLennan and McLeod, 1929) and the gas (Rasetti, 1929). The persistence of the 3 to 1 ratio for the intensities of the lines due to ortho- and para-states, respectively, in liquid hydrogen implies, as already indicated, that the normal proportions of the two forms remain at low temperatures, because of the slowness of the establishment of equilibrium. If liquid hydrogen is kept for some time, however, the line corresponding to the $0 \rightarrow 2$ transition,* due to para-molecules, increases in intensity, showing that some spontaneous ortho–para conversion does occur. It is of interest to record that the Raman spectrum of liquid hydrogen at 20° K. shows lines corresponding *only* to the transitions of J which are $0 \rightarrow 2$ and $1 \rightarrow 3$: the molecules at this temperature thus have

* It should be noted that in the Raman spectrum the rational quantum number changes by two units (see "Recent Advances in Physical Chemistry," Chapter IV.).

only sufficient rotational energy to occupy the two lowest levels. If equilibrium had been attained nearly all the molecules would have occupied the lowest, that is, $J = 0$, level, and the hydrogen would be almost exclusively in the para-form.

Vapour Pressures, Boiling and Triple Points. The vapour pressure of liquid para-hydrogen is definitely greater than that of the normal liquid, and consequently the former has the lower boiling point, namely, 20·26° K., as compared with a value of 20·39° K. for the latter. The results in Table IX. were obtained by Bonhoeffer and Harteck, who worked with a number of mixtures containing from 80 to 98·5 per cent. of para-hydrogen and extrapolated the measured vapour pressures in order to give the value for the pure para-form. The temperatures, 13·95° K. and 20·39° K., are the triple point and boiling point, respectively, of normal hydrogen.

TABLE IX

Vapour Pressures of Normal- and Para-Hydrogen.

Temp.	Vapour Pressure (mm. Hg.).	
	Normal-H_2.	Para-H_2.
13·95° K.	53·9	57·0
20·39°	760·0	787·0

It will be recalled that Giauque and Johnston (p. 100) found that the vapour pressure of hydrogen at its triple point *decreased* on standing : this is at first sight surprising, since the para-form, which is slowly accumulating, has the higher vapour pressure. There must be taken into consideration, however, the fact that the triple point of para-hydrogen is about 0·12° lower than that of the normal form. At their *respective* triple points, the vapour pressure of the latter is actually 0·9 mm. of mercury higher than that of the former. If the vapour pressure of liquid hydrogen is measured at some *definite temperature*, the value should increase on standing, and Keesom and his co-workers (1931) have found that this actually occurs ; at about 20° K. the rate of increase of

pressure is approximately 0·15 mm. of mercury per hour. It may be mentioned, finally, that the vapour pressure of pure ortho-hydrogen has been estimated, by extrapolation, to be 751 mm. of mercury at 20·39° K., the boiling point of the normal liquid.

Magnetic Properties. An essential consequence of the difference in the nuclear-spin orientations of the ortho- and para-forms of hydrogen is a difference in the magnetic properties : the magnetic moment is determined by the nuclear spins and by the rotational quantum number. In para-hydrogen the nuclear spins are anti-parallel and compensate one another, so that they do not contribute to the magnetic moment, and since at low temperatures these molecules all accumulate in the lowest rotational level ($J = 0$), the moment should be zero. This has been verified by the observation that at liquid-air temperatures para-hydrogen molecules are not deflected in an in-homogeneous magnetic field, and so they are not magnetic. The magnetic moment of ortho-hydrogen, apart from the effect due to rotation, should be twice that of the proton : the actual value, estimated from the deflection of normal hydrogen, appears to be somewhat greater than this estimate, but there is as yet no adequate explanation of the discrepancy.

Ortho–Para Ratios. It has been seen in the previous chapter that for a system obeying the Maxwell-Boltzmann distribution law, the number of molecules present in any given state is proportional to $pe^{-\varepsilon/kT}$, where p is the statistical weight and ε the energy in excess of the zero-point value, for the given state. The sum of all these terms for the different states present in the given system is the partition function (p. 57). In para-hydrogen, as already observed, only even rotational levels are possible, in the electronic ground state, whereas in the ortho-form only odd levels occur ; it is apparent, therefore, that the ratio of the number of molecules of hydrogen in the para- to that in the ortho-form is given by the ratio of the partition functions for odd and even values, respectively, of the rotational quantum numbers, J ; thus

$$\frac{[\text{para-H}_2]}{[\text{ortho-H}_2]} = \frac{\Sigma p_J e^{-\varepsilon_J/kT}}{\Sigma p_J e^{-\varepsilon_J/kT}} \underset{J=1,3,5,7\ldots}{\overset{J=0,2,4,6\ldots}{}} = \frac{\Sigma i(2i+1)(2J+1)e^{-\varepsilon_J/kT}}{\Sigma(i+1)(2i+1)(2J+1)e^{-\varepsilon_J/kT}} \underset{J=1,3,5,7\ldots}{\overset{J=0,2,4,6\ldots}{}} \quad \text{(i.)}$$

In determining the statistical weight of each level it must be remembered that the normal weight $2J + 1$ must be multiplied by the nuclear-spin factor $i(2i + 1)$ for even values of J, and by the factor $(i + 1)(2i + 1)$ for odd values, where i, equal to $\frac{1}{2}$, is the spin of the hydrogen nucleus; these spin factors are equal to 1 and 3 respectively, for even and odd rotational levels. It follows, therefore, that

$$\frac{[\text{para-H}_2]}{[\text{ortho-H}_2]} = \frac{1 + 5e^{-\epsilon_2/kT} + 9e^{-\epsilon_4/kT} + 13e^{-\epsilon_6/kT} \ldots}{3(3e^{-\epsilon_1/kT} + 7e^{-\epsilon_3/kT} + 11e^{-\epsilon_5/kT} \ldots)} \quad \text{(ii.)}$$

where ε_J represents the rotational energy of the Jth level. By means of this equation it is possible to calculate the ratio of para- to ortho-molecules in hydrogen gas at equilibrium at any temperature, the value of the rotational energy being determined from the band spectra of molecular hydrogen. This calculation was carried out by Giauque (1930), and the results are given in Table X.; the terms in both numerator and denominator of equation (ii.) are summed as long as they contribute appreciably to the total. Since the magnitude of the rotational energy increases rapidly with increasing values of J, the $e^{-\epsilon_J/kT}$ term becomes smaller, and for the higher levels is only appreciable if the temperature is high, that is, when T is large. At 300° K. the contribution beyond the sixth rotational level is so small as to be negligible.

TABLE X

Ortho–Para Composition of Equilibrium-Hydrogen.

Temp.	Ortho/Para Ratio.	Para-H_2, %.	Ortho-H_2, %.
20° K.	$1{\cdot}835 \times 10^{-4}$	99·82	0·18
40°	$1{\cdot}285 \times 10^{-1}$	88·61	11·39
50°	$3{\cdot}006 \times 10^{-1}$	76·89	23·11
60°	$5{\cdot}291 \times 10^{-1}$	65·39	34·61
70°	$7{\cdot}911 \times 10^{-1}$	55·83	44·17
80°	1·066	48·39	51·61
90°	1·338	42·75	57·25
100°	1·596	38·51	61·49
120°	2·042	32·87	67·13
170°	2 691	27·99	72·01
230°	2·933	25·42	74·58
273°	2·979	25·13	74·87
∞	3·000	25·00	75·00

The use of ε values determined from actual spectroscopic frequencies makes allowance for the increase in the moment of inertia, and for other effects, as the rotational quantum number increases. If as an approximation it is assumed that the hydrogen molecule is rigid, then the rotational energy can be expressed by the well-known equation, $\varepsilon_J = J(J+1)h^2/8\pi^2 I$, and taking the magnitude of I as $0{\cdot}467 \times 10^{-40}$ c.g.s. units the rotational energy for a series of values of J can be determined. The calculations can be considerably simplified in this manner and the results obtained are not very different from those given by the more accurate procedure.

It will be observed from Table X. that as the temperature is raised the porportion of the para-form in equilibrium hydrogen decreases from 100 per cent. to a limiting value of 25 per cent.; that is to say, at ordinary temperatures hydrogen should contain ortho- and para-forms in the ratio of 3 parts to 1. This is in agreement with the experimental facts considered in the introductory section. It may be noted that the ortho–para ratio of 3 to 1 at appreciable temperatures is to be expected from the fact, mentioned in the previous chapter (p. 73), that if the temperature is not too low the sum of the $(2J+1)e^{-\varepsilon_J/kT}$ terms for odd values of J is equal to the sum for even values. The ratio of the odd to even partition functions, giving the ratio of ortho- to para-molecules, is then determined only by the corresponding ratio of the nuclear-spin factors, namely, 3 to 1. At low temperatures, as is to be anticipated from general considerations, equilibrium hydrogen contains larger proportions of the para-form, and below 25° K. exists almost exclusively in this state.

Heat Capacity. The equations connecting the heat capacity of an ideal gas with the partition function have been already considered in Chapter II., and these may now be applied to the different forms of hydrogen. If the rotational heat capacity of *equilibrium*-hydrogen is to be calculated then the total partition function, for both even and odd levels, including the appropriate allowance for nuclear spin, must be used; thus

$$Q_{\text{equil.}} = \sum_{J=0,2,4,6\ldots}(2J+1)e^{-\varepsilon_J/kT} + 3\sum_{J=1,3,5,7\ldots}(2J+1)e^{-\varepsilon_J/kT} \quad . \quad . \quad \text{(iii)}$$

On the other hand, if individual heat capacities of either pure para- or ortho-forms are required the partition functions over odd and even values of J, respectively, should be used ; thus

$$Q_{\text{para}} = \sum_{J=0,2,4,6\ldots}(2J+1)e^{-\epsilon_J/kT} \quad . \quad . \quad . \quad . \quad . \quad \text{(iv}a\text{.)}$$

and

$$Q_{\text{ortho}} = 3\sum_{J=1,3,5,7\ldots}(2J+1)e^{-\epsilon_J/kT} \quad . \quad . \quad . \quad . \quad . \quad \text{(iv}b\text{.)}$$

Since the partition functions can be evaluated, either by the aid of ϵ_J values obtained directly from spectroscopic data, or else by calculation from the known moment of inertia, assuming a rigid molecule, the molar heat capacities of para- and ortho-hydrogen and of their equilibrium mixtures, at various temperatures, can be determined by means of equation (xii.) of the previous chapter. The calculations are rendered relatively simple by the fact that at temperatures up to 300° K. only a negligible proportion of the hydrogen molecules is in rotational levels above that for which J is 6, so that no more than the first seven levels contribute appreciably to the partition function. The values obtained in this manner (Giauque, 1930) for the rotational heat capacity are quoted in Table XI., the last column in the table is for " normal " hydrogen, that is, for a mixture containing the ortho- and para-forms in the constant proportion of 3 to 1 at *all* temperatures, the heat capacities being obtained by the relationship :

$$C_{\text{normal}} = \tfrac{3}{4}C_{\text{para}} + \tfrac{1}{4}C_{\text{ortho}}$$

TABLE XI

Molar (Rotational) Heat Capacities of Hydrogen Gas (Calculated).

Temp.	Para.	Ortho.	Equilibrium.	Normal.
0° K.	0·0000	0·0000	0·0000	0·0000
20°	0·0000	0·0000	0·0028	0·0000
30°	0·0001	0·0000	1·8795	0·0000
50°	0·0399	0·0000	4·1042	0·0100
100°	1·5014	0·0731	1·7498	0·4309
150°	2·8451	0·5271	1·4131	0·7871
200°	2·7674	1·1512	1·5965	1·5553
250°	2·4056	1·6049	1·8101	1·8051
298·1°	2·1862	1·8377	1·9254	1·9248

There is no appreciable contribution of the vibrational levels to the heat capacity at temperatures below 300° K., and so the molar heat capacity of hydrogen at constant volume is obtained by adding the translational contribution, namely, $3R/2$ per gm.-mol., to the values given in the table.

The heat capacity of normal-hydrogen is that to be expected

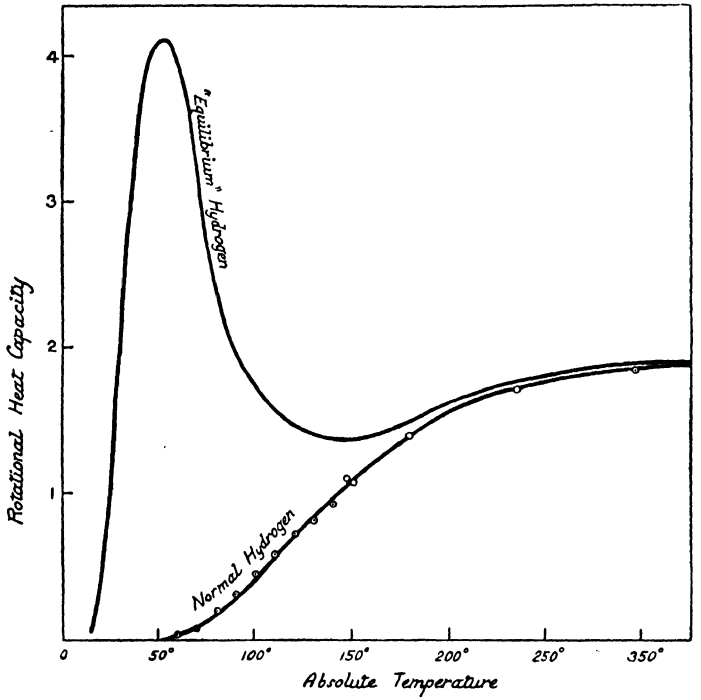


FIG. 6.—Calculated heat capacities for "equilibrium" and "normal" forms of hydrogen. Experimental values are indicated by circles.

from ordinary hydrogen which has been cooled down from room temperatures without equilibrium being established during the cooling process. The values, according to Dennison, should correspond to those determined experimentally with hydrogen gas, provided it has not been kept at low temperatures for lengthy periods; that this is actually the case has been already mentioned.

The calculated values for the molar heat capacity of equilibrium-hydrogen are represented graphically in Fig. 6, which shows more clearly than the data in Table XI. the remarkable variation of the heat capacity with temperature, the maximum at 75° K. being accounted for by the para → ortho conversion which should, theoretically, be taking place. The discrepancy between this curve and that for normal-hydrogen, which approximates to the experimental data, is very striking, and brings out clearly the nature of the problem presented by the heat capacity of hydrogen until the ideas of the existence of the ortho- and para-forms, and of their slow interconvertibility under normal conditions, were developed. The molar heat of almost pure para-hydrogen, prepared by the use of charcoal as catalyst (p. 101), has been determined at low temperatures (Clusius and Hiller, 1929); the results are in excellent agreement with those calculated from the partition functions involving even rotational states only, which are given in Table XI.

Entropy. The entropy of hydrogen has been determined calorimetrically by adding the dQ/T(or $Cd\ln T$) terms involved in raising the temperature of 1 gm.-mol. of hydrogen to 298·1° K. from the solid state at 0° K., the entropy of the latter state being assumed to be zero, in accordance with the third law of thermodynamics. The experimental value determined in this manner (Giauque, 1930) is 29·64 cals./degree per gm.-mol., after applying a correction of 0·03 units, based on van der Waals' equation, for deviation from ideal-gas behaviour. The entropy calculated by the statistical method, as already described (p. 84), is 33·98 units, and the difference between the two values is of considerable importance. One obvious source of this discrepancy is the fact that the thermal measurements at low temperatures were made on normal-, instead of equilibrium-hydrogen, whereas the calculations by the use of partition functions imply that equilibrium is established at all temperatures. It appears, further, that the rotational levels which characterise the ortho- and para-molecules are carried over into the solid state: the molecular arrangement in the latter is, therefore, not perfectly ordered, and the entropy cannot be zero. This behaviour, namely rotation in the solid,

is very rare and appears only to be definitely established for hydrogen itself and possibly for one or two compounds containing hydrogen.

At very low temperatures para-hydrogen will be almost exclusively in the lowest even rotational level, for which $J = 0$; ortho-hydrogen under the same conditions would exist in the $J = 1$ level, so that their respective entropies in the solid state, if rotational levels are maintained, will be different. For para-hydrogen the statistical weight, $2J + 1$, is unity, since at temperatures below about 20° K. the molecules will all be in the $J = 0$ level, and application of equation (xix.) of Chapter II. (p. 58) shows that the internal entropy, that is, apart from translational entropy, should be $R\ln 1$, which is zero. At low temperatures, therefore,

$$S^{\text{int.}}_{\text{para}} = 0.$$

Under the same conditions the ortho-molecules will all be in the $J = 1$ level, and the statistical weight, which is now $3(2J + 1)$, the factor 3 allowing for the nuclear-spin degeneracy, is 9, so that the internal entropy is given by

$$S^{\text{int.}}_{\text{ortho}} = R\ln 9.$$

The entropy (S) of a mixture of two substances, A and B, is obtained by the relationship

$$S = n_A S_A + n_B S_B - R\,(n_A \ln n_A + n_B \ln n_B) \quad . \quad . \quad . \quad \text{(v.)}$$

where n_A and n_B are the molar fractions, and S_A and S_B the entropies, of A and B, respectively. The third term on the right-hand side of equation (v.) is the entropy of mixing, which must be included. Applying this equation to determine the entropy of normal-hydrogen, containing one part of para- to three parts of the ortho-form, at low temperature, it follows that

$$\begin{aligned} S^{\text{int.}}_{\text{normal}} &= 0 + \tfrac{3}{4} R\ln 9 - R(\tfrac{1}{4}\ln\tfrac{1}{4} + \tfrac{3}{4}\ln\tfrac{3}{4}) \\ &= 4{\cdot}39 \text{ cals./degree per gm.-mol.} \end{aligned}$$

As a consequence, therefore, of the rotational levels of hydrogen being carried over into the solid state at low temperatures, it follows that ordinary hydrogen will have an internal entropy of

4·39 units, instead of zero, as would have been the case if all the molecules had passed over into the para-form, as they theoretically should do for the third law of thermodynamics to be applicable. The difference of 4·39 units should therefore be added to the experimental entropy value of 29·64, to give a total of 34·03 units, as the true absolute entropy of hydrogen at 298·1° K. This result would, of course, have been obtained if the ortho–para equilibrium were always rapidly established in hydrogen at all temperatures; there would then be no rotation in the solid, since all the molecules would be in the zero rotational level. The adjusted entropy value is so close to that calculated (33·98 units) that the latter may be regarded with confidence as being correct. If the entropy of hydrogen is to to be used in conjunction with values determined calorimetrically for other substances, which do not rotate in the solid state, the nuclear-spin contribution, viz., $R\ln 4$ (see p. 75), should be subtracted, giving 31·23 units for the virtual entropy of hydrogen at 298·1° K.

Energy of Ortho–Para Conversion. From the appropriate rotational partition functions it is possible to calculate the rotational energies of para-, ortho-, and equilibrium-hydrogen, and from the results of the first two of these the values for normal-hydrogen, viz., one-quarter para + three-quarters ortho, can be determined at a series of temperatures. Some of the results obtained in this way, with the aid of equation (xi.) of Chapter II., are given in Table XII.

TABLE XII

Potential Energy of Hydrogen (cals. per gm.-mol.).

Temp.	Para.	Ortho.	Equilibrium.	Normal.
0° K.	0·00	337·17	0·00	252·88
20°	0·00	337·17	0·63	252·88
50°	0·20	337·18	78·38	252·94
100°	30·56	338·59	219·78	262·17
150°	146·61	351·40	292·94	300·20
200°	290·22	393·59	366·76	367·75
250°	419·27	463·46	452·30	452·41
298·1	529·12	546·92	542·46	542·47

The small values for the energies of the para- and equilibrium-forms at low temperatures are to be ascribed to the fact that nearly all the molecules in the para-state are in the lowest rotational level, viz., $J = 0$, and consequently have no rotational energy; under these conditions, further, equilibrium-hydrogen consists mainly of the para-form, so that its energy will be zero.

It will be observed from the table that as the temperature increases the difference between the rotational energies for the various kinds of hydrogen diminishes; at about 400° K. the values are, in fact, indistinguishable, but at low temperatures the differences are appreciable and should become evident as heat evolved when normal-hydrogen is made to attain the equilibrium condition. This conclusion has been confirmed by the measurements of von Elbe and Simon (1930): normal-hydrogen was adsorbed, at low temperature, on charcoal capable of bringing about rapid ortho–para conversion, and then the gas was desorbed in the equilibrium-form. The difference between the heat evolved on adsorption and that taken up on desorption is clearly equal to the heat of conversion from normal to equilibrium states. The experimental difficulties involved in this work are very considerable, liquid hydrogen or nitrogen being used as calorimetric liquid; nevertheless, the observed heats of conversion are in satisfactory agreement with the calculated values, as is shown by the results in Table XIII.

TABLE XIII

Heat Evolved in the Conversion of Normal- to Equilibrium-Hydrogen.

Temp.	Heat Evolved (Experimental).	Difference in Rotational Energies (Calculated).
77·5° K.	74 ± 16 cals.	83 cals.
20·4°	214 ± 4	252

Free Energy Changes. The differences in the free energy of the the various kinds of hydrogen are also of interest, and the values can be readily calculated, especially for appreciable temperatures. The equation (xxvi*a*.) of Chapter II. (p. 59), giving the standard

free energy in terms of the partition function (Q) and of other quantities, may be simplified for the different forms of molecular hydrogen. The zero-point energy ($E_0°$), which depends on the vibrations within the molecule is very probably independent of the nuclear spins, and the masses of the various kinds of hydrogen are the same ; hence at constant temperature, and at atmospheric pressure, the equation may be written in the form

$$-F° = RT\ln Q + a \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi.)}$$

where a is a constant for all forms of hydrogen. At reasonably high temperatures, namely, above 273° K., the partition function, including spin, Q_{ortho} is equal to $3Q_{\text{para}}$ (see p. 108), and hence Q_{normal}, which is virtually the same as $Q_{\text{equil.}}$ at these temperatures, is equal to $4Q_{\text{para}}$. It follows, therefore, that

$$-F°_{\text{para}} = RT\ln Q_{\text{para}} + a$$
$$= RT\ln Q_{\text{normal}}/4 + a$$

and $$-F°_{\text{normal}} = RT\ln Q_{\text{normal}} + a$$

and, consequently, for the process

$$H_2(\text{para}) \rightarrow H_2(\text{normal})$$

the free energy change $\Delta F°$ is given by

$$-\Delta F° = RT\ln 4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii.)}$$
$$\text{para} \rightarrow \text{normal}$$

This difference in the free energy must result in a difference of reactivity of the two forms of hydrogen ; for example, in the dissociation of hydrogen molecules

$$H_2 = 2H,$$

the free energy changes, according as the molecules are in the para- or in the normal-forms, may be written in terms of the equilibrium constants ; thus,

$$-\Delta F° = RT\ln K_{\text{para}} \quad \text{and} \quad -\Delta F° = RT\ln K_{\text{normal.}}$$
$$\text{para-}H_2 \rightarrow 2H \qquad \text{normal-}H_2 \rightarrow 2H$$

Since the hydrogen atoms are the same in both cases, irrespective of the combination of the nuclear spins in the molecules from which they are formed, it follws that

$$-\Delta F° = RT\ln K_{\text{para}}/K_{\text{normal}} \quad . \quad . \quad . \quad . \quad \text{(viii.)}$$
$$\text{para} \rightarrow \text{normal}$$

Comparing this result with equation (vii.) it follows that K_{para}/K_{normal} is equal to 4, at appreciable temperatures. For the reaction under consideration the equilibrium constant is directly related to the fraction x of the molecules dissociated at the particular temperature by the equation

$$K = \frac{4x^2}{1 - x^2} P$$

where P is the total pressure. It is evident, therefore, that under the same conditions of temperature and pressure para-hydrogen will be dissociated to twice the extent of normal-hydrogen, provided the total extent of dissociation is not large. This result is probably mainly of theoretical interest, since for temperatures at which there is a significant concentration of hydrogen atoms, the rate of conversion of the para-form to the equilibrium, that is, normal, state, *viâ* the atoms (*cf.* p. 119), is so great that the equilibrium between molecular para-hydrogen and the atoms cannot be realised. The larger concentration of hydrogen atoms in equilibrium with para-hydrogen might be made evident by the influence of the gas, as compared with that of normal-hydrogen, in the initiation of reaction chains, many of which can be set off by hydrogen atoms. As an example might be taken the effect of the two kinds of hydrogen on the explosion limits of the hydrogen–oxygen reaction ("Recent Advances in Physical Chemistry," Chapter V.), but in this case the oxygen itself catalyses the para–ortho conversion. The same difficulty arises in other cases, and consequently no direct proof is yet available for the increased dissociation of para-hydrogen relative to that of the normal gas.

Analysis of Ortho–Para Mixtures. The difference in the heat capacities of ortho- and para-hydrogen, especially at low temperatures, has been applied in a relatively simple method for determining the proportions of the two forms present in any given specimen of hydrogen (Bonhoeffer and Harteck, 1929). The heat conductivity (λ) of a gas can be directly related to its molar heat capacity (C_v) by an equation of the form

$$\lambda = \eta(k + C_v)/M \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix.)}$$

where η is the viscosity of the gas, M its molecular weight and k a

constant. For the different forms, both the molecular weight and viscosity are the same, and so the heat conductivities are directly related to the respective heat capacities. If a given quantity of electricity is passed through a wire in a closed vessel containing a definite amount of hydrogen under constant conditions of temperature and pressure, the wire will attain a higher temperature the smaller the heat conductivity, or the heat capacity, of the gas. In the experimental method the hydrogen is passed into a small vessel, able to contain a few cubic centimetres of gas at a definite low pressure, consequently only a relatively small quantity is required. The heating element consists of a fine platinum wire connected to accumulators so as to permit the passage of a definite quantity of electricity. The cell is placed in a Dewar vessel containing liquid air, or liquid hydrogen, and the amount of heating current is chosen so as to bring the wire to a temperature in the vicinity of 160° K., if possible, because it is then that the difference in the heat capacities of the two forms of hydrogen is greatest (see Table XI.). The temperature attained by the wire immediately after the passage of the current is measured by determining the resistance in the usual way, by means of a Wheatstone-bridge arrangement. The apparatus is calibrated with a number of mixtures of almost pure para-hydrogen and normal-hydrogen, containing 75 per cent. of the ortho-form, and so the ortho–para ratio of any specimen of hydrogen gas can be read off directly from the resistance of the platinum wire. A number of modifications of the method described have been employed ; in one of these only about 0·003 c.c. of gas at N.T.P. is required (Farkas, 1933), the pressure being approximately 0·05 mm. of mercury.

CHEMICAL REACTIONS

Homogeneous Ortho–Para Conversion.* The alternations of the rotational lines in the band spectrum of normal hydrogen, even

* The general term " ortho–para conversion " is used for conversion in either direction ; at the lowest temperatures it is the change from ortho to para which is under consideration, whereas at higher temperatures the reverse change is of importance.

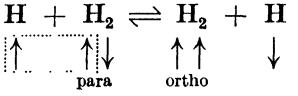
at low temperatures, implies, as already noted, that the absorption of radiation does not result in appreciable conversion of ortho- to para-states; calculations by Wigner (1929), based on wave mechanics, show that the transition probability of a hydrogen molecule from the rotational level J to the level $J + 1$, within the same electronic state, that is, the ortho–para conversion, as a result of the absorption of radiation, is about one molecule in 10^{10} seconds. If the probability of transition as a result of collisions is taken into consideration, the half-life period of the ortho–para conversion process can be calculated as approximately 10^8 seconds, that is, about three years, under normal conditions (Hall and Oppenheimer, 1930). Since increase of pressure favours the number of collisions, the rate of conversion of ortho- to para-forms should be greater at higher pressures than under atmospheric conditions; in their earliest work Bonhoeffer and Harteck kept hydrogen gas under a pressure of 150 atmospheres, at liquid-air temperature, and obtained appreciable conversion in a relatively short time. This result was, however, shown later to be due to the catalytic effect of the walls of the brass vessel in which the hydrogen had been enclosed. Similarly, the increase in concentration of the para-molecules observed by Eucken and Hiller (p. 101) is probably to be attributed to catalytic action. There is little doubt that at low temperatures the spontaneous homogeneous ortho–para conversion in hydrogen gas is an extremely slow process: there is evidently very considerable reluctance to the reversal of nuclear spins. The homogeneous conversion in the liquid and solid phases occurs more readily, but special conditions are here operative, to which reference will be made later (p. 124).

High Temperature Conversion. As the temperature is raised above 600° C., the conversion of para- to ortho-states occurs readily as a homogeneous gas reaction in vessels of quartz or of glazed porcelain; in an unglazed porcelain tube the process is almost completely heterogeneous and is catalysed by the walls of the vessel. The homogeneous conversion of para-hydrogen has been studied by A. Farkas (1930), who found the time of half-change to be inversely proportional to the square-root of the

initial pressure of hydrogen ; the reaction is consequently of the order 1·5, implying a mechanism represented by the equation

$$H + \text{para-}H_2 \rightleftharpoons \text{ortho-}H_2 + H,$$

so that hydrogen atoms play a part in the conversion process. The hydrogen atoms are produced by ordinary thermal dissociation of the molecules, and suitable collisions can result in the change from para- to ortho-forms, *without any actual reversal of nuclear spin* having occurred ; this process may be depicted thus



where arrows represent the spins of the three hydrogen nuclei involved in a collision. The energy of activation of the process, determined from the influence of temperature on the velocity constant, after making due allowance for the variation of the concentration of hydrogen atoms with temperature, is 5500 cals. in the temperature range of 600° to 750° C.

Conversion by Atomic Hydrogen. The reaction between para-hydrogen and hydrogen atoms specially produced by extraneous means, for example, by the passage of an electrical discharge through the gas, should be kinetically similar to the para–ortho conversion first considered. In the experiments of Geib and Harteck (1931), hydrogen containing 3 to 19 per cent. of hydrogen atoms, compared with 10^{-8} to 10^{-6} per cent. resulting from thermal dissociation at about 700° C., was allowed to interact with para-hydrogen at temperatures between 10° and 100° C., and at a pressure of about 0·5 mm. of mercury. The resulting gas was passed through a liquid-air trap to remove the hydrogen atoms and then analysed, by the thermal conductivity method, to determine the final ortho–para ratio. The kinetics of the reaction was found to be similar to that for the para–ortho conversion already discussed ; the activation energy, however, was determined as 7000 cals., instead of 5500 cals. In view of the very different conditions of the two sets of experiments it is not certain if any definite significance is to be attached to this discrepancy. In neither case was the reaction velocity constant equal to the value calculated

from the equation $k = Ze^{-E/RT}$ (see Chapter VII.), where Z is the number of collisions in which each para-hydrogen molecule is involved and E is the energy of activation ; in the high temperature " spontaneous " conversion experiments the calculated velocity was 0·06 times, and in the other experiments in which hydrogen atoms were deliberately added the velocity was 0·13 times, the observed values.

The equilibrium constant of the reaction $H + \text{para-}H_2 \rightleftharpoons \text{ortho-}H_2 + H$ is written as [ortho-H_2]/[para-H_2], and this is equal, almost exactly, to 3·00 at temperatures above 300° K., that is, the normal ortho–para ratio. It follows, therefore, that the reaction between hydrogen atoms and ortho-hydrogen molecules is three times as fast as that between the atoms and para-molecules, at all temperatures above 300° K. This result is of special theoretical interest as showing the different reactivities to be expected from the two types of hydrogen molecules.

Conversion by Electrical Discharge. The passage of an electrical discharge through para-hydrogen gas results in partial conversion into ortho-hydrogen at appreciable temperatures : this is probably due to the dissociation of the molecules of the former into atoms, which bring about conversion either by the reaction already considered, or by recombining in pairs to yield both ortho- and para-molecules in equilibrium amounts. According to this suggested mechanism, it is to be expected that an electrical discharge should be capable of facilitating the attainment of equilibrium, by the conversion of ortho- to para-states, if passed through normal-hydrogen at liquid-air temperatures : actually no such facilitation is observed. The explanation of this anomaly is based on the fact that at low temperatures the conversion rate resulting from the interaction of atoms with ortho-hydrogen molecules is negligibly small, so that the ortho–para change could only result from the recombination of hydrogen atoms. This process, however, is accompanied by the evolution of a large amount of energy, namely, over 100,000 cals. per gm.-mol. of hydrogen, so that the molecules formed are virtually at a high temperature, since they carry a portion of this energy in the kinetic form. The ortho- and para-molecules cannot thus be

obtained in the low temperature equilibrium-ratio amounts in spite of the fact that the bulk of the gas is being cooled in liquid air.

It may be noted that the atom recombination process is probably of little importance in the " spontaneous " para–ortho conversion at temperatures about 700° C., to which reference was made earlier (p. 118). Under the conditions of these experiments the concentration of hydrogen atoms is very small, and the rate of combination would be negligibly low, especially as reaction only takes place as the result of a ternary collision between two atoms and a molecule capable of removing part of the energy liberated in the process (see " Recent Advances in Physical Chemistry," Chapter V.).

Photo-sensitised Conversion. If hydrogen containing a trace of mercury vapour is exposed to the 2536 Å. wavelength radiation from a mercury-vapour lamp, the hydrogen molecules undergo dissociation into atoms, and the latter are capable of bringing about the conversion of the para- into the ortho-form. Some conversion also results from the recombination of hydrogen atoms : for the para- to ortho- transformation at appreciable temperatures the excess energy carried by the resulting molecules is, of course, an advantage.

Detection of Hydrogen Atoms. The para–ortho-hydrogen conversion process can be used to determine the concentration of hydrogen atoms present in various chemical reactions ; the photochemical hydrogen–chlorine union has been studied in this manner by Geib and Harteck (1931). Chlorine gas was admitted through a capillary tube into the middle of a large bulb containing para-hydrogen at approximately atmospheric pressure ; by using an intense source of illumination the chlorine was completely used up immediately on entering, and so was prevented from reacting with hydrogen atoms in the remainder of the bulb. The rate of conversion of para- to ortho-molecules was determined in the usual manner by analysis of the gas, and since the kinetics of the atomic hydrogen–para-hydrogen reaction is known, the stationary concentration of hydrogen atoms produced in the hydrogen–chlorine union could be determined. This was found to be 1 to 5 $\times$ 10^{-5} mm. of mercury, partial pressure, depending on the

experimental conditions. The result, although it proves that hydrogen atoms are formed in the system, can only be regarded as very approximately quantitative, since some ortho-hydrogen will be obtained from the reaction

$$H + HCl = H_2 + Cl,$$

which may occur to an appreciable extent. The presence of hydrogen atoms in detectable amounts seems, however, to be established, and this lends support to the Nernst chain mechanism (see "Recent Advances in Physical Chemistry," Chapter VI.) for the photochemical hydrogen–chlorine reaction; thus

$$Cl_2 + \text{radiation} \rightarrow 2Cl$$

followed by $Cl + H_2 \rightarrow HCl + H$

and $H + Cl_2 \rightarrow HCl + Cl.$

By a similar method to that described, the production of hydrogen atoms has been proved in the photochemical decomposition of hydrogen bromide, water vapour and ammonia. In the latter reaction the primary process has been shown to be:

$$NH_3 + \text{radiation} \rightarrow NH_2 + H,$$

but the hydrogen atoms are rapidly removed in subsequent stages, so that their stationary concentration is always low. The energy of activation of the ortho–para conversion produced by these atoms, calculated from the temperature coefficient, is about 7000 cals. (L. Farkas and Harteck, 1934); this is the same as the value obtained by direct experiments with hydrogen atoms (p. 119), and indicates that in the photochemical decomposition of ammonia the stationary concentration of hydrogen atoms is independent of the temperature. The process by means of which these atoms are removed from the ammonia system thus involves no energy of activation.

Homogeneous Catalysis of Conversion Process. The conversion of para-hydrogen into the normal form is markedly accelerated by the presence of oxygen or of other paramagnetic molecules and ions (L. Farkas and Sachsse, 1933); the process is undoubtedly homogeneous, and is evidently brought about by actual reversal of the nuclear spin by the exceptionally powerful in-homogeneous

magnetic field in the close vicinity of the paramagnetic molecules (Wigner, 1933). The rate of para- to ortho-hydrogen conversion in the presence of oxygen is proportional to the concentration of the latter, and the reaction appears to be unimolecular with respect to hydrogen, allowing for the fact that a definite equilibrium between ortho- and para-states is being approached. It appears that the conversion from para- to ortho-hydrogen, and *vice versâ*, occurs at suitable collisions between one oxygen and one hydrogen molecule. Both nitric oxide and nitrogen dioxide, but not the associated tetroxide form, which are paramagnetic behave in a manner similar to that of oxygen in bringing about the para–ortho conversion. Nitrogen, nitrous oxide, carbon monoxide, ammonia, sulphur dioxide and other diamagnetic gases, however, have no influence on the conversion process.

Since ortho-hydrogen is itself to some extent magnetic (p. 106), although only very slightly in comparison with oxygen, it should be capable of bringing about a slow conversion of para-molecules, The process can, however, only take place at a very small rate. although it may play some part in the spontaneous homogeneous conversion of para-hydrogen to the normal form.

Paramagnetic molecules or ions in solution are also able to catalyse the attainment of equilibrium in hydrogen ; the velocity constant of the para–ortho conversion brought about by oxygen dissolved in water is almost identical with that in the gas phase. In these experiments allowance had to be made for the fact that water is itself able to catalyse the conversion, as also are other solvents, *e.g.*, benzene, aniline, methyl alcohol and hexane, all of which contain hydrogen : the reaction, in these cases, is supposed to be due to the magnetic moments of the hydrogen nuclei present in the solvent molecules. The bivalent cations of copper, nickel, cobalt, iron and manganese are all paramagnetic and capable of accelerating the change from para- to ortho-hydrogen in solution ; the tervalent ions of the rare-earth elements are similarly effective. Zinc ions have no magnetic moment and solutions of zinc salts have no influence on the conversion process.

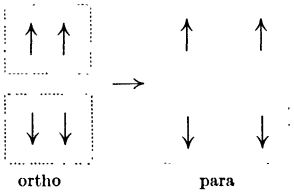
Applications. The structure of the boron hydride B_2H_6 has long presented a problem in valency (" Recent Advances in

Physical Chemistry," Chapter I.), and a formula involving two single-electron linkages has been proposed : if this is correct then the molecule should be paramagnetic. The direct measurement of the magnetic properties of the hydride, in view of its instability, would be a matter of some difficulty, but the study of its influence on the para- to ortho-hydrogen conversion should give definite information on the subject. Farkas and Sachsse (1934) found the rate of the reaction to be so slow in the presence of the boron hydride as to indicate that the molecules, in the ground state, were definitely not paramagnetic.

Free radicals, such as methyl, possessing odd electrons should be paramagnetic and should, consequently, affect the para–ortho conversion, and this expectation has been confirmed (West, 1935). The photochemical decomposition of acetone is known to produce free radicals, and the products of illumination of acetone are actually capable of accelerating the attainment of equilibrium in a mixture of ortho- and para-hydrogen. Methyl iodide gives similar results, presumably because of photochemical decomposition into a methyl radical and an iodine atom, but illuminated propaldehyde is ineffective ; this is in agreement with the view arrived at from photochemical experiments that free radicals are not formed to any great extent in the decomposition of this compound. The influence of acetone, formaldehyde, acetaldehyde, propaldehyde and ethane, at 750° to 850° C., on the ortho–para conversion has been studied by Sachsse and Patat (1935) : only with acetone was any considerable acceleration observed, indicating that of the substances studied this was the only one giving an appreciable concentration of free radicals on thermal decomposition. Further reference to this subject is made in Chapter IX.

Homogeneous Conversion in Liquid and Solid Phases. Spontaneous homogeneous ortho–para conversion occurs in liquid hydrogen : this results in the well-known change in the vapour pressure of the liquid, and in the specific heat of the gas obtained from it, on keeping. The rate of removal of ortho-hydrogen is proportional to the square of its concentration (Cremer and Polanyi, 1933). In solid hydrogen the ortho to

para change also occurs spontaneously, but the rate which is initially higher than in the liquid, falls off when a concentration of about 70 per cent. of the para-form is attained in the crystal. On melting and freezing again the original rate of conversion is re-established. The conversion in both solid and liquid phases appears to be brought about by the reversal of the nuclear spin of an atom in one ortho-molecule under the influence of the magnetic forces of another : these forces become effective because of close packing of the molecules in the crystal and of their proximity in the liquid. This mechanism would be in harmony with the observed kinetics, according to which the rate of conversion varies with the square of the concentration of the ortho-molecules. A chemical reaction according to the scheme,



which would also be kinetically bimolecular is improbable because of the high energy of activation, probably about 100,000 cals. that would be necessary ; this would make the process strongly temperature dependent, whereas actually it is not.

The falling off in the conversion rate in the solid phase as the para-molecules accumulate has been attributed to the small mobility of the hydrogen molecules in the crystal, so that the statistical distribution of ortho- and para-forms is not maintained as the conversion proceeds. The chance of two ortho-molecules being in juxtaposition, a necessity for the conversion process to occur, diminishes with time, and so the rate falls off. If the crystal is melted and resolidified the probability of two ortho-molecules being together is increased, and so, consequently, is the rate of conversion into the para-form. It must be admitted, however, that this cannot be a complete explanation of the experimental facts (Cremer, 1935).

Heterogeneous Ortho–Para Conversion. The observation that

charcoal is able to bring about rapid ortho–para conversion at liquid-air temperatures—the process used by Bonhoeffer and Harteck to obtain para-hydrogen in quantity—but is a poor catalyst for the re-establishment of equilibrium at ordinary temperatures, whereas for platinum black the reverse is the case, has led to the discovery that many catalysts exhibit a negative temperature coefficient of velocity at lower temperatures and a

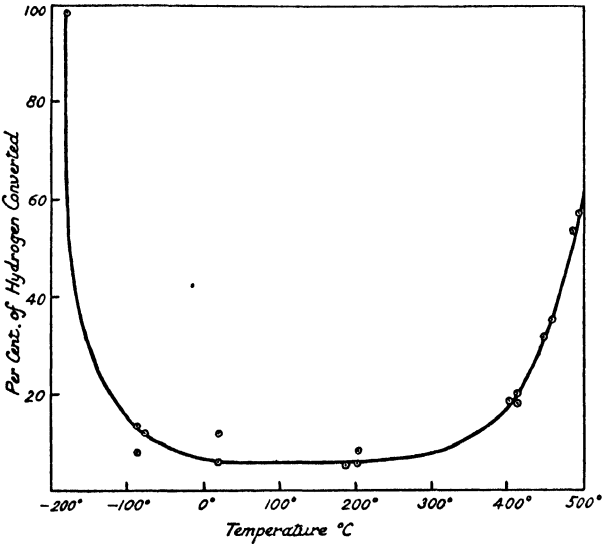


FIG. 7.—Rate of the ortho–para conversion on charcoal at various temperatures. (After Bonhoeffer, Farkas and Rummel.)

positive value at higher temperatures (Bonhoeffer, Farkas and Rummel, 1933). The rate of the ortho–para conversion obtained at various temperatures with 7 gm. of charcoal over which hydrogen was passed at the rate of 10 c.c. per minute is shown in Fig. 7. In some cases the negative temperature coefficient range is not easily observed if the rate of reaction is in any case very small at low temperatures. The general behaviour of catalysts leads to the conclusion that conversion takes place by two independent mechanisms which are effective over different temperature ranges ;

these are referred to generally as the " low temperature " and " high temperature " mechanisms, respectively.

It will be observed that there is a striking parallelism between the influence of temperature on the heterogeneous catalysed ortho–para conversion and on the sorption of hydrogen. At low temperatures the gas is adsorbed, *e.g.*, on nickel, to an appreciable extent, as a result of the operation of van der Waals' forces, but the amount adsorbed falls off with increasing temperature because of the exothermic nature of the process. According to Taylor's theory (" Recent Advances in Physical Chemistry," Chapter VII.) an " activated adsorption," probably involving dissociation into atoms, which requires an appreciable energy of activation, becomes manifest at higher temperatures ; the rate of adsorption, as with an ordinary chemical reaction, increases as the temperature is raised. It will be seen that the two types of ortho–para conversion are closely related to the two types of adsorption.

Low-temperature Heterogeneous Conversion. The experimental results (Rummel, 1933) suggest that in the ortho–para catalysis by charcoal at low temperatures the gas molecules are held on the surface by physical forces, since hydrogen can remain adsorbed on certain charcoals for some time and yet show only relatively little adjustment towards equilibrium when desorbed. Although the adsorptive power of a catalyst and its activity have not yet been correlated, probably because of the influence of factors not completely understood, the falling off in the catalytic effectiveness of charcoal as the temperature is raised appears to be caused by a decrease in the amount of gas adsorbed. The rate of the conversion process is directly proportional to the concentration of hydrogen molecules on the surface, and the action of the catalyst is probably to produce magnetic perturbations which are able to bring about reversal of the nuclear spin, in a manner similar to that whereby paramagnetic substances influence the ortho–para change. This view is in harmony with the observation that catalysis by adsorbing materials which are themselves paramagnetic, as, for example, sesquioxides of chromium and of rare earth metals, and vanadium trioxide, is very rapid (Taylor and Diamond, 1933, 1935).

When a charcoal catalyst is allowed to adsorb oxygen at liquid-air temperatures, the rate of attainment of the ortho–para equilibrium is markedly increased: this is probably to be attributed to the paramagnetism of the adsorbed oxygen molecules. If the gas is taken up at higher temperatures, however, viz., above — 80° C., the catalytic activity of the charcoal is decreased: this "poisoning" effect appears to be caused by direct chemical combination between the oxygen and the charcoal, so that the "free valencies" of the latter become satisfied and, consequently, the intensity of the magnetic field in the vicinity of the atoms is diminished. The influence of the paramagnetic oxygen molecules themselves is also lost as a result of the combination. At low temperatures, on the other hand, the paramagnetism of the oxygen molecules is effective, even if the residual fields of the carbon atoms are to a great extent saturated.

Under certain conditions adsorption of hydrogen itself results in a diminution of the activity of a catalyst for the low-temperature ortho–para conversion; with charcoal the adsorption must take place over 20° C., but with a nickel catalyst adsorption of hydrogen at — 78° C. brings about a marked diminution of activity, although the effect is greater if the hydrogen is taken up at higher temperatures (Emmett and Harkness, 1935). Other substances show a similar effect, and the phenomenon is attributed to the saturation of the free valencies of the catalyst by hydrogen in the "activated," probably atomic, form (*vide infra*). Iron catalysts, promoted by oxides of aluminium and potassium, such as are used in the production of ammonia by the Haber synthesis, are also effective for the ortho–para conversion at low temperatures; the adsorption of hydrogen by these catalysts above 100° C. diminishes their effectiveness to a considerable extent. The exposure to oxygen at temperatures up to 450° C., on the other hand, has no such effect on the low-temperature catalysis: this is not surprising when it is realised that the product is the magnetic oxide, Fe_3O_4, which would be expected, according to the view already expressed, to have a high catalytic activity (Harkness and Emmett, 1933).

High-temperature Heterogeneous Conversion. The high

temperature para–ortho conversion reaction has been studied on metals in various forms, on salts, and on oxides ; the observations are rendered difficult by the poisoning effects of oxygen, of hydrogen sulphide, of other typical catalytic poisons, and of tap-grease. There appears to be a parallelism between the effectiveness of catalysts for the high-temperature establishment of the ortho–para equilibrium and for hydrogenation processes ; platinum, nickel and iron are far more effective in both cases than are silver, copper or gold. In both types of reaction also, oxygen in small amounts appears to enhance the efficiency of platinum as a catalyst. Metallic oxides, *e.g.*, gadolinium, neodymium and vanadium sesquioxides, which show activated adsorption of hydrogen, are effective in bringing about the conversion of para- to ortho-hydrogen at temperatures above 100° C. (Taylor and Sherman, 1931, 1932). In all cases, the kinetic order of the conversion process is apparently between zero and unity, indicating that the reaction proceeds in the adsorption layer (" Recent Advances in Physical Chemistry," Chapter VII.).

The simplest explanation of the high-temperature catalysis is that at these temperatures the hydrogen molecules acquire activation energy from the surface of the catalyst, so that the bond between the atoms in the molecule is loosened, and consequently hydrogen exists on the surface to a great extent in the atomic form. In the adsorbed phase there is a continual interchange between molecules and atoms, and it is clear that this will result in a tendency for the establishment of the ortho–para equilibrium at the temperature of the catalyst surface. The para–ortho conversion results, in this way, through the intermediate formation of atoms, and so the change is chemical and does not involve the reversal of nuclear spins, as in the low-temperature process. The molecules of hydrogen in the gas phase are continually interchanging with those in the adsorption layer ; thus,

$$\underset{\text{gas}}{H_2} \rightleftarrows \underset{\text{adsorbed}}{H_2 \rightleftharpoons 2H}$$

and consequently the action of the catalyst will be to establish the ortho–para equilibrium in the bulk of the gas. The observed order of the reaction is in harmony with this explanation : the process, at low pressures, will appear to be of the first order, but as the extent of adsorption increases, and the surface becomes almost entirely covered with hydrogen, the reaction rate will be independent of the gas pressure, and so will tend to become apparently of zero order. It may be noted that this interpretation of the kinetic observations implies that the ortho–para equilibrium is established mainly by the process of recombination of hydrogen atoms (p. 120). The parallelism between the proposed mechanism for the high-temperature ortho–para process and that suggested by Taylor for the so-called " activated adsorption " is very striking ; the increased rate of adsorption as the temperature is raised results in an increase in the number of activated adsorbed molecules, and so accounts for the positive temperature coefficient of the conversion reaction.

A high-temperature establishment of the ortho–para equilibrium occurs on alumina at 300° C., although the catalyst does not show activated adsorption of hydrogen at this temperature (Taylor and Diamond, 1935). It is suggested that the mechanism involved is an exchange reaction between the molecules of hydrogen gas and the hydrogen in water, which is known to be strongly adsorbed by a surface of alumina.

An interesting application of the heterogeneous para–ortho conversion has been made in connection with the catalytic union of nitrogen and hydrogen to form ammonia. The conversion process takes place rapidly on a finely divided iron catalyst at about 40° C., the reaction being evidently of the high-temperature type, since activated adsorption of hydrogen commences at a lower temperature. The same catalyst, however, was not able to bring about appreciable combination of nitrogen and hydrogen until the temperature was between 300° and 400° C. It appears, therefore, that in the synthesis of ammonia the catalyst must bring the nitrogen into a reactive state before combination with hydrogen, even in the atomic form, can occur (Emmett and Harkness, 1932).

OTHER ORTHO–PARA SYSTEMS

All molecules consisting of two *identical* atoms should exist in ortho- and para-states, provided the nuclei possess spin momentum. Since the nuclei of ^{12}C and ^{16}O have no spin, the molecules $^{12}C_2$ and $^{16}O_2$ exist in one form only; so also does the molecule $^{35}C^{37}Cl$, for in this case the nuclei, although possessing spin, are not identical. There is definite evidence that the molecules $^{35}Cl_2$, $^{14}N_2$ and $^{79}Br_2$, amongst others, exist in ortho- and para-forms because alternations have been observed in the intensities of their spectral lines. It will be seen later that the relative intensities of alternate lines at appreciable temperatures should be given by the ratio $i + 1$ to i, where i is the number of units of spin momentum possessed by the nucleus. For the $^{35}Cl_2$ molecule this ratio has been found experimentally to be about 1·36 to 1, so that the spin of the ^{35}Cl nucleus is $\frac{5}{2}$ units. If i is zero then alternate rotational lines of the molecular spectrum should be missing; this is in fact the case for the $^{16}O_2$ molecules, which does not occur in ortho- and para-forms. Certain symmetrical polyatomic molecules, such as C_2H_2 and H_2O, behave in a similar manner to hydrogen molecules, since the nuclei of the other atoms present, namely, carbon or oxygen, have no spin. The band spectra of both acetylene and water vapour show an alternation in intensity of the rotational lines, and so these substances exist in ortho- and para-states.

If the spin of each nucleus in a homonuclear molecule is i, then there are theoretically $2i + 1$ values for the resultant spin of the molecule as a whole: these may be represented by the series $2i$, $2i-1$, $2i-2$, . . . 2, 1, 0, of which the first, third, fifth, and so on, values correspond to symmetrical spin functions, and the second, fourth, sixth, etc., values to antisymmetrical functions. In general, the resultant molecular spin (t) may be written as $2i-n$, where n is an integer which cannot exceed $2i$, so that $2i-n$ remains positive; for ortho-states (symmetrical) the value of n is even, including zero, and for para-states (antisymmetrical) it is odd. Each resultant molecular spin is $2t + 1$-fold degenerate, that is to say, the various molecular states have a multiplicity of $2t + 1$, and since t is equal to $2i-n$ the multiplicities of the

various states for different values of n are given by $2(2i - n) + 1$. When n is zero or even the states are ortho, and when n is odd they are para ; hence it follows that

$$\frac{\text{Statistical weight of ortho-states}}{\text{Statistical weight of para-states}} = \frac{\sum_{n=0,2,4,6\ldots} 2(2i-n)+1}{\sum_{n=1,3,5,7\ldots} 2(2i-n)+1} = \frac{(i+1)(2i+1)}{i(2i+1)}$$

This ratio of the statistical weights, which is equal to $(i + 1)/i$, gives the limiting ratio of the amounts of ortho- to para-forms at appreciable temperatures, and incidentally also represents the ratio of the intensities of alternate lines in the spectrum under normal conditions. As already shown (p. 108), this limiting ratio is only attained at about 273° K. for hydrogen, but for other molecules, except deuterium (see Chapter IV.), which have much larger moments of inertia, the limit is reached at such low temperatures that the substances are solid. Most molecules do not rotate in the solid state, and so there is little hope of obtaining evidence for a change in the ortho–para ratio by experiments with the solids.

It has been stated earlier in the present chapter that the ortho- and para-states are associated with alternate rotational levels, but no indication was given as to the factors determining the relationship between the rotational quantum number and the two states. In the first place it has to be known whether the molecule obeys the Bose-Einstein (total eigenfunction is symmetrical) or the Fermi-Dirac (total eigenfunction is antisymmetrical) statistics. It now appears certain that the former apply to molecules consisting of two identical atoms with even atomic weights (mass numbers), whereas the latter are applicable when the atomic weights are odd. The next factor to consider is whether the electronic level, generally the ground state of the molecule for ordinary purposes, is " even " or " odd," represented by the symbols g and u, respectively ; that is, if the sum of the individual values of l, the orbital quantum number, for all the electrons is even or odd. Finally, for a Σ-state it must be known

whether the rotational levels are to be classified as " positive " or " negative " ; this is determined by wave-mechanical considerations and depends on whether the rotational eigenfunction remains the same or changes its sign when the positional coordinates of nuclei and electrons have their signs changed, that is, when the line joining the nuclei is turned in the opposite direction. The distribution of ortho- and para-states amongst the rotational levels is then given in Table XIV.

TABLE XIV

Distribution of Ortho- and Para-States.

Statistics.	Electronic Level.	Rotational Classification.	Rotational Quantum No.	State.
Fermi-Dirac	Even (g)	Positive	Even	Para
			Odd	Ortho
		Negative	Even	Ortho
			Odd	Para
	Odd (u)	Positive	Even	Ortho
			Odd	Para
		Negative	Even	Para
			Odd	Ortho
Bose-Einstein	Even (g)	Positive	Even	Ortho
			Odd	Para
		Negative	Even	Para
			Odd	Ortho
	Odd (u)	Positive	Even	Para
			Odd	Ortho
		Negative	Even	Ortho
			Odd	Para

The ground state of the hydrogen molecule is Σ_g^+, that is to say, the electronic level is even, and the rotational classification is positive ; since the atomic weight is odd the Fermi-Dirac statistics are obeyed, and so it is seen from Table XIV. that the even rotational levels ($J = 0, 2, 4, 6 \ldots$) will be para-states and the odd levels ($J = 1, 3, 5, 7 \ldots$) ortho-states. For the deuterium

molecule, on the other hand, the atomic weight is even and the Bose-Einstein statistics are followed; the ground state is also Σ_g^+, and so in this substance the even rotational levels represent ortho-states. At low temperatures all molecules tend to congregate in the lowest ($J = 0$) rotational level; hence, at low temperatures equilibrium-hydrogen consists almost exclusively of the para-form, whereas deuterium is almost entirely in the ortho-state. At high temperatures, however, the ortho-molecules predominate in both cases, since the ratio of the statistical weights of ortho to para is always $i + 1$ to i, and this gives the limiting ratio of the two forms, as already stated. For hydrogen and deuterium i is $\frac{1}{2}$ and 1, respectively, and the limiting high temperature ortho/para ratio is 3/1 and 2/1, respectively.

It may be noted, as a matter of general interest, that the distribution shown in Table XIV. applies, in an appropriate sense, to symmetrical molecules consisting of nuclei without spin. The oxygen molecule $^{16}O^{16}O$, for example, has a Σ_g^- ground state, and obeys the Bose-Einstein statistics; the para-state should, theoretically, be associated with even rotational quantum numbers, but the statistical weight of this state, viz., $i(2i + 1)$, is zero, since $i = 0$, and so the rotational lines of the spectrum for which J is even in the ground state are missing.

REFERENCES

BEUTLER. *Z. Physik*, 1928, **50**, 581.

BONHOEFFER *et al.* *Z. physikal. Chem.*, 1929, [*B*], **4**, 113; **5**, 292; 1931, [*B*], **12**, 231; 1933, [*B*], **21**, 225; *Z. Elektrochem.*, 1929, **35**, 621; *Trans. Faraday Soc.*, 1932, **28**, 242, 561.

CLUSIUS and HILLER. *Z. physikal. Chem.*, 1929, [*B*], **4**, 158.

CREMER. *Ibid.*, 1935, [*B*], **28**, 199.

DENNISON. *Proc. Roy. Soc.*, 1927, [*A*], **115**, 483.

VON ELBE and SIMON. *Z. physikal. Chem.*, 1930, [*B*], **6**, 79.

EUCKEN and HILLER. *Ibid.*, 1929, [*B*], **4**, 142.

FARKAS. "Orthohydrogen, Parahydrogen and Heavy Hydrogen," 1935*; *Z. physikal. Chem.*, 1930, [*B*], **10**, 419; 1931, [*B*], **14**, 371; 1933, [*B*], **22**, 344.

FARKAS and SACHSSE. *Trans. Faraday Soc.*, 1934, **30**, 331; *Z. physikal. Chem.*, 1933, [*B*], **23**, 1, 19; 1934, [*B*], **27**, 111.

GEIB and HARTECK. *Ibid.*, Bodenstein Festband, 1931, 849; 1931, [*B*], **15**, 116.

GIAUQUE. *J. Amer. Chem. Soc.*, 1930, **52**, 4816.

GIAUQUE and JOHNSTON. *Ibid.*, 1928, **50**, 3221.

HARKNESS and EMMETT. *Ibid.*, 1932, **54**, 403 ; 1933, **55**, 3496 ; 1935, **57**, 1624.
HEISENBERG. *Z. Physik*, 1927, **41**, 239.
HORI. *Ibid.*, 1927, **44**, 834.
HUND. *Ibid.*, 1927, **42**, 93.
KEESOM *et al.* *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 1223.
MCLENNAN and MCLEOD. *Nature*, 1929, **123**, 160.
MECKE. *Z. Physik*, 1924, **28**, 261 ; 1925, **31**, 709.
RASETTI. *Physical Rev.*, 1929, **34**, 366.
RUMMEL. *Z. Physikal. Chem.*, 1933, **167**, 221.
SACHSSE and PATAT. *Z. Elektrochem.*, 1935, **41**, 493.
TAYLOR and DIAMOND. *J. Amer. Chem. Soc.*, 1933, **55**, 2613 ; 1935, **57**, 1251.
TAYLOR and SHERMAN. *Ibid.*, 1931, **53**, 1614 ; *Trans. Faraday Soc.*, 1932, **28**, 247.
WEST. *J. Amer. Chem. Soc.*, 1935, **57**, 1931.
WIGNER. *Z. physikal. Chem.*, 1929, [*B*], **4**, 126 ; 1933, [*B*], **23**, 28.

* Review papers and books, wherein further references can be found, are marked with an asterisk.

CHAPTER IV

DEUTERIUM AND ITS COMPOUNDS

Historical Introduction. When Aston in 1927 determined the atomic weight of hydrogen by means of the mass-spectrograph, he obtained a value of 1·00778, which was apparently in excellent agreement with the accepted chemical atomic weight 1·00777, based on the assumption that oxygen was 16·0000. The discovery by Giauque and Johnston (1929) that oxygen had isotpes of masses 17 and 18, showed that the average atomic weight of chemical oxygen must be greater than 16, and from the relative proportions of the three isotopes the value was calculated to be 16·0035,* so that the true atomic weight of hydrogen, determined chemically, was 1·00799. A careful examination of these results led Birge and Menzel (1931) to suggest as a possible explanation that there was present in ordinary hydrogen a heavier isotope of mass 2 ; about one part of the latter in 4500 of hydrogen would be sufficient to account for the discrepancy actually existing between the mass-spectroscopic and chemical atomic weights. The former, of course, gives the atomic weight of the isotope of mass number unity, whereas the latter gives the mean atomic weight of the two isotopes.†

It may be noted that as long ago as 1920, Harkins had suggested the possibility of the existence of a hydrogen isotope of mass 2 from an examination of the regularities to be observed in the masses of known nuclei, and more recently it had been shown that by plotting atomic masses, for known isotopes, against the difference between these numbers and the atomic numbers, the

* More recent determinations of the isotopic ratios give an average atomic weight of 16·0042,

† In Chapter I., p. 29, it is seen that the atomic weights quoted here are probably inaccurate ; nevertheless, the conclusions drawn from them have proved to be fundamentally correct.

plot is quite regular but for certain gaps which might be filled by three then unknown isotopes, namely, ^2H, ^3H and ^5He (see Fig. 8). Stern and Volmer had sought for the presence of a heavier isotope in ordinary hydrogen in 1919 in order to determine whether the departure of the atomic weight from exactly unity might be accounted for in this manner; they attempted a partial separation by a diffusion process, but were unable to detect any change of density, although it is now evident that if the experiment had been carried out in a suitable manner some variation would have been observed.

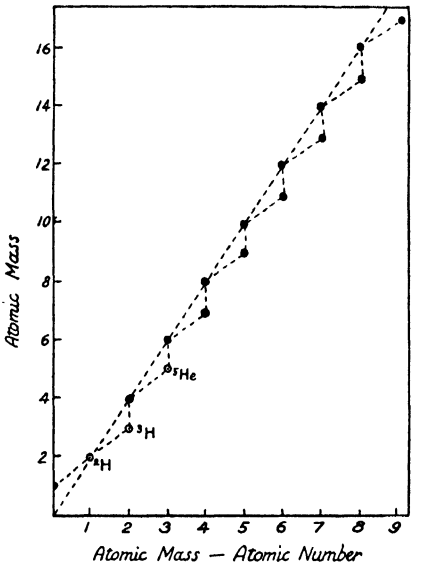


FIG. 8.—Plot of atomic mass against difference between mass and atomic number. Isotopes known in 1931 shown as black dots, and those required to complete the regularity as circles.

Discovery of the Heavy Isotope of Hydrogen. Encouraged by the calculations based on the difference in the atomic weights mentioned above, Urey, Brickwedde and Murphy, in the United States of America, realising that an isotope present to the extent of only one part in about five thousand could not be easily detected by ordinary methods, set out in 1931 to concentrate the heavier isotope by the evaporation of 4 litres of liquid hydrogen to about 1 c.c., since calculations had shown that fractional distillation in the vicinity of the triple-point should permit the concentration of the heavier isotope in the residual liquid. The attempt was successful, for the Balmer (atomic) spectrum of the gas from this residue showed very clearly a line in the position required for an atom having a mass of two and an atomic number of unity; by careful examination the same line, although very much fainter,

was detected in the spectrum of ordinary hydrogen. The concentration of the heavier isotope of hydrogen by fractional distillation was verified by a number of workers in Europe, and further confirmation was obtained shortly afterwards (Bleakney, 1932) by means of the mass-spectrograph, when the lines for an atom of mass 2 were detected in electrolytic hydrogen and in the samples enriched by evaporation of the liquid. Further, the band due to ^2HCl was found in the expected position in the rotation-vibration spectrum of hydrogen chloride, having its origin at 4·8 μ (Hardy, Barker and Dennison, 1932), thus showing that compounds of the heavier isotope were present in hydrogen compounds.

Concentration of the Heavier Isotope. A most important development, with remarkable consequences, was made when Washburn and Urey, in the spring of 1932, reported that the water obtained from industrial electrolytic cells, which had been used for the production of oxygen and hydrogen, had a markedly higher density than ordinary water. This difference was attributed to the presence in the former case of an excess, above the normal proportion, of molecules containing the heavier hydrogen isotope, namely, ^2H_2O, or "heavy water." It was suggested, consequently, that on electrolysis of an aqueous solution, light hydrogen is evolved more readily than the heavier isotope, so that the latter accumulates in the residual water, and that by continued electrolysis it might be possible to prepare almost pure heavy water. This was actually achieved by G. N. Lewis and Macdonald (1933) who, starting with 20 litres of water from an old commercial electrolytic cell, obtained by continued electrolysis about 0·5 c.c. of water having a density of 1·073. Since the molecular weight of ^2H_2O is 20, compared with 18 for H_2O, the former should have a density about 10 per cent. greater than ordinary water, namely, 1·10 at room temperature; consequently the heavy water obtained by electrolysis contained about 70 per cent. of the hydrogen in the form of the heavier isotope. Following on this observation numerous workers in various parts of the world undertook the prolonged electrolysis of water and small quantities containing relatively large proportions of ^2H_2O became available, although at a high cost: these were sufficient, however, to show

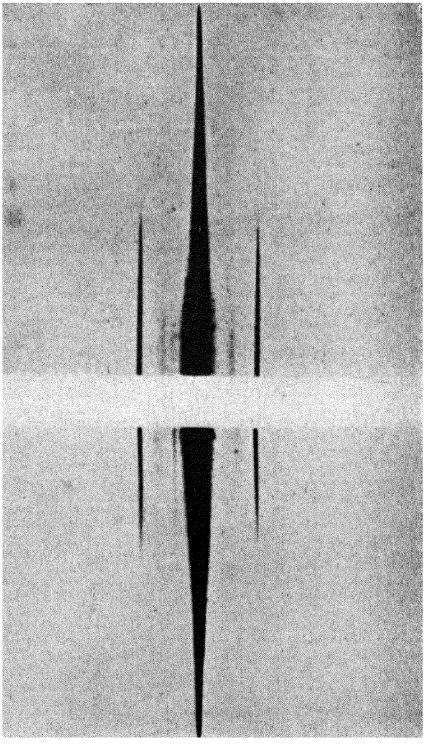


FIG. 9.—Balmer spectrum of ordinary hydrogen (upper) and of the residue from the evaporation of liquid hydrogen (lower). The line due to ^2H is seen to the left of the central line. (After Urey, Brickwedde and Murphy.)

[*To face p.* 138.

that the heavier isotope of hydrogen exhibited some remarkable differences in properties from those of the lighter isotope.

Deuterium. The possibility of obtaining such a unique isotope, in so far as it is twice as heavy as the other isotopic form, in appreciable amounts and in relatively pure form, attracted a great deal of attention, and the subject of " heavy hydrogen " has become one of the most important of recent years : in fact it has been suggested that its discovery and isolation marks " possibly the greatest advance in chemistry in the present century." Water, containing at least 99 per cent. of its hydrogen in the form of the isotope of mass 2, is now obtainable commercially at a relatively low price, and is being used not only for the study of the properties of inorganic and organic compounds containing the heavier form of hydrogen, but also for throwing light, as will be seen subsequently, on various chemical problems. Because of the difference between the two isotopes, and the possibility of studying each separately, it has become necessary to use separate names and symbols for them : the names " haplogen " (single) and " diplogen " (double), for the isotopes of mass 1 and 2, respectively, were proposed, but they have not met with general acceptance. It has become the practice to retain the term hydrogen and the symbol H for the lighter isotope, and to use " deuterium " (the second), with the symbol D, for the isotope of mass 2. The adjectives " light " and " heavy " are still sometimes employed to describe the two isotopes. The normal mixture of isotopes, which contains the light form almost exclusively, is still called " hydrogen," and there is generally no confusion by the use of the same name for two somewhat different substances. The name " protium " (the first) has been proposed for ^1H, but this has not been widely adopted, probably because the corresponding symbol might lead to confusion. " Heavy water " is given the formula D_2O and is called deuterium oxide, and the analogue of benzene, viz., C_6D_6, is termed hexadeuterobenzene ; corresponding names have been devised for other deuterium compounds which are becoming known in increasing numbers.

It may be noted that a mixture of hydrogen and deuterium does not consist of H_2 and D_2 only, neither does water contain

only H_2O and D_2O molecules : one atom of each isotope can be present in the molecule instead of two of the same kind, viz., HD in hydrogen, and HDO in water. Actually there is always an equilibrium between the three types of molecules, thus

$$H_2 + D_2 \rightleftharpoons 2HD \quad \text{and} \quad H_2O + D_2O \rightleftharpoons 2HDO,$$

and it is clear from an application of the law of mass action that in a system rich in the lighter isotope the deuterium will be mainly in the form of HD, or HDO ; similarly, the light hydrogen will be mainly present as these same molecules if there is an excess of the heavier isotope.

ANALYSIS OF MIXTURES OF HYDROGEN AND DEUTERIUM

Spectroscopic Method. (*a*) The first method used for determining the ratio of the two isotopes was by examining the β- and γ-lines of the Balmer spectrum : the ratio of the exposure times required for the intensities of the lines due to H and D to be of the same intensity is approximately inversely proportional to the amounts of H and D present. There are a number of difficulties associated with this method, however, which render it of minor importance in comparison with other means for determining the ratio of hydrogen to deuterium.

Mass-spectroscopic Method. (*b*) The mass-spectrograph obviously presents a means for the isotopic analysis of hydrogen, and a method which permits of accurate quantitative estimation of the relative proportions of the two isotopes has been devised by Bleakney (1932) for mixtures containing relatively small amounts of deuterium. Positive ions having m/e values of 3, and consisting of H_3^+ and HD^+ particles are sorted out by electric and magnetic fields, and their total amount estimated by collecting the charges on a long electrode and measuring the positive-ion current ; the amount of the HD^+ ions is directly proportional to the pressure, whereas the number of H_3^+ ions depends on its square, and by determining the ion-current for the particles for which m/e is equal to 3, at different total pressures, the ratio of deuterium to hydrogen can be determined. Since the gas consists mainly of H_2, the

intensity of the H_2^+ ion-current is used as a measure of the pressure. By this method Bleakney and Gould (1933) determined the D to H ratio in normal hydrogen, for example, as in ordinary water, to be 1 to 5000, in surprisingly good, even if fortuitous, agreement with the value calculated by Birge and Menzel on the basis of the atomic weight discrepancy. It may be mentioned that the earliest estimates by Bleakney in 1932 indicated the presence of only one part of deuterium in 30,000 of normal hydrogen, but this result was due to the use of the electrolytic gas : it has been already seen that on electrolysis the lighter isotope is evolved more readily than the heavier one, and in fact the rates of evolution are roughly in the ratio of 6 to 1 (*vide infra*).

Thermal-Conductivity Method. (*c*) A very convenient method for the analysis of small quantities of hydrogen gas is based on the differences in the specific heats, and consequently in the thermal conductivities of the two isotopes (*cf.* p. 116) : it can only be used for mixtures containing more than 1 per cent. of deuterium, when it is capable of an accuracy of $\pm$ 0·1 per cent., with only about 0·002 c.c. of gas at N.T.P. The principle of the method is identical with that already described for the analysis of mixtures of ortho- and para-hydrogen (Chapter III.). The apparatus is calibrated either by means of mixtures containing known proportions of H_2 and D_2 only, or else by the use of equilibrium mixtures of H_2, D_2 and HD. If the gas used is not at equilibrium, it may be brought into this state by passage over a hot nickel wire. Should it be necessary to determine the D/H ratio in a specimen of water, the whole of the vapour of the latter is decomposed by passage over a heated tungsten filament : the oxygen is retained in the form of tungstic oxide, which can be readily volatilised from the wire and condensed on a cold surface, thus presenting a fresh surface of the metal. Other methods have also been employed.

Density Method. (*d*) The general practice at the present time, unless only small amounts are available, is to determine the deuterium content of water by measurement of its density : pure D_2O has a specific gravity at 25° C. of 1·1048 compared with ordinary water at 4°, or 1·1079 compared with water at 25°, and from the observations of Lewis and Luten (1933) the specific

gravity of any mixture of H_2O and D_2O is given by the following equation, which differs somewhat from a linear relationship :

$$d_{4^\circ}^{25^\circ} = 0{\cdot}9970 + 0{\cdot}1066N_2 + 0{\cdot}0012N_2^2$$

where N_2 is the molar fraction of D_2O in the mixture. By means of this equation it is possible to determine the relative amounts of the two isotopes in water containing appreciable proportions of both. When only small quantities of deuterium are present, however, the density must be measured with greater precision than the equation implies. The density can be obtained with the aid of a suitable pyknometer with an accuracy of one part per million ; and even greater precision results, with more convenience, by the use of a buoyancy method, as first employed for the purpose by Lewis and Macdonald (1933). In this method a glass or silver float is employed which will remain just suspended in the sample under consideration at a convenient temperature or under a convenient pressure : in the latter case the principle of operation is that of the " Cartesian diver," and in the former case it depends on the different coefficients of expansion of glass and water. Each float is best calibrated, either against temperature or pressure according to the type, by means of normal water and of solutions of known density. The buoyancy permits of an accuracy as great as one part in five millions in the determination of density, and suitable forms of float permit of measurement being made with as little as 0·1 c.c. of water. In calculating the proportion of D_2O present it may be assumed, as a first approximation, that the density of the deuterium oxide is 10 per cent. greater than that of ordinary water, and that the change in the density is a linear function of the composition : that is to say, an increase of 10^{-6} in the density implies an increase of ten parts per million in the D_2O content. It is perhaps unnecessary to mention that before the density is determined the specimen of water must be carefully freed from all impurities, including dissolved air ; this is generally achieved by distillation.

Miscellaneous Methods. (*e*) In conclusion, brief mention may be made of other methods which have been used to some extent. The refractive indices of H_2O and D_2O differ by about 0·0045 for

the sodium-*D* line at 25° C., and in view of the great accuracy with which this quantity can be measured, a method for determining all but the most minute proportions of D_2O becomes available. The difference in refractive indices of the specimen and of normal water is best determined by means of a Zeiss interferometer, which has to be calibrated with mixtures of known composition (Crist, Urey and Murphy, 1933). The determination can be carried out rapidly, and requires at most 1·5 c.c. of liquid of low deuterium oxide content: a precision as high as 0·02 per cent. is claimed for the method. Another procedure which may prove of value where the proportion of deuterium in the water is not extremely small is to take advantage of the difference of 3·82°. in the freezing points of light and heavy water. The actual freezing point of as little as 0·4 gm. is determined with an error of $\pm$ 0·005°, equivalent to about $\pm$ 0·13 per cent. of D_2O content, by making use of the fact that a mixture of ice and water changes considerably in volume if melted or frozen: at the actual freezing point the volume should remain constant. The liquid under examination is placed in a capillary tube in which the meniscus can be observed; the tube is attached to a Beckmann thermometer and placed in a bath the temperature of which can be changed gradually. All traces of air must be removed from the water and the tube, as otherwise appreciable errors will result (King, James, Lawson and Briscoe, 1935). A method for determining the deuterium oxide content of water, depending on the difference in the vapour pressures of the light and heavy forms, has also been described (Reitz and Bonhoeffer, 1935).

SEPARATION OF THE ISOTOPES

Fractionation of Liquid Hydrogen and Water. (*a*) As already mentioned, deuterium in ordinary hydrogen was first concentrated by utilising the difference in vapour pressure of the liquids: the process was not very efficient, however, as the 1 c.c. of residue obtained from the evaporation of 4 litres of liquid hydrogen contained only one part of deuterium in a thousand. With the aid of an efficient rectifying column, which had previously been

employed for the partial separation of the isotopes of neon, Keesom, van Dijk and Haantjes (1933) obtained from 40 litres of ordinary liquid hydrogen, 2 litres of gas containing about 1·5 per cent. of deuterium. This procedure is not likely to develop into a laboratory method for obtaining heavy hydrogen, but it may have industrial possibilities. The difference in the vapour pressures of H_2O, HDO and D_2O leads to some separation of the isotopes when water is distilled : the H/D ratio in the vapour to that in the liquid has been calculated to be 1·025 at the boiling point at atmospheric pressure. Although this is not large it should be sufficient to bring about satisfactory separation of hydrogen from deuterium if a number of efficient rectifying columns were used. It has been stated that the fractional distillation of water may prove an important competitor of the electrolytic method for obtaining heavy water on the large scale.

Electrolytic Method. (*b*) Next in historical sequence, and at present the most widely used for concentrating the deuterium oxide in water, is the electrolytic process ; it is employed industrially for the preparation of the heavy water of commerce. The conditions of electrolysis are by no means critical : almost any electrode material, except perhaps platinised platinum, may be used, and the electrolyte may be acid or alkali. The most common procedure is to employ 0·5*N*-sodium hydroxide as electrolyte with a cathode of nickel or steel, and anodes, generally of nickel, but sometimes, especially for the last stages, of platinum The cooled solution is electrolysed continuously in a number of cells with as large a current as convenient, until the volume is reduced to approximately one-tenth of the original. Almost pure H_2O, containing very little deuterium, can be obtained by burning the hydrogen evolved in this stage of the process. Since the electrolyte has now become concentrated in alkali, the process is stopped and nine-tenths of the liquid treated with carbon dioxide gas until completely converted into carbonate. The solution is now distilled to dryness and the resulting distillate added to the remaining one-tenth of electrolyte, thus regaining approximately the original alkali concentration. The process of electrolysis and removal of alkali is then continued in as many

stages as necessary to obtain water with the desired deuterium content. Although light hydrogen is evolved more readily than deuterium on electrolysis, the electrolytic gas begins to contain appreciable amounts of the latter isotope as the deuterium content of the water increases, and it is not desirable to lose this : the gases, oxygen and hydrogen, evolved in the later stages of the electrolysis, are burned in a suitable manner, with the aid of a heated platinum spiral, and the water condensed, collected and used again. In order to avoid the risk of explosion as a result of the

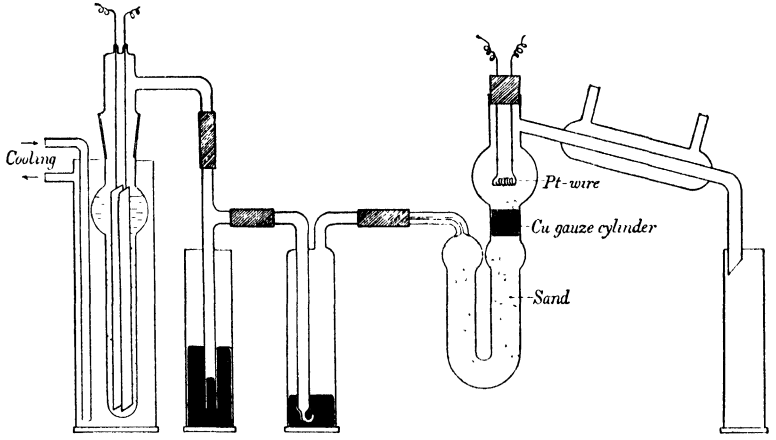


FIG. 10.—Diagrammatic representation of apparatus for concentrating the deuterium in water by electrolysis. (After Farkas.)

flame striking back, if the supply of gas should diminish, mercury bubblers, bulbs filled with fine sand, and capillary tubes are placed between the electrolytic cell and the point at which the gas is burned (Fig. 10). The results in Table XV. were obtained by Taylor, Eyring and Frost (1933); the initial electrolyte was procured from a commercial cell and contained about 0·03 per cent. of deuterium, and the whole of the remainder of each stage of electrolysis was passed on to the next stage.

In this process actually only 10 per cent. of the deuterium initially present was finally obtained. Various modifications of the process have been devised which permit of obtaining larger

TABLE XV

Concentration of Deuterium by Electrolysis.

Stage.	Volume of Electrolyte.	Specific Gravity ($d^{20°}_{4°}$).	Deuterium.
I.	2311 litres	0·998	0·03 per cent.
II.	341 ,,	0·999	0·5 ,,
III.	52 ,,	1·001	2·5 ,,
IV.	10 ,,	1·007	8·0 ,,
V.	2 ,,	1·031	30·0 ,,
VI.	420 c.c.	1·098	93·0 ,,
VII.	82 ,,	1·104	99·0 ,,

quantities of heavy water more rapidly, but the fundamental principle remains the same.

Separation Factor. If the relative rates of evolution of hydrogen and deuterium on electrolysis remain constant, irrespective of the composition of the water in the electrolyte, it is possible to write

$$\frac{dn_1}{dn_2} = s\frac{n_1}{n_2} \text{ or } d\ln n_1 = sd\ln n_2 \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

where n_1 and n_2 are the number of gm.-mols. of hydrogen and deuterium in the water, and s is a constant known as the "separation factor" or "separation coefficient." The quantity dn_1/dn_2 is a measure of the H/D ratio in the evolved gas, and n_1/n_2 is the ratio in the liquid; consequently, the separation coefficient may be written in the form

$$s = \frac{[\text{Hydrogen}]_{\text{gas}}}{[\text{Deuterium}]_{\text{gas}}} \Big/ \frac{[\text{Hydrogen}]_{\text{liquid}}}{[\text{Deuterium}]_{\text{liquid}}} \quad . \quad . \quad . \quad \text{(ii.)}$$

where the square brackets are employed, as usual, to represent concentrations. If v represents the volume of the electrolyte, then the concentrations of hydrogen (c_1) and of deuterium (c_2) in the water are n_1/v and n_2/v, respectively; or

$$n_1 = c_1 v \text{ and } n_2 = c_2 v,$$

and hence

$$d\ln c_1 v = sd\ln c_2 v \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

by equation (i.). If $c_1°$ and $c_2°$ represent the concentrations of hydrogen and deuterium at the commencement of the electrolysis

when the volume is v_0, and c_1 and c_2 are the concentrations after the electrolysis has reduced the volume to v, then integration of equation (iii.) gives the result

$$\frac{c_1^{\circ}}{c_1}\left(\frac{c_2}{c_2^{\circ}}\right)^{s} = \left(\frac{v_0}{v}\right)^{s-1} \quad \ldots\ldots\ldots \text{(iv.)}$$

It is thus possible to calculate the value of s, either by an analysis of the gases evolved at any stage of the electrolysis and the use of equation (ii.), or by determination of the composition of the electrolyte after the volume has been appreciably reduced and inserting the data in equation (iv.). This equation can also be used, if s is known, to give some idea of the extent to which the volume must be reduced by electrolysis in order to give water of a particular D_2O content. A common value of s, as will be seen later, is about 5; starting with ordinary water, containing 0·02 per cent. of the hydrogen as deuterium, it can be calculated that to obtain water with 90 per cent. of D_2O, the volume must be reduced about 66,000-fold.

Although the separation factor has been the subject of considerable investigation the data are not yet sufficiently definitive to have any real significance: different results have been obtained under apparently identical conditions, and it is evident that the possible factors, which may vary during the course of the electrolysis, will have to be rigorously controlled. Apart from the fact that platinised platinum electrodes generally give a low separation factor, there does not seem to be any direct connection between

TABLE XVI

Separation Factors for Electrolysis under Different Conditions.

Electrode.	Electrolyte.	Separation Factor.
Lead . . .	0·5 N-KOH	7·2—7·4
Platinum . .	,,	6·5—7·6
Platinum . .	0·5 N-H_2SO_4	5·7
Iron . . .	0·5 N-KOH	6·9—7·6
Nickel . .	,,	5·5
Copper . .	,,	6·8
Silver. . .	,,	5·3—5·8

this factor and the nature of the metal; acid electrolytes appear to give lower values of s than do alkaline solutions, but this is by no means quite certain. The results in Table XVI. are taken from the work of Topley and Eyring (1933); the apparent current density used was 1 amp. per sq. cm. in each case.

Increasing the current density generally increases the separation coefficient, but this is not always the case: raising the temperature apparently lowers the coefficient, and this may account for the relatively low efficiency of commercial electrolytic cells which are generally operated at an elevated temperature. At one time it was believed that the separation factor remained constant, even though the deuterium oxide content of the electrolyte might vary, but recent work (Applebey and Ogden, 1936) has shown that this view is probably incorrect, as the following results, obtained with a nickel cathode in a 5 per cent. sodium hydroxide solution, indicate:

Mean concentration of D_2O in electrolyte	3·7	29·5	58·75	86·5 per cent.
Separation Factor	5·26	5·56	4·35	3·45 ,,

Although observed separation coefficients are commonly about 5, values covering the range from 2·7 to 17 (Eucken and Bratzler, 1935), and possibly higher, have been recorded. Two circumstances tend to make the measured values somewhat smaller than they should be: in the first place, the gases evolved are not dry, being saturated with both H_2O and D_2O, according to their vapour pressures above the electrolyte. The fractionation factor for the vaporisation of water is only 1·025 (see p. 144), and consequently the apparent electrolytic separation factor observed when the gases are wet will be lower than the theoretical value for the dry gases. In the second place, the equilibrium

$$\underset{\text{liquid}}{H_2O} + \underset{\text{gas}}{HD} \rightleftharpoons \underset{\text{liquid}}{HDO} + \underset{\text{gas}}{H_2}$$

should theoretically be established whenever hydrogen and water are in contact, and consequently should exist when hydrogen is evolved by electrolysis. The equilibrium constant

$$K = \frac{[HDO]_l[H_2]_g}{[H_2O]_l[HD]_g} = \frac{[H_2]_g}{[HD]_g} \Big/ \frac{[H_2O]_l}{[HDO]_l}$$

has a value of about 3·0 at ordinary temperatures (see p. 176), and an examination of the alternative method of writing the fraction

shows that it is effectively the same as the separation factor. Provided the water does not contain more than about 30 per cent. of the heavy isotope the deuterium is present in the liquid phase mainly as HDO, and as HD in the gas. If the equilibrium under discussion were established in electrolysis, therefore, the separation factor should have a value of about 3·0; for most electrodes, it is evident that the equilibrium is not attained, but with a platinised platinum cathode, at relatively low current densities, a separation factor of 3 has actually been observed. It is obvious, however, that in any case there will be a tendency towards the establishment of equilibrium, even if it is not actually reached: any separation factor above 3·0 will, therefore, tend to be reduced, the extent of reduction depending on the catalytic effect of the electrode material on the establishment of equilibrium. As might be anticipated platinised platinum is very effective in this connection, especially when the gas is being evolved slowly, and the observed separation coefficient is equal to the equilibrium constant. The decrease in the separation factor with increasing deuterium content, recorded above, has been attributed to the more rapid attainment of equilibrium as the electrolyte, especially in the vicinity of the cathode, becomes enriched in HDO.

Theory of the Electrolytic Separation. Calculations of free energy show that the *reversible* discharge potentials of hydrogen and deuterium are very little different, so that theoretically the two isotopes should be liberated in almost equal amounts, and the separation factor, apart from the tendency of the equilibrium already mentioned to be established, should be about unity. It is evident, therefore, that the discharge of the ions to form hydrogen and deuterium molecules is not reversible, that one of the processes involved is a slow one, and that the rates are different for the two isotopes. In other words, the explanation of the separation factor is to be sought in the difference in the "overvoltages" of the cathode for the liberation of hydrogen and deuterium gases. It is well known that on electrolysis of an aqueous solution hydrogen is not liberated at the theoretically reversible potential, for an excess potential, known as the overvoltage, must be applied before the gas can be evolved. The

discharge of a hydrogen ion, which is actually present in solution in the hydrated form, H_3O^+, to yield molecular hydrogen at a cathode may be represented by two stages, viz.,

(1) $H_3O^+ + e \rightarrow H + H_2O$

and (2) $2H \rightarrow H_2$,

and the overvoltage is due to the slowness of one or other of these stages. Until recent years it was generally believed that the formation of molecular hydrogen from the atoms on the electrode surface was the slow process responsible for overvoltage: but latterly (Erdey-Grúz and Volmer, 1930) the view that the first stage, involving the union of the ion and an electron, takes place slowly has gained considerable support, especially as a quantum-mechanical interpretation of the process, in terms of the penetration of electrons through a potential barrier between the electrode and the positive ions in solution, has been proposed (Gurney, 1932). Since the ions H_3O^+ and DH_2O^+ (or D_3O^+) will have different zero-point energies (see p. 166), that of the H_3O^+ ion being the greater, different amounts of energy will be required to bring the ions into an activated state which is necessary before the discharge can occur; this amount of energy will be less for the hydrated H^+ ion than for the corresponding D^+ ion, and so the rate of discharge of the former should be greater than that of the latter. Working along these and similar lines it has been shown that separation factors of the correct order, namely, about 10 ± 5, are normally to be expected.

It must be remembered, further, that according to wave mechanics there is a definite probability of the permeability of an energy barrier to particles having less energy than would be considered requisite in classical mechanics; this is the so-called "tunnel effect." The permeability factor should decrease with increasing mass of the particle, and will be much greater for hydrogen than for deuterium; consequently the existence of the tunnel effect would tend to increase the rate of evolution of hydrogen with respect to deuterium, and so increase the separation factor. The actual influence depends on the height and width of the energy barrier, and assuming reasonable values for them it has

been shown that separation coefficients as high as 74 could be attained (Bawn and Ogden, 1934). No such value had been reported until Applebey and Ogden (1936) showed that apparent s values of the order of 70 to 100 were obtainable with water containing relatively small amounts of deuterium, on the assumption that normal water contains one part of the heavier isotope in 5500 parts of hydrogen. The calculated separation coefficient is very sensitive to changes in this isotopic proportion in normal water, and a H/D ratio of 4500/1 would bring the coefficient down to a reasonable value. For the present the position remains in doubt: if the 1 to 5500 proportion is proved correct then the tunnel effect must be regarded as being established in the case of the discharge of hydrogen ions, but until further results are available an open mind must be preserved.

Although most workers accepted the different rates of combination of the isotopic hydrogen ions with electrons as the cause of the discrepancy between the separation factor and the hydrogen–water equilibrium constant, there has been recently a tendency on the part of some authors to reconsider the idea, originally envisaged by Eyring and Sherman (1933), that the ratio of the velocities of combination of hydrogen and of deuterium atoms on the electrode surface is the essential factor in the different rates of gas evolution (Urey and Teal, 1935; Gross and Halpern, 1935). On this hypothesis it can be shown, by making reasonable assumptions, that a separation factor of about 4 might be expected from purely kinetic considerations, and this would be increased by allowing for the difference in the zero-point energies of the combination between the electrode metal (M) and the atoms, that is, M—H and M—D, and possibly also by the permeability of the barrier representing the energy of activation which the atoms must acquire before they can combine. The electrolytic separation of hydrogen and deuterium can thus be accounted for by either of two commonly accepted theories of overvoltage, and so does not permit, at present, of a choice between them as was at one time considered possible.

Related to the separation of hydrogen and deuterium by electrolysis is the preferential liberation of the lighter isotope

when metals react with water or with aqueous solutions of acids. It appears that for strongly electropositive elements, such as lithium, sodium and calcium, the separation factor is low, about 2, but when the hydrogen is evolved in acid solution only, as for example with zinc, magnesium and iron, a higher factor, about 4 to 5 is obtained. It has been suggested that different mechanisms are operative in the two cases, but the subject appears to require re-investigation before definite conclusions can be drawn from the observations.

It may be noted finally that only a limited number of actual measurements have been made of the overvoltages required for the liberation of light hydrogen only and of deuterium only, from solutions containing the hydrogen almost exclusively in one form or the other. The results so far indicate quite definitely, in accordance with the views outlined above, that the overvoltage in connection with the discharge of deuterium ions is greater than that with hydrogen ions (Bowden and Kenyon, 1935).

Miscellaneous Methods. (*c*) Other methods for the fractionation of the isotopes of hydrogen may be considered briefly. The difference in masses of the H_2 and D_2 molecules leads to a ratio of 1·41 to 1 for their diffusion coefficients ; advantage has been taken of this difference by Hertz (1933) to obtain a specimen of deuterium gas so pure that its Balmer spectrum showed no trace of the lines due to the lighter isotope. The gas at the commencement contained 0·1 per cent. of the heavier isotope, obtained by electrolytic enrichment, and was allowed to diffuse through porous clay tubes in a series of forty-eight units. Since the original gas consisted of H_2 and HD, with an almost negligible amount of D_2, an electric discharge was passed through the gas at a suitable point in order to establish the equilibrium $H_2 + D_2 \rightleftharpoons 2HD$, and so permit of the isolation of pure deuterium. The diffusion method, although it can be made very effective, operates with only relatively small quantities of material, and so is more of academic than of practical interest. The failure of early workers (Stern and Volmer, 1920) to effect an isotopic separation by the process of diffusion (p. 137) must be ascribed either to the use of electrolytic hydrogen, containing only one part of deuterium in thirty-thousand of gas, as

the starting material, or to an exchange reaction with steam, used as the carrying gas, which would tend to restore the D/H ratio.

Hydrogen also diffuses more rapidly through heated palladium than does deuterium : the difference in the rates does not depend primarily on the difference in the speeds of the molecules, since the gas probably passes through in the atomic form, and a certain activation energy is required. Owing to the difference in the zero-point energies, the energy required for H_2 will be less than for HD or D_2 molecules, and so the former will diffuse through the palladium more rapidly (Rideal and Melville, 1935). An eight- to ten-fold enrichment of the deuterium concentration in hydrogen gas has been effected by this diffusion process.

Both deuterium itself and deuterium oxide (heavy water), especially in the form of vapour, are more readily adsorbed by charcoal or by silica gel than are light hydrogen and light water, respectively. A partial separation of the isotopes has been achieved in this way, but the results are apparently of little direct practical value.

Finally, mention must be made of the possibility of separating the isotopes by chemical means. If hydrogen gas were passed through water and the equilibrium

$$H_2O + HD \rightleftharpoons H_2 + HDO$$

were attained, it is clear, from what has already been said (p. 148), that partial enrichment of the water would occur, since the H/D ratio in the gas would be about 3·0 times the value in the liquid. In other words, this process would give a separation factor almost as good as that obtained in electrolysis, and there is every possibility that this reaction, or a similar one, may eventually prove to be a convenient method for obtaining heavy water. It will, however, be necessary to find a catalyst which facilitates the establishment of equilibrium, as mere bubbling of hydrogen gas through water is by no means adequate. Palladium and platinum black are known to be effective in this connection (see p. 175), but it is doubtful whether they accelerate the reaction to a sufficient extent to find application on a large scale.

PROPERTIES OF DEUTERIUM

Physical Properties. Pure deuterium can be obtained by the electrolysis of pure heavy water, containing a suitable electrolyte, or by the action on it of metallic sodium, or in other ways. Since its density is approximately twice that of hydrogen, its diffusion coefficient and heat conductivity are $1/\sqrt{2}$ times the corresponding value for the light isotope; this factor also gives the ratio of the number of collisions between deuterium molecules to that between hydrogen molecules, in the two gases under the same conditions.

Partly as a result of the higher molecular weight, and partly for other reasons, liquid deuterium has a lower vapour pressure than liquid hydrogen at the same temperature; for example, at 13·95° K., the triple point of light hydrogen, the ratio of the vapour pressures is 2·42. Deuterium has, therefore, the higher boiling point and also a higher triple point. Some of the physical properties of " normal "* hydrogen and deuterium in the liquid and solid states are given in Table XVII.

TABLE XVII

Physical Properties of Hydrogen and Deuterium.

Property.	Hydrogen.	Deuterium.
Boiling point	20·38° K.	23·50° K.
Triple point	13·92°	18·58°
Heat of vaporisation at triple point	218 cals./gm.-mol.	308 cals./gm.-mol.
Heat of fusion	28 ,, ,, ,,	47 ,, ,, ,,
Molecular volume of solid . .	26·15 c.c.	23·17 c.c.

Mixtures of liquid hydrogen and deuterium behave almost as ideal systems, so that the vapour pressures and freezing points vary in a linear manner with the molar fraction; the vapour pressure of any given mixture is almost unchanged when the equilibrium between H_2, D_2 and HD is established, showing that the value for HD is the mean of those for H_2 and D_2 molecules.

Atomic Spectra. Deuterium was first detected by means of its

* The term " normal " here refers to the appropriate mixtures of ortho- and para-forms, see p. 109.

Balmer (atomic) spectrum, and the positions of the lines are in excellent agreement with the calculated frequencies. The lines in the spectra of atomic hydrogen may be represented by the equation

$$\nu = R\left(\frac{1}{n_A} - \frac{1}{n_B}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (v.)$$

where n_A is equal to 1 for the Lyman series and 2 for the Balmer series, and n_B has a series of integral values greater than n_A; R is the Rydberg constant which, according to Bohr's calculations, is given by

$$R = \frac{2\pi^2 me^4}{ch^3} \cdot \frac{M}{M+m}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (vi.)$$

where m and M represent the masses of an electron and of the nucleus of the atom respectively, c is the velocity of light, e the electronic charge, and h the Planck constant. Since the value of M is different for the two hydrogen isotopes, different values of the Rydberg constant are obtained; these are $R_H = 109677{\cdot}76$ and $R_D = 109707{\cdot}62$ in cm.$^{-1}$ units, and consequently it is a simple matter to calculate the isotopic shift of corresponding lines in the spectrum. The first four lines in the Balmer series and the first six in the Lyman series have been examined and very satisfactory agreement found between the observed and calculated differences in wavelength for the two isotopes. Although the lines are correctly spaced, according to the simple Bohr theory (equation v.), there are still some difficulties in connection with the fine structure of the lines for which a satisfactory solution is not yet available.

Molecular Spectra. The frequency ν of the origin of the vibrational bands for a diatomic molecule, assumed to be a harmonic oscillator, is given by

$$\nu = \omega_e(v + \tfrac{1}{2})c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (vii.)$$

where ω_e cm.$^{-1}$ is the equilibrium vibration frequency and v the vibrational quantum number. The value of ω_e will be related to the restoring force f by the expression

$$2\pi\omega_e = (f/\mu)^{1/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (viii.)$$

where μ, the " reduced mass," is defined by $1/\mu = 1/m_a + 1/m_b$, m_a and m_b being the masses of the two atoms constituting the molecule. It is assumed, on the basis of general experience in the study of the spectra of isotopic molecules, that the restoring force for a given substance is independent of the particular isotope present; consequently, for two isotopes, represented by the suffixes 1 and 2, it follows that

$$(\omega_e)_1/(\omega_e)_2 = (\mu_2/\mu_1)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix.)}$$

Since the μ values can be determined from the atomic weights, if ω_e for one isotopic molecule is known the corresponding vibration frequency for the other can be determined, and hence the isotopic shift in the vibrational bands can be readily calculated (" Recent Advances in Physical Chemistry," Chapter IV.). In accurate computations allowance must be made for the anharmonicity of the vibrations. As noted in previous chapters, the rotational energy of a rigid molecule can be written as $E_{\text{rot.}} = J(J+1)h^2/8\pi^2 I$ where J is the rotational quantum number, and I the moment of inertia of the molecule: the factor $h/8\pi^2 Ic$ is frequently represented by the term B, which is virtually a measure of the frequency separations in cm.$^{-1}$ units of the rotational lines in the spectrum. For a diatomic molecule $I = \mu r^2$, where r is the distance between the two nuclei, which may be assumed constant irrespective of the particular isotope present in the molecule. For two isotopic substances, therefore,

$$B_1/B_2 = \mu_2/\mu_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(x.)}$$

Allowance is made in practice for the non-rigidity of the molecule, and the separation of the rotational lines in the spectrum of one isotope can be evaluated if that for the other is known. The band spectrum of H_2 has been carefully studied and the various constants are well established; it is consequently possible to calculate the corresponding values for the spectra of the HD and D_2 molecules, and these have been found to be in striking agreement with the actual experimental observations. In Table XVIII. (quoted from Urey and Teal, 1935) are given the spectroscopic constants for the equilibrium vibrations in the ground state of the

molecules H_2, HD and D_2; the term x represents the anharmonicity constant.

TABLE XVIII

Band Spectroscopic Constants for Hydrogen Isotopes in the Ground State.

	H_2	HD	D_2
ω_e . .	4415·64 cm.$^{-1}$	3824·99 cm.$^{-1}$	3124·07 cm.$^{-1}$
$x\omega_e$ . .	131·203 ,,	98·36 ,,	65·67 ,,
B_e . .	60·848 ,,	45·655 ,,	30·46 ,,

A definite alternation of the intensity of the lines has been observed in certain bands of the D_2 molecule, implying that this substance can exist, like H_2 molecules, in ortho- and para-states; the ratio of the intensities has been measured (Murphy and Johnston, 1934) and found to be almost exactly 1 to 2, which as already seen (p. 134) corresponds to a spin of unity for the deuterium nucleus. Further reference to this subject will be made later. Since the HD molecule is unsymmetrical, all the spectral lines in a given band have, of course, the same intensity.

The zero-point energy of a diatomic molecule can be calculated by the relationship (p. 60).

$$E_0^\circ = Nhc(\tfrac{1}{2}\omega_e - \tfrac{1}{4}x\omega_e) \quad \text{(xi.)}$$

where E_0° is the zero-point energy in ergs per gram-molecule. Using the data in Table XVIII. the following values, in calories per gm.-mol., have been calculated for the three isotopic forms of molecular hydrogen :

H_2 6,181 cals. HD 5,365 cals. D_2 4,392 cals.

The markedly different zero-point energies for the different isotopic forms of hydrogen have an important influence on their physical and chemical properties. Since atoms have no zero-point energies, the energies of H and D atoms may be taken as being identical, *i.e.*, zero, at 0° K., and consequently the heats of

dissociation of the HD and D_2 molecules can be calculated from the known value for the H_2 molecule. The latest spectroscopic data give the heat of dissociation of H_2 at 0°K. as 102,680 ± 120 cals. per gm.-mol., and so the corresponding value for HD is 103,550 cals., and for D_2 it is 104,460 cals.

Ortho- and Para-Deuterium. Like all symmetrical molecules, the nuclei of which possess spin, deuterium can exist in symmetrical (ortho) and antisymmetrical (para) states. As explained in the previous chapter (p. 134), odd rotational levels represent para-states, having statistical weights of $i(2i + 1)$ due to nuclear spin, and even rotational levels constitute the ortho-states, with nuclear-spin weights of $(i + 1)(2i + 1)$. Using the same nomenclature as employed in Chapter III., p. 106, it is seen that

$$\frac{[\text{para-}D_2]}{[\text{ortho-}D_2]} = \frac{\sum_{J=1,3,5,7\ldots} p_J e^{-\epsilon_J/kT}}{\sum_{J=0,2,4,6\ldots} p_J e^{-\epsilon_J/kT}} = \frac{\sum_{J=1,3,5,7\ldots} i(2i+1)(2J+1)e^{-\epsilon_J/kT}}{\sum_{J=0,2,4,6\ldots} (i+1)(2i+1)(2J+1)e^{-\epsilon_J/kT}} \quad \text{(xii.)}$$

Since $i = 1$ for the deuterium nucleus, as found from spectroscopic and other observations, it follows that

$$\frac{[\text{para-}D_2]}{[\text{ortho-}D_2]} = \frac{3(3e^{-\epsilon_1/kT} + 7e^{-\epsilon_3/kT} + 11e^{-\epsilon_5/kT} + \ldots)}{6(1 + 5e^{-\epsilon_2/kT} + 9e^{-\epsilon_4/kT} + 13e^{-\epsilon_6/kT} + \ldots)}. \quad \text{(xiii.)}$$

where ε_J represents the rotational energy of the Jth level, the values of which for different quantum numbers J can be calculated from spectroscopic data. The calculation of the relative amounts of ortho- and para-deuterium in equilibrium at various temperatures, by means of equation (xiii.), has been carried out by Johnston and Long (1934), and by others; some of the results obtained are recorded in Table XIX. The results in this table may be compared with those for light hydrogen given in Table X., on p. 107.

At very low temperatures nearly all the molecules occupy the lowest ($J = 0$) rotational level, and consequently in the equilibrium state deuterium exists almost exclusively in the ortho-form, but as the temperature is raised the equilibrium composition approaches that at normal temperatures, namely, 2 parts of ortho-deuterium to 1 part of para-deuterium. The limiting ratio of

TABLE XIX

Ortho–Para Composition of Equilibrium-Deuterium.

Temp.	Ortho/Para Ratio.	Para-D_2, %.	Ortho-D_2, %.
10° K.	3332	0·03	99·97
20°	48·22	2·03	97·97
40°	5·758	14·78	85·12
60°	2·966	25·21	74·79
80°	2·316	30·18	69·82
100°	2·107	32·18	67·82
140°	2·018	33·19	66·81
180°	2·001	33·32	66·68
300°	2·000	33·33	66·67

2 to 1 follows, as already explained, from the ratio of the nuclear-spin multiplicities, which is 6 to 3, that is 2 to 1. A general comparison of the results for deuterium with those for hydrogen has been made at the close of the previous chapter (p. 133).

Ortho–Para Interconversion. The establishment of the ortho–para equilibrium in deuterium at low temperatures, involving conversion of para-deuterium to the ortho-form is, like the corresponding change for hydrogen, a slow process : it can, however, be catalysed by charcoal (Farkas, Farkas and Harteck, 1934). By using the thermal-conductivity method already described (p. 116), the equilibrium mixtures were analysed at 20·4°, 53° and 78° K., and the results found to be in excellent agreement with those calculated in the manner explained above and recorded in Table XIX. The rate of formation of ortho-deuterium from the para-form on charcoal at low temperatures is too great to be easily measurable, but on glass, in the presence of some solid oxygen, the process is slower : it is found that the conversion process takes place somewhat less rapidly than the corresponding ortho–para-hydrogen conversion, the half-reaction times being 19 mins. and 11 mins., respectively. The reconversion of ortho- into para-deuterium molecules at room temperatures, like the reverse process with hydrogen, is catalysed by paramagnetic oxygen molecules, although the speed of the former reaction is only one-sixteenth of that of the latter (Farkas and Farkas, 1935).

This marked difference in the velocities is due chiefly to the smaller magnetic moment of the deuterium nucleus, it being only about one-quarter of the moment of the proton, the light hydrogen nucleus.

The high-temperature reconversion of ortho-deuterium to the equilibrium state has been studied over a range of 850° to 1,000° K., at pressures from 3 to 74 mm. of mercury ; the order of the reaction, as in the corresponding para–ortho-hydrogen reconversion, is 1·5, indicating a process

$$\mathrm{D} + \text{ortho-}\mathrm{D_2} \rightleftharpoons \text{para-}\mathrm{D_2} + \mathrm{D}.$$

It is evident that the mechanisms of the reactions whereby ortho- and para-deuterium are interconverted are similar to those for the corresponding processes taking place with the lighter isotope. This subject is considered more fully in connection with chemical reactions involving deuterium (p. 169).

Heat Capacity, Entropy and Free Energy. The rotational partition functions for the ortho- and para-states are represented by

$$Q_{\text{para-}\mathrm{D_2}} = 3\sum_{J=1,3,5,7\ldots}(2J+1)e^{-\varepsilon_J/kT}$$

$$Q_{\text{ortho-}\mathrm{D_2}} = 6\sum_{J=0,2,4,6\ldots}(2J+1)e^{-\varepsilon_J/kT}$$

and the function for equilibrium-deuterium is the sum of these, namely, $Q_{\text{para}} + Q_{\text{ortho}}$. For the HD molecule there are, of course, no ortho- and para-states, but treating this as being heteronuclear, the respective spins being $\frac{1}{2}$ and 1, it follows that

$$Q_{\mathrm{HD}} = 6\sum_{J=0,1,2,3,4\ldots}(2J+1)e^{-\varepsilon_J/kT}$$

the values of ε_J being determined from the spectroscopic data for this molecule. Since it is possible to evaluate the partition functions, the rotational molar heat capacities and entropies can be calculated, at various temperatures, for ortho-$\mathrm{D_2}$, para-$\mathrm{D_2}$, equilibrium-$\mathrm{D_2}$, normal-$\mathrm{D_2}$, and for HD molecules (Johnston and Long, 1934). Some of the heat capacities determined in this manner are quoted in Table XX.

TABLE XX

Molar Rotational Heat Capacities (Calculated).

Temp.	Ortho-D_2.	Para-D_2.	Equilibrium-D_2.	Normal-D_2.	HD.
0° K.	0·000	0·000	0·000	0·000	0·000
10°	0·000	0·000	0·039	0·000	0·000
20°	0·002	0·000	0·726	0·000	0·401
30°	0·137	0·000	1·307	0·091	1·406
50°	1·455	0·064	1·973	0·991	2·179
70°	2·693	0·383	2·325	1·923	2·106
100°	2·775	1·116	2·273	2·222	2·028
140°	2·249	1·745	2·084	2·081	2·009
190°	2·037	1·964	2·013	2·013	2·004
300°	2·007	2·007	2·007	2·007	2·008

The rotational specific heats of HD and normal-deuterium have been determined experimentally (Clusius and Bartholomé, 1935) between 30° and 120° K., using two samples of gas containing H_2, D_2 and HD molecules in different proportions; the heat capacity of H_2 being known, the values for normal-deuterium and for HD were estimated by assuming the mixture law to apply. The results obtained were in agreement with those given by the calculations from the spectroscopic constants.

The entropy of deuterium at 298·1° K. has been determined (Clusius and Bartholomé, 1935) by thermal measurements, based on the third law of thermodynamics, and found to be 33·65 cals./degree per gm.-mol. The calculated value, including the complete allowance for nuclear spin, is 38·73 units. As in the case of hydrogen (p. 112), the difference is to be attributed to the fact that measurements were made on normal-deuterium and that the rotational levels, characterising the ortho- and para-forms, are carried over into the solid state. The correction to be applied can be calculated in the same manner as that already described for the lighter isotope. At very low temperatures all the ortho-molecules will be in the $J = 0$ level, and so the statistical weight will be 6, and the internal entropy will be given by

$$S_{\text{ortho}}^{\text{int.}} = R\ln 6,$$

and similarly all the para-molecules will be in the $J = 1$ level, with a statistical weight of 9, so that

$$S^{\text{int.}}_{\text{para}} = R\ln 9.$$

The entropy of the normal mixture, consisting of two parts of ortho- to one of para-deuterium, will be

$$\begin{aligned} S^{\text{int.}}_{\text{normal}} &= \tfrac{2}{3} R\ln 6 + \tfrac{1}{3} R\ln 9 - R(\tfrac{2}{3}\ln\tfrac{2}{3} + \tfrac{1}{3}\ln\tfrac{1}{3}) \\ &= 5{\cdot}09 \text{ cals./degree per gm.-mol.} \end{aligned}$$

Hence, if the rotational levels of deuterium are carried over into the solid state at low temperatures, the internal entropy will be 5·09 units, instead of zero, as required by the third law of thermodynamics. The experimental absolute entropy should consequently be 33·65 + 5·09 = 38·74 units, which is in almost perfect agreement with the calculated value. For use in the determination of equilibrium constants, or in conjunction with other thermal entropies, except that for hydrogen and hydrogen deuteride (HD) molecules, the nuclear-spin factor, $R\ln 9 = 4{\cdot}366$, should be subtracted, giving a value of 34·36 cals./degree per gm.-mol.

Equilibrium Constants. With the aid of the complete partition functions and the known heats of dissociation of HD and D_2 at 0° K. (p. 158), it is possible to calculate, as shown in Chapter II., the equilibrium constants of the reactions :

$$HD \rightleftharpoons H + D \quad \text{and} \quad D_2 \rightleftharpoons 2D.$$

The results, for a number of temperatures, taken from the calculations of Johnston and Long (1934) are given in Table XXI. ; the corresponding values for the dissociation of hydrogen (H_2) are recorded for comparison.

TABLE XXI

Equilibrium Constants (K_p) for Dissociation into Atoms.

Temp.	H_2	HD	D_2
1,000° K.	$6{\cdot}45 \times 10^{-18}$	$2{\cdot}48 \times 10^{-18}$	$3{\cdot}71 \times 10^{-18}$
1,500	$3{\cdot}60 \times 10^{-10}$	$1{\cdot}57 \times 10^{-10}$	$2{\cdot}70 \times 10^{-10}$
2,000	$2{\cdot}96 \times 10^{-6}$	$1{\cdot}36 \times 10^{-6}$	$2{\cdot}49 \times 10^{-6}$
2,500	$6{\cdot}91 \times 10^{-4}$	$3{\cdot}28 \times 10^{-4}$	$6{\cdot}17 \times 10^{-4}$
3,000	$2{\cdot}69 \times 10^{-2}$	$1{\cdot}29 \times 10^{-2}$	$2{\cdot}47 \times 10^{-2}$

It will be observed that, although at low temperatures the degree of dissociation of hydrogen molecules is greater than that of deuterium molecules, the values approach one another as the temperature is increased: this is because the differences in the heats of dissociation become of less importance at high temperatures. The dissociation constant for HD molecules approaches a value which is half that for either H_2 or D_2.

PHYSICAL PROPERTIES OF DEUTERIUM COMPOUNDS

Deuterium Oxide. The most important deuterium compound at present available is, of course, deuterium oxide, D_2O. Its physical properties have been carefully studied, and some of these are recorded in Table XXII., together with the corresponding values for ordinary water for comparison.

TABLE XXII

Physical Properties of Light and Heavy Water.

	H_2O.	D_2O.
Density $\frac{25°}{25°}$	1·000	1·1079
Max.-density temp.	4·0° C.	11·6° C.
Surface tension	72·75	67·8 dynes. per cm.
Viscosity (20°)	10·09	12·60 millipoises.
Refractive index (20°)	1·33300	1·32828 for Na-*D* line.
Freezing point	0·00° C.	3·82° C.
Boiling point	100·00° C.	101·42° C.
Equiv. conductivities (20°)—		
Potassium ions	64·2	54·5
Chlorine ions	65·2	55·3
Hydrogen ions	315·2 (H_3O^+)	213·7 (D_3O^+)
Solubilities (25°)—		
Sodium chloride	0·359	0·305 gm. per gm.
Barium chloride	0·357	0·289 gm. per gm.
Critical solution temp.—		
Phenol	68·3° C.	70·1° C.

It is evident from the higher boiling and freezing points that the vapour pressure of deuterium oxide at any temperature is less

than that of ordinary water: at 20° C. the ratio is 0·87, and at 100° C. it is 0·949. Mixtures of liquid H_2O and D_2O behave almost as ideal, the specific gravities (see p. 142), refractive indices, viscosities and freezing points (see p. 143), being nearly linear functions of the molar fractions of the constituents.

Other Deuterium Compounds. Deuterammonia, ND_3, has been prepared by the action of heavy water on magnesium nitride: it is generally contaminated with some NHD_2 and NH_2D. Deuterium chloride, DCl, forming deuterochloric acid in solution, is obtained by allowing D_2O vapour to react with anhydrous magnesium chloride at 600° C., and deuterium fluoride, DF, results by the heating of deuterium gas in contact with silver fluoride at 110° C. Deuteromethane, CD_4, is made by the action of heavy water on aluminium carbide. A number of other organic compounds of deuterium have been isolated, and a few of the more interesting may be mentioned. When D_2O reacts with calcium carbide, deuteroacetylene, C_2D_2, is formed, and acetic deuteracid, $CH_3{\cdot}CO_2D$, results from the interaction of silver acetate and deuterium chloride. From carbon suboxide and D_2O, in dry benzene, it is possible to obtain dideuteromalonic deuteracid, $CD_2(CO_2D)_2$, and on heating at 140° to 150° C. this gives trideuteracetic deuteracid, $CD_3{\cdot}CO_2D$. Pure hexadeuterobenzene, C_6D_6, is prepared by distilling the calcium salt of mellitic acid with calcium deuteroxide, $Ca(OD)_2$, and also by an exchange reaction between D_2O and C_6H_6 on a nickel-kieselguhr catalyst. The melting and boiling points of some corresponding hydrogen and deuterium compounds are recorded in Table XXIII.

The boiling points of ND_3 and DCl are, like that of D_2O, higher than the values for the corresponding hydrogen compounds, but that for DF is definitely less than that for HF, and the same is probably the case for the acetic acids. The unexpected result for the latter compounds is probably to be connected with the fact that these substances are not only associated in the liquid phase, but also in the vapour. There is good reason to believe that the deuterium bond, the analogue of the co-ordinated hydrogen bond ("Recent Advances in Physical Chemistry," Chapter I.), is definitely stronger than the latter, so that deuterium derivatives

TABLE XXIII

Melting and Boiling Points of Hydrogen and Deuterium Compounds.

Compound.	M. Pt.	B. Pt.	Compound.	M. Pt.	B. Pt.
NH_3	— 77·9° C.	— 33·3° C.	HI	—	— 35·6° C.
ND_3	— 74°	— 30 8°	DI	—	— 36·1°
HF	—	20·0°	HCN	— 14°C.	25·4°
DF	—	18·7°	DCN	— 12°	26·1°
HCl	— 114·2°	— 85·0°	$CH_3{\cdot}CO_2H$	16·6°	—
DCl	— 114·9°	— 81·5°	$CH_3{\cdot}CO_2D$	13·3°	—
HBr	—	— 65·8°	C_6H_6	5·5°	80·12°
DBr	—	— 65·8°	C_6D_6	6·8°	79·4°

are more highly associated than the corresponding hydrogen compounds. The vapour pressures and boiling points depend on the relative degrees of association of the liquid and the vapour : for $CH_3{\cdot}CO_2D$, $CD_3{\cdot}CO_2D$ and DF the vapour pressures are higher and the boiling points lower than for the hydrogen compounds. It has been stated that theoretically the curves showing the variation of vapour pressure with temperature for analogous hydrogen and deuterium compounds should cross at some temperature, so that for *every* compound there should be a range over which the heavier isotopic form has the higher vapour pressure, even for non-associated substances (Urey and Teal, 1935). Actually for most compounds this theoretical range is above the boiling point and so cannot be observed, but it is possible that the almost identical boiling points of hydrogen and deuterium bromides are due to a coincidence between this temperature and that at which the vapour pressure curves intersect.

The dissociation constants of acetic deuteracid and of deuterammonium deuteroxide are less than for the analogous hydrogen compounds; similarly, the ionic product of D_2O, *i.e.*, $[D_3O^+][OD^-]$, is smaller than that for H_2O, *i.e.*, $[H_3O^+][OH^-]$. These phenomena are probably related to the factors which result

in the increased strength of the deuterium bond as compared with that of co-ordinated hydrogen.

Spectra. The study of deuterium compounds is already having an important influence in spectroscopy, which is likely to be extended in the future. In general, the results for diatomic molecules, which give the simplest spectra, are in agreement with expectation, assuming the force constants and equilibrium distances of the nuclei to remain the same, as already discussed in connection with the spectra of HD and D_2 molecules. As with these substances the change in the fundamental vibration frequency and in the anharmonicity constant is such as to make the zero-point energy of the D—X bond less than that of the corresponding H—X linkage. In some instances, however, such as AlH and AlD, there are definite discrepancies in both vibrational and rotational constants, which must be attributed to hitherto unsuspected factors operative in the production of the spectra : no completely satisfactory explanation of these phenomena has yet been proposed. The study of the spectra of polyatomic molecules containing deuterium is proving of value in the assignment of frequencies to particular modes of vibration in the molecule, where they had previously been in doubt. By the use of unsymmetrical molecules, as for example, C_2HD and CH_3D, certain frequencies which are forbidden in the spectra of acetylene and of methane, respectively, become active, and so fuller information is made available, permitting the interatomic distances and force constants for the molecules to be calculated without the need for making assumptions which have hitherto been necessary.

REACTION KINETICS AND EQUILIBRIA

Activation and Zero-Point Energies. Probably the most important aspect to date of the study of deuterium and its compounds has been in connection with the reactions in which these substances are involved : not only have new facts in chemical kinetics been discovered, but it has been possible to throw light on the mechanisms of a number of reactions. As a general rule deuterium compounds react more slowly than do the correspond-

ing hydrogen compounds, but the difference is much greater than can be explained by the smaller collision number for the deuterium compound, resulting from its larger mass and consequently smaller velocity. Other explanations must be sought and two appear probable (Cremer and Polanyi, 1932). In the reaction between a hydrogen molecule and a molecule AB, for example, the molecules H_2 and AB must acquire a certain energy of activation before reaction can occur : this may be interpreted in the sense that the reactants must combine to form an intermediate activated complex, H_2AB, possessing potential energy in excess of the normal value for $H_2 + AB$. The situation may be represented diagrammatically in the form of a potential-energy curve (Fig. 11), the left-hand side representing the reactants and the right the resultants, whereas the height of the peak, or energy barrier, is the energy of the activated complex, which may be called E^*. The energy of activation is then the difference between E^* and the combined energy of the molecules. In comparing reactions between H_2 and AB, and between D_2 and AB, it may be assumed, as a first approximation, that the potential energies of the intermediate states H_2AB and D_2AB are the same, so that the difference in the energies of activation for the processes

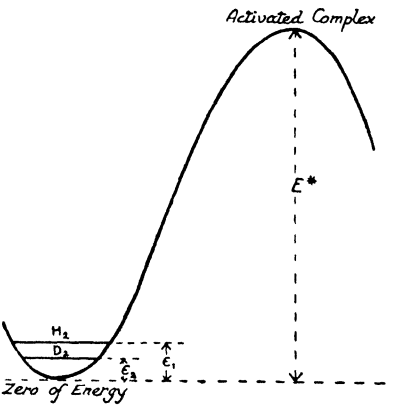


FIG. 11.—Diagrammatic representation of potential-energy change in reactions involving hydrogen and deuterium molecules.

$$H_2 + AB = HA + HB$$

and

$$D_2 + AB = DA + DB$$

will depend on the difference in the fundamental energies, that is, in the zero-point energies, of the H_2 and D_2 molecules. If it is supposed that these must acquire the whole of the requisite energy

necessary to pass over the barrier, then the activation energies E_1 and E_2, for the hydrogen and deuterium reactions, respectively, may be written

$$E_1 = E^* - \varepsilon_1$$

and

$$E_2 = E^* - \varepsilon_2$$

where ε_1 and ε_2 are the respective zero-point energies. The velocity constant k of a reaction may be written in the form (see p. 271),

$$k = PZe^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv.)}$$

where Z is the number of collisions per molecule, P the steric factor and E the energy of activation. Hence, assuming P and Z to be the same for hydrogen and deuterium, although for the latter Z will be the smaller, it follows that

$$k_1 = PZe^{-E_1/RT} \quad \text{and} \quad k_2 = PZe^{-E_2/RT}$$

for the velocity constants of the two reactions. Dividing one by the other, and inserting the values of E_1 and E_2 in terms of E^* and ε_1 and ε_2, it is seen that

$$\frac{k_1}{k_2} = e^{(\varepsilon_1 - \varepsilon_2)/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xv.)}$$

Since $\varepsilon_1 - \varepsilon_2$ for H_2 and D_2 is about 1790 cals. (p. 157), there will be a marked difference in the rates of the two reactions, especially if the temperature is not too high. An analogous difference in reaction velocity, due to differences in energy of activation, should be found for all compounds containing H and D: the zero-point energies for the particular compounds can be calculated from spectroscopic data, and hence the ratio of the velocity constants determined.

It is important to note that since atoms have virtually no zero-point energy, this difference in reactivity between hydrogen and deuterium is not to be expected when the atoms react, as for example in reactions of the type

$$H + AB = HA + B$$

and

$$D + AB = DA + B;$$

in such cases the difference in the velocity constants would depend

only on the fact that collisions between H and AB will occur more frequently than between D and AB. In this discussion it has been assumed that the intermediate activated complexes possess the same potential energy for hydrogen and deuterium compounds : this is not necessarily the case, as will be seen later, and the difference may have an important effect.

The "Tunnel Effect." The second factor which may favour reactions with H_2 over those with D_2 is the quantum-mechanical "tunnel" effect already mentioned in connection with the separation of the isotopes by electrolysis (p. 150). The expression for the permeability of a potential barrier by a given particle contains the term $e^{1/m}$, where m is the mass of the particle : with a heavy atom or molecule leakage through the barrier should be much smaller than for the lighter isotopic form of the same substance. It is evident, therefore, that this effect would tend to increase the velocity of a reaction involving hydrogen *molecules or atoms*, as compared with the same reaction in which deuterium molecules or atoms take part. There is, as yet, no clear indication that this tunnel effect does occur in chemical reactions : an experiment to provide evidence for it, namely, the catalytic reduction of styrene by hydrogen, and by deuterium (Cremer and Polanyi, 1932), failed to give any positive result, but the possibility of its existence must be borne in mind.

Having considered some general aspects of reactions involving deuterium, a few interesting cases will now be discussed in more detail.

Ortho–Para-Deuterium Conversion. One of the simplest reactions involving deuterium is the homogeneous conversion, at high temperatures, of the ortho- to the para-form. By making use of the catalytic effect of charcoal at the temperature of liquid hydrogen, almost pure ortho-deuterium can be obtained, and this remains unchanged, in a metastable state, for some time at ordinary temperatures. By heating to about 600° C., however, the re-establishment of the equilibrium proportions, viz., two parts of ortho to one part of para, takes place at a measurable velocity. The order of the reaction, as with the corresponding para- to ortho-hydrogen conversion (p. 118), has been found to be 1·5

(Farkas and Farkas, 1935), so that the mechanisms of the two processes are probably similar, that for deuterium being

$$D + \text{ortho-}D_2 = \text{para-}D_2 + D.$$

The velocity of this reaction, over the temperature range 600° to 750° C., is about 2·5 times as slow as that of the analogous change

$$H + \text{para-}H_2 = \text{ortho-}H_2 + H.$$

By making allowance for the difference in the collision frequencies for hydrogen and deuterium, atoms and molecules, and

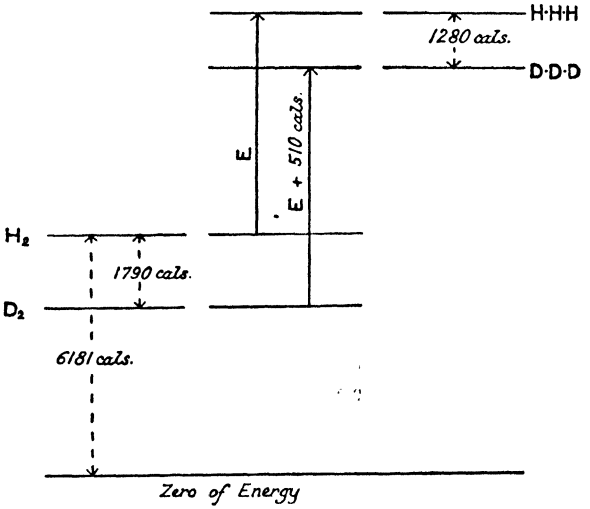


FIG. 12.—Diagrammatic representation of energy levels of initial and activated states for the ortho–para conversion of hydrogen and of deuterium. (After Farkas and Farkas.)

the difference in the extent of dissociation of the molecules, it appears that the energies of activation differ by only 510 cals., instead of the expected value of 1790 cals., representing the difference in the zero-point energies of hydrogen and deuterium molecules. This anticipation, however, is based on the supposition that the activated complexes, which will be different for the two reactions, thus DDD and HHH, respectively, have the same zero-point energies. The intermediate complexes probably possess, to some extent, the properties of real molecules, and consequently

definite vibrational frequencies must be ascribed to the various bonds present in them, leading to definite zero-point energies. If this is the case, it must follow that the zero-point energy of DDD, involving the heavier atoms, is less than that for HHH, assuming the force constants to remain almost unchanged. If the zero-point energy of the DDD complex is 1280 cals. less than the energy for the complex HHH, the activation energies for the two reactions under discussion will only differ by 1790 — 1280 = 510 cals., the observed value. From general considerations Farkas and Farkas (1935) have shown that this difference in the zero-point energies of the hydrogen and deuterium complexes, required to account for the observations, is quite reasonable. The ortho- to para-deuterium conversion is, therefore, a reaction of great importance as it emphasises the necessity of making allowance for the zero-point energy of the intermediate complex in a chemical reaction.

The Molecular Hydrogen–Deuterium Reaction. The homogeneous reaction between hydrogen and deuterium molecules,

$$H_2 + D_2 = 2HD,$$

takes place readily at temperatures between 600° and 750° C., and in this range the process, like the high-temperature homogeneous ortho- to para-conversion, is kinetically of the order 1·5 ; the rate of the former reaction is, however, about 1·6 times as fast as that of the latter over the range of temperature mentioned. It appears, therefore, that the molecular hydrogen–deuterium reaction probably takes place in two stages, each involving an atom and a molecule ; thus

$$D + H_2 = HD + H$$

and

$$H + D_2 = HD + D,$$

the D atoms resulting from the dissociation of deuterium molecules. The zero-point energies of the intermediate complexes involved in the two stages, namely, DHH and HDD, are probably almost identical (Farkas and Farkas, 1935), and so the activation energies of the two reactions differ by about 1,700 cals. As is to be expected, the second stage is the slower process, requiring the

higher energy of activation. It is of some interest that the first step mentioned above is probably as rapid as, if not more rapid than, the corresponding reaction involving a hydrogen atom and molecule: this may be accounted for by the lower zero-point energy of the DHH complex as compared with that of HHH.

Heterogeneous Hydrogen–Deuterium Reaction. Although the reaction $H_2 + D_2 \rightleftharpoons 2HD$ does not occur on charcoal at low temperatures, it does take place with measurable speed on chromium sesquioxide and on finely divided nickel catalysts at temperatures as low as −190°C. (Gould, Bleakney and Taylor, 1934). The heterogeneous reaction is also rapid on a heated nickel wire. A very definite parallelism has been observed between the molecular hydrogen–deuterium reaction and the para-hydrogen to ortho-hydrogen conversion on nickel catalysts at ordinary temperatures; the observed order of both reactions is about 0·7 at 14° C., and the ratio of the velocities is approximately constant at 3 to 1 for catalysts of widely varying activity (Bonhoeffer, Bach and E. Fajans, 1934; E. Fajans, 1935). The apparent heats of activation are 7400 cals. for the $H_2 + D_2 = 2HD$ reaction, and 6000 cals for the para-H_2 = ortho-H_2 conversion. The latter process probably involves the intermediate formation of atoms, as a result of activated adsorption, and in view of the similarity of the two reactions, the former must have a similar mechanism. The adsorbed hydrogen and deuterium molecules are dissociated on the surface and the resulting atoms can re-combine to form either H_2, D_2 or HD, thus establishing the equilibrium. The difference in the apparent heats of activation, 1400 cals., is approximately equal to the difference in the zero-point energies of the hydrogen and deuterium molecules, and so it appears that the dissociation in each case involves passage through the same, or similar, activated state. From these observations it must be concluded that activated adsorption occurs on the chromium sesquioxide and finely divided nickel catalysts at low temperatures, since they are able to bring about the hydrogen–deuterium reaction. On charcoal, however, no such catalysis is to be expected, since the efficacy of this substance in connection with the ortho- to para-hydrogen process at low

temperatures is not due to its facilitation of dissociation into atoms, but to the actual reversal of the nuclear spin by the paramagnetic surface (p. 122).

Equilibrium Constants. The equilibrium constant of the $H_2 + D_2 \rightleftharpoons 2HD$ reaction at various temperatures can be readily calculated by the methods described in Chapter II. (Urey and Rittenberg, 1933); substituting the appropriate values in equation (lv.), p. 93, it is seen that

$$-\ln K = \frac{\Delta E_0^\circ}{RT} - \frac{3}{2}\ln\frac{M_{HD}^2}{M_{H_2}M_{D_2}} - \ln\frac{I_{HD}^2}{I_{H_2}I_{D_2}} - \ln 4 \quad \text{(xvi.)}$$

where K is equal to $[HD]^2/[H_2][D_2]$. The symmetry numbers (s) involved are 2 for H_2 and D_2 and 1 for HD. The term ΔE_0° is the difference in the zero-point energies of resultants and reactants, thus,

$$\begin{aligned}\Delta E_0^\circ &= 2(E_0^\circ)_{HD} - (E_0^\circ)_{H_2} - (E_0^\circ)_{D_2} \\ &= 157 \text{ cals.}\end{aligned}$$

The moments of inertia may be calculated from the B_e values given in Table XVIII., which may be put equal to $h/8\pi^2 Ic$. The equlibrium constants for a number of temperatures determined by means of equation (xvi.) are given in Table XXIV. (Farkas, 1935).

TABLE XXIV

Equilibrium Constants of the $H_2 + D_2 \rightleftharpoons 2HD$ Reaction.

Temp.	K.	Temp.	K.
50° K.	1·345	400°K.	3·494
100°	2·265	575°	3·710
298°	3·269	700°	3·800

The value of the equilibrium constant has been determined experimentally in a number of ways: by allowing a mixture of hydrogen and deuterium to attain equilibrium in contact with a catalyst, as for example, chromium sesquioxide or nickel, at various temperatures, viz., —190°, —78°, 0° and 100° C. (Gould, Bleakney and Taylor, 1934); by decomposing mixtures of HI

and DI with mercury at 25°, or by heating to 397° or 468° C.; in each case the proportion of H_2, D_2 and HD in the gas was determined by means of the mass spectrograph (Rittenberg, Bleakney and Urey, 1934). The observed and calculated results, for a number of temperatures, are quoted in Table XXV.

TABLE XXV

Observed and Calculated Equilibrium Constants for the Reaction

$$H_2 + D_2 \rightleftharpoons 2HD.$$

Temp.	Equilibrium Constant.	
	Observed.	Calculated.
− 190°C.	2·30	2·2
− 78°	2·80–3·01	2·88
0°	2·96–3·37	3·19
25°	3·28	3·27
110°	3·45–3·67	3·46
397°	3·35–4·20	3·78
468°	3·68–3·82	3·82

In view of the difficulties in analysing the equilibrium mixtures the agreement between the experimental and calculated equilibrium constants is very satisfactory. It should be noted that if there had been no zero-point energies, that is, according to classical treatment, since the existence of a definite zero-point energy follows from the application of wave mechanics or from the " uncertainty principle," the equilibrium constant of the molecular hydrogen–deuterium reaction would have depended on kinetic factors only, and the value would have been 4, at all temperatures. This value is only approached at high temperatures, when the effect of the difference in the zero-point energies becomes negligible.

Hydrogen–Water Reactions. The complete equilibrium between the isotopic forms of both hydrogen and water can be made to depend on two reactions, in addition to the one between hydrogen and deuterium molecules already considered; they are

(1) $HD + H_2O \rightleftharpoons HDO + H_2$

and (2) $H_2O + D_2O \rightleftharpoons 2HDO,$

the equilibrium constants being written K_1 and K_2, respectively. From these three it is possible to derive all the exchange equilibria involving the three forms of hydrogen, namely, H_2, D_2 and HD, and the three isotopic forms of water, viz., H_2O, D_2O and HDO.

Although there is no appreciable homogeneous exchange reaction between hydrogen and water, the presence of a catalyst, such as platinum or palladium black, is able to facilitate the process. By passing hydrogen gas, enriched with respect to deuterium, into an aqueous solution in which platinum black is suspended, the exchange reaction

$$HD + H_2O \rightleftharpoons HDO + H_2$$

takes place (Horiuti and Polanyi, 1933, 1934): the mechanism suggested is that the hydrogen is adsorbed by and ionised on the catalyst, and the ions enter the solution, whilst at the same time an equivalent number of ions from the solution are discharged. This interchange will result in the setting up of the equilibrium between light and heavy hydrogen and light and heavy water, mentioned above. A rapid exchange between water adsorbed on the surface of chromium sesquioxide, zinc oxide, zinc chromite, alumina and platinised asbestos, and heavy hydrogen has been noted (Taylor and Diamond, 1935) at temperatures between 200° and 400° C. The ionic mechanism, postulated for the reaction with liquid water, is unlikely to apply here, and it is supposed that since activated adsorption of hydrogen occurs on all the catalysts, except aluminium oxide, it is presumably atomic deuterium which reacts with the water molecule. It is not impossible that the same mechanism may apply to the exchange reaction involving liquid water, for which the ionisation process has been suggested. Alumina is a good dehydration catalyst, and so it may be assumed that on it the water molecules are activated and react with HD molecules.

At high temperatures a homogeneous exchange reaction between water vapour and light and heavy hydrogen molecules takes place, but the velocity is relatively slow, for the process appears to require a large energy of activation, viz., about 65,000 cals.

The equilibrium constants K_1 and K_2 of the reactions

mentioned at the beginning of this section have been calculated by the statistical methods of Chapter II., but the results are not so precise as those involving diatomic molecules only, because of the uncertainty in the vibration frequencies and in the anharmonicity constants. Some of the values determined in this way are to be found in Table XXVI.; the constants quoted are for the reactions involving gases and vapours only. It may be noted that the "classical" values for K_1 and K_2 are 1 and 4, respectively, and these are approached at high temperatures. The significance of K_1' in the table is explained below.

TABLE XXVI

Equilibrium Constants for Hydrogen–Deuterium Exchange Reactions.

Temp.	3°	20°	65°	100°	450° C.
K_1 Calc. .	2·89	2·67	2·24	1·98	1·23
K_1 Obs. .	2·97	2·67	2·37	2·00	1·15
K_1' . .	3·46	3·05	2·57	2·13	—
K_2 . .	—	3·21	—	3·40	3·76

The values of K_1 have been determined experimentally by allowing liquid heavy water, or its vapour, to react in a closed vessel with light hydrogen gas in the presence of a platinum or palladium catalyst until equilibrium was attained at a given temperature; the gas phase was removed from the catalyst, the water vapour extracted by rapid freezing, and the D/H ratio in the hydrogen gas and in the water determined by the thermal-conductivity method.

If the reaction

$$HD\ (gas) + H_2O\ (liquid) \rightleftharpoons HDO\ (liquid) + H_2\ (gas)$$

is considered, the equilibrium constant (K_1') may be represented by

$$K_1' = \left(\frac{[H_2]}{[HD]}\right)_{gas} \Big/ \left(\frac{[H_2O]}{[HDO]}\right)_{liquid.}$$

The experimental values, the importance of which in connection with the partial separation of hydrogen and deuterium has been

already discussed (p. 148), are also given in Table XXVI. above; they are obtained by analysis of the hydrogen gas phase, after removing the water vapour, and of the liquid water left in contact with the catalyst. When the deuterium content of the water is small, it may be assumed that in the gas the deuterium is all present as HD, and in the liquid phase as HDO, molecules. At higher concentrations the amounts of these substances can be calculated from known equilibrium constants.

When hydrogen and deuterium gases are evolved from any specimen of water, the equilibrium represented by the constant K_1' should be established : in electrolysis this is true, at least approximately, only when the electrode is of platinised platinum and the current density is low. When hydrogen is liberated from enriched water, by the action of certain salts, *e.g.*, potassium cobaltocyanide, viz.,

$$K_4Co(CN)_6 + H_2O = K_3Co(CN)_6 + KOH + \tfrac{1}{2}H_2,$$

or by the catalytic decomposition of sodium formate by palladium black, or by certain enzymes, viz.,

$$H{\cdot}CO_2Na + H_2O = H_2 + CO_2 + NaOH,$$

the expected equilibrium is established, a value of K_1' of the order of 3 being obtained at room temperatures.

Hydrogen–Halogen Reactions. The thermal reactions of deuterium and of hydrogen with bromine have been studied, and the rates compared : they are expressible by the relationships

$$k_1 = 6{\cdot}92 \times 10^{10} \times e^{-17{,}740/RT}$$

and

$$k_2 = 8{\cdot}34 \times 10^{10} \times e^{-19{,}870/RT}$$

where k_1 and k_2 are the velocity constants for hydrogen and deuterium, respectively. These results imply that the energies of activation differ by about 2000 cals., and this is in agreement with the accepted mechanism. The first stage in the hydrogen–bromine reaction is undoubtedly the dissociation of the bromine molecules into atoms, followed by

$$Br + H_2 = HBr + H$$

as the rate-determining stage in the process, which is actually somewhat complicated and follows a chain mechanism (see

" Recent Advances in Physical Chemistry," Chapter VI.). The corresponding stage for the deuterium reaction should be

$$Br + D_2 = DBr + D,$$

and the energy of activation of this process should differ from that for the lighter isotope by the difference in the zero-point energies of the hydrogen and deuterium molecules, that is, about 1800 cals. In view of the complexity of the reaction the agreement with the observed values is as close as could be expected.

The photochemical union of chlorine and hydrogen, or deuterium, has been studied both directly (Farkas and Farkas, 1934) and also in the presence of carbon monoxide (Rollefson, 1934), and marked differences in velocity found. In the latter case, the relative velocities for hydrogen and deuterium were 13·4 to 1 at 0°, and 9·75 to 1 at 32° C. It is well known that the hydrogen–chlorine combination involves a chain mechanism, and one of the stages must consequently involve the breaking of a hydrogen or deuterium linkage. The essential reactions in the chain propagation have been suggested as being

$$Cl + H_2 = HCl + H$$

and

$$H + Cl_2 = HCl + Cl.$$

The second step will have very nearly the same velocity for hydrogen and deuterium since molecules are not involved, but the first step will be more rapid for the lighter isotope. Applying the equation (xv.), p. 168, to the ratio of the observed velocity constants, the difference in the zero-point energies is found to be 1630 cals., which is in excellent harmony with the known difference for hydrogen and deuterium. These results tend to confirm the generally accepted mechanism for the main stages of the photochemical hydrogen–chlorine reaction.

The equilibrium

$$H_2 + 2DI \rightleftharpoons D_2 + 2HI$$

has been studied both theoretically and practically. From the statistical equation (p. 93) it follows that

$$-\ln K = \frac{\Delta E_0^\circ}{RT} - \tfrac{3}{2}\ln\frac{M_{D_2}M_{HI}^2}{M_{H_2}M_{DI}^2} - \ln\frac{I_{D_2}I_{HI}^2}{I_{H_2}I_{DI}^2}.$$

The s term cancels out, since the symmetry numbers of H_2 and D_2 are both 2, and those of HI and DI are both unity. Since the spectroscopic constants of H_2, DI, D_2 and HI are known with some accuracy, reliable zero-point energies and moments of inertia are available, and so the equilibrium constant at various temperatures can be calculated. The constant K for this reaction is the ratio of the dissociation constants of HI and DI, and the calculated values have been confirmed experimentally by measuring the amount of iodine formed on heating mixtures of hydrogen and deuterium iodides (Rittenberg and Urey, 1934). In evaluating K from the experimental data it must be remembered that the equilibrium $H_2 + D_2 \rightleftharpoons 2HD$ is probably established at the same time, and allowance must be made for this.

The equilibrium constants of the corresponding reaction with hydrogen chloride

$$H_2 + 2DCl \rightleftharpoons D_2 + 2HCl$$

have been calculated and also verified experimentally (Cross and Leighton, 1936; Gross and Steiner, 1936). A mixture containing known amounts of hydrogen and deuterium was allowed to react with a definite quantity of hydrogen chloride in a quartz vessel at temperatures between 500° and 570° C., and pressures somewhat less than atmospheric. Under these conditions the reaction is mainly homogeneous and bimolecular. After equilibrium was attained, which took some time, the hydrogen and deuterium chlorides were removed by condensation and the hydrogen and deuterium content of the residual gas determined. From these data the requisite equilibrium constant can be evaluated.

Hydrogen–Oxygen Reaction. The homogeneous combination of hydrogen and oxygen at temperatures of about 500° C. is a very complex process, involving a branching chain mechanism ("Recent Advances in Physical Chemistry," Chapter V.); as the pressure is increased, at a given temperature, a point is attained at which the reaction suddenly becomes explosive. At lower pressures the chain-propagating radicals are de-activated by impacts with the walls of the vessel, but when the rate of propagation of chains just exceeds the rate of de-activation a rapid

explosive reaction sets in. This rapid-reaction stage continues over a range of pressure, but with further increase a condition is reached when the rate of breaking the chains, by collisions between molecules in the gas phase, just compensates the rate of propagation : the reaction velocity, at this pressure, then falls to a normal value. There are consequently two pressure limits, lower and upper, between which the chain reaction is explosive. When hydrogen is replaced by deuterium the lower pressure limit, under given conditions, remains almost unchanged ; this is to be expected from the theory that chains terminate at the walls, provided no hydrogen bonds are broken in the chain-branching process, for otherwise the different zero-point energies of the radicals or molecules concerned would result in a difference in the rate of chain propagation. The upper explosive limit is, however, definitely raised when deuterium replaces hydrogen ; at any given temperature, for mixtures consisting of $2D_2 + O_2$, or of $2H_2 + O_2$, the limiting pressures bear a ratio to one another of 1·31 to 1. This result is in harmony with the theory of the upper limit given above ; since the deuterium molecules have a smaller velocity, the collisions between them and the activated complexes are less frequent than with hydrogen molecules, so that the rate at which chains are broken, at a given pressure, is less. A higher pressure of deuterium is, therefore, necessary to produce the same rate of breaking chains, and so suppress the explosive reaction. By making a number of reasonable assumptions the ratio of the upper limiting pressure for deuterium to that for hydrogen has been calculated as 1·29 to 1. The velocity of the steady non-explosive reaction between hydrogen and oxygen, at a temperature of about 560° C., and a total pressure of 450 mm. of mercury is found to be up to 2·5 times as fast as the corresponding reaction with deuterium ; under these conditions molecules containing hydrogen and deuterium bonds are evidently involved in the chain mechanism, and the difference in their zero-point energies results in the different reaction velocities (Frost and Alyea, 1934 ; Hinshelwood, Williamson and Wolfenden, 1934).

Hydrogen and deuterium atoms in excess, produced by the mercury-photosensitised decomposition of the corresponding

molecules, react at the same speed with molecular oxygen at a temperature of 20° C.; the rate-determining step is evidently a reaction between hydrogen or deuterium atoms and oxygen molecules, probably in a three-body collision. The energies of activation are then almost the same. The larger number of collisions in which hydrogen atoms are involved, as compared with deuterium atoms, is probably compensated by the lower concentration of the former, resulting from their diffusion to the walls of the vessel where they combine to form molecules (M. G. Evans, 1934; Melville, 1934). From a study of the photochemical oxidation of hydrogen and deuterium iodides, it has been concluded that the two processes, $H + O_2 + O_2$ or $D + O_2 + O_2$, also take place at almost the same velocity (Cook and Bates, 1935). At higher temperatures, between 250° and 400° C., chains are propagated in the reaction between atomic hydrogen and molecular oxygen; the speeds are then different for the two isotopes, showing that molecules or radicals with hydrogen or deuterium bonds having different zero-point energies are involved. The rate-determining stages may then be

$$OH + H_2 = H_2O + H,$$

and

$$OD + D_2 = D_2O + D,$$

followed by a series of reactions in which the OH or OD radicals are regenerated. The reaction is then probably analogous to that occurring between molecular hydrogen and oxygen at 530° C., to which reference has already been made.

Nitrous Oxide–Hydrogen Reaction. Nitrous oxide behaves in a similar manner to oxygen in its reaction with hydrogen and deuterium atoms, the rates being the same at 20° C.; they are, however, also very close at higher temperatures when a chain reaction is occurring. It is evident that in this process no linkages involving hydrogen or deuterium are broken, and this is in agreement with the suggestion, made previous to this work (Melville, 1934), that the rate-determining stage in the chain process is

$$H + N_2O = N_2 + OH.$$

The reactions of light and of heavy hydrogen with oxygen and with

nitrous oxide have also been studied on various surfaces: the lighter isotope always reacts more rapidly, and the results are readily explicable when allowance is made for the different masses of hydrogen and deuterium, and the difference in the zero-point energies, either of the molecules or of complexes formed on the surface between the catalyst and hydrogen or deuterium atoms.

The Hydrogen–Ethylene Reaction. When investigating the catalytic hydrogenation of ethylene, by means of a mixture of light and heavy hydrogen, on a nickel wire catalyst, the surprising observation was made by measuring simultaneously the change in pressure and in the deuterium content of the gas, that under certain conditions an exchange reaction,

$$C_2H_4 + HD \rightleftharpoons C_2H_3D + H_2$$

takes place in addition to the hydrogenation process

$$C_2H_4 + H_2 = C_2H_6.$$

At 20° C. the latter reaction predominates, but at 120° considerable exchange, resulting in a decrease of the deuterium content of the hydrogen, can be detected (Farkas, Farkas and Rideal, 1934). It appears that when the ethylene is adsorbed on the nickel surface it becomes activated and dissociated into one or more hydrogen atoms and a radical, *e.g.*, $C_2H_3\cdot$; the HD molecules are simultaneously dissociated into H and D atoms, and consequently there is a possibility, when the $C_2H_3\cdot$ radical and a D atom meet on the surface, for C_2H_3D to be formed. Benzene and HD exchange similarly, on platinum black and nickel catalysts, at a greater rate than that of the hydrogenation process (Horiuti, Ogden and Polanyi, 1934).

Decomposition of Ammonia. The photochemical decomposition of ammonia is another example of a reaction upon which light has been thrown by the use of deuterium. Radiation of wavelength 2100 Å. alone is capable of bringing about photochemical decomposition of ammonia, and the primary reaction has generally been regarded as

$$NH_3 + \text{radiation} \rightarrow NH_2 + H.$$

The quantum efficiency is low, so that the reverse reaction, $NH_2 + H = NH_3$, no doubt occurs to a considerable extent. In

the presence of mercury vapour, hydrogen and deuterium molecules are known to be dissociated into atoms, when illuminated by light of 2537 Å. wavelength. Consequently when a mixture of deuterium and ammonia, containing a little mercury, is exposed to both these wavelengths simultaneously, the reaction

$$NH_2 + D = NH_2D$$

should take place to some extent, and the hydrogen atoms in the ammonia should be gradually replaced by deuterium atoms (Taylor and Jungers, 1934). This change has, in fact, been observed by the examination of the absorption spectra of the gases. The exchange reaction

$$NH_3 + D = NH_2D + H,$$

which has been suggested by some authors, probably does not occur, since when the 2100 Å. radiation is completely eliminated there appears to be no alteration in the ammonia.

The heterogeneous exchange reaction between ammonia and deuterium has been examined on a finely divided iron catalyst at 160° to 230° C. (A. Farkas, 1936); the process is much slower, requiring a higher energy of activation, than either the ortho- to para-deuterium conversion or the molecular hydrogen–deuterium reaction on the same catalyst, both of which probably involve dissociation into atoms (see p. 172). It appears that the following stages occur rapidly on the catalytic surface :

$$NH_3 = NH_2 + H, \quad D_2 = 2D \quad \text{and} \quad H + D = HD,$$

but the rate-determining step is

$$D + NH_2 = NH_2D,$$

which is a slow process.

The homogeneous ammonia–deuterium exchange reaction at 680° to 780° C. involves a mechanism of quite a different type; the rate is determined by the stage

$$D + NH_3 = NH_2D + H,$$

the requisite deuterium atoms being formed by thermal dissociation of the deuterium molecules. It may be noted that under the

conditions of the experiments the reaction $NH_3 = NH_2 + H$ occurs only to a negligible extent (A. Farkas, 1936): this has been shown by calculation of the equilibrium constant by the partition-function method; and also by the fact that the ammonia, in the appropriate temperature range, has no influence on the para- to ortho-hydrogen conversion (*cf.* p. 122).

Reactions in Solution. The hydrolysis of sucrose and of methyl and ethyl acetates, catalysed by D_3O^+ ions, takes place about 1·7 times more rapidly than when H_3O^+ ions are the catalysts; it appears that the intermediate complex, between the molecule X being hydrolysed and the deuteron, thus X—D^+, is formed more readily than that involving a proton, thus X—H^+. The rate of reaction may be taken as proportional to the concentration of the critical activated complex (see Chapter VII.), and so it will be greater for catalysis by D_3O^+ than for H_3O^+. It is possible that the lower zero-point energy of the X—D^+ complex, compared with that of X—H^+, may be a factor to be taken into consideration (Wynne-Jones, 1935).

The mutarotation of *d*-glucose, whether catalysed by D_2O or D_3O^+, is slower than when the catalyst is H_2O or H_3O^+. The differences in the reaction rates can be accounted for by alterations in the molecular velocities and by differences in the zero-point energies. The reaction of nitroethane with OH^- and OD^- ions has been studied (Wynne-Jones, 1935); the process

$$CH_3{\cdot}CH_2{\cdot}NO_2 + OD^- = CH_3{\cdot}CH{:}NO_2^- + HDO$$

takes place 1·5 times as fast as the corresponding stage

$$CH_3{\cdot}CH_2{\cdot}NO_2 + OH^- = CH_3{\cdot}CH{:}NO_2^- + H_2O,$$

indicating that the removal of a proton by the OD^- ion is more probable than the removal by OH^- ions, that is, OD^- is a stronger base than is OH^-. The latter process is much more rapid than the one involving

$$CH_3{\cdot}CD_2{\cdot}NO_2 + OD^- = CH_3{\cdot}CD{:}NO_2^- + D_2O,$$

the ratio of the velocities being accounted for by differences in zero-point energies, since in one case a C—H bond, and in the other a C—D bond, is broken.

The rate of alcoholic fermentation of α-glucose is about eight or nine times more rapid in light water than in heavy water : on the other hand the enzyme emulsin hydrolyses salicin 25 per cent. more rapidly in heavy than in light water. Hydrogen peroxide decomposes more rapidly when catalysed by iodine ions than does the deuterium peroxide : the energies of activation appear to be the same in spite of the difference in the zero-point energies. It is evident that the study of catalytic reactions in heavy water requires a great deal of further attention, and that such investigations are likely to yield results of interest.

Exchange Reactions in Heavy Water. A number of substances containing hydrogen exchange one or more of their hydrogen atoms for deuterium when dissolved in heavy water ; thus,

$$HX + HDO \rightleftharpoons DX + H_2O$$

and

$$HX + D_2O \rightleftharpoons DX + HDO.$$

The hydrogen atoms in the —OH groups of ethylene glycol, glucose, sucrose and other carbohydrates exchange rapidly, and so also do the hydrogen atoms of acetone and acetylene in alkaline solutions. The acetone apparently reacts in the enolic-form, $CH_3{\cdot}C(OH){:}CH_2$, whereas acetylene probably behaves as a weak acid, so that in alkaline solutions C_2H^- ions are present, which unite with deuterium ions to form C_2HD. Numerous other compounds, *e.g.*, formaldehyde, acetaldehyde, hydrogen peroxide, acetyl acetone, egg albumin and cellulose, all exchange to a greater or lesser extent. All the hydrogen atoms in the amines $[Co(NH_3)_6](NO_3)_3$ and $[Cu(NH_3)_4]SO_4.H_2O$ exchange readily with deuterium when dissolved in heavy water : in the second of these compounds the hydrogen atoms present both in the NH_3 and H_2O groups undergo exchange. No reaction, however, has been observed with the hypophosphite KH_2PO_2. Studies of this kind may prove useful in the elucidation of many reaction mechanisms, in providing information concerning the structures of molecules containing hydrogen, and for the preparation of various deuterium compounds.

Benzene and ethylene, like hydrogen gas, do not exchange with liquid water in the absence of a catalyst, but they do so in

the presence of hydrogenation catalysts, such as nickel, palladium or platinum. Of special interest is the exchange reaction between benzene and the vapour of heavy water on a nickel-kieselguhr catalyst at 200° C.; in four stages it has been found possible to convert C_6H_6 into pure C_6D_6.

TRITIUM

The graphical methods which indicated the possibility of the existence of a hydrogen isotope of mass 2, show that a still heavier isotope of mass number 3 might be expected (see Fig. 8). Preliminary investigation by both band-spectroscopic and mass-spectroscopic methods implied that if it existed it was present to the extent of less than two parts in 10^9 of ordinary hydrogen. More careful examination, by means of an improved mass spectrograph, of the hydrogen from 99 per cent. deuterium oxide, obtained by the electrolytic method, showed definitely a line corresponding to a hydrogen isotope of atomic mass 3 (Lozier, Smith and Bleakney, 1934; Tuve, Hafstad and Dahl, 1934). In accordance with the nomenclature used for the isotope of mass 2, the new isotope has been called " tritium," and given the symbol T. The intensity of the line in the mass spectrograph showed it to exist to the extent of only one part, or less, in 10^9 of ordinary hydrogen. It should be possible to concentrate tritium by electrolysis, in a manner analogous to that used for deuterium, and in spite of the very small proportion present, Selwood, Taylor, Lozier and Bleakney (1935) have reported that from the electrolysis of 75 metric tons of ordinary water they have obtained 0·5 c.c. of a residue containing one part of tritium to 4000 of hydrogen, the latter almost entirely as deuterium. The separation coefficient (*cf.* p. 146) for tritium and deuterium was found to be about 2·0 at a nickel cathode, and so the separation is not so efficient as for deuterium and hydrogen.

It has been seen in Chapter I. (p. 26) that the impact of high-speed deuterons on deuterium is supposed to lead to disintegration, represented by the expression

$$ {}^{2}_{1}\mathrm{D} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{T}, $$

and consequently it should be possible after a time to detect the presence of tritium. After passing a positive-ray discharge through deuterium gas for several hours it was examined in the mass spectrograph and a definite increase in the ratio of tritium to deuterium was observed, namely, from one part in 20,000 to one part in 5000 (Harnwell, Smyth, van Voorhis and Kuper, 1934).

REFERENCES

APPLEBEY and OGDEN. *J. Chem. Soc.*, 1936, 163.
BAWN and OGDEN. *Trans. Faraday Soc.*, 1934, **30**, 432.
BELL. *Ann. Reports Chem. Soc.*, 1934, **31**, 13.*
BLEAKNEY. *Physical Rev.*, 1932, **40**, 496 ; **41**, 32.
BLEAKNEY and GOULD. *Ibid.*, 1933, **44**, 265 ; 1934, **45**, 281.
BONHOEFFER, BACH and FAJANS. *Z. physikal. Chem.*, 1934, **168**, 313.
CLUSIUS and BARTHOLOMÉ. *Ibid.*, 1935, [*B*], **29**, 162 ; **30**, 237.
COOK and BATES. *J. Amer. Chem. Soc.*, 1935, **57**, 1775.
CREMER and POLANYI. *Z. physikal. Chem.*, 1932, [*B*], **19**, 443.
CRIST and DALIN. *J. Chem. Physics*, 1933, **1**, 677 ; 1934, **2**, 442, 548.
CRIST, MURPHY and UREY. *Ibid.*, p. 112 ; *J. Amer. Chem. Soc.*, 1933, **55**, 5060.
CROSS and LEIGHTON. *J. Chem. Physics*, 1936, **4**, 28.
EUCKEN and BRATZLER. *Z. physikal Chem.*, 1935, **174**, 279.
EVANS. *J. Chem. Physics*, 1934, **2**, 445.
EYRING and SHERMAN. *Ibid.*, 1933, **1**, 345.
FAJANS. *Z. physikal. Chem.*, 1935, [*B*], **28**, 239.
FARKAS. "Orthohydrogen, Parahydrogen and Heavy Hydrogen," 1935 ;* *Trans. Faraday Soc.*, 1935, **31**, 821 ; *J. Chem. Soc.*, 1936, 26.
FARKAS, FARKAS *et al.* *Proc. Roy. Soc.*, 1934, [*A*], **144**, 16, 467, 481 ; **146**, 623, 630 ; 1935, [*A*], **152**, 124, 152 ; *Trans. Faraday Soc.*, 1934, **30**, 1071 ; *J. Chem. Physics*, 1934, **2**, 468.
FOWLER. *Proc. Roy. Soc.*, 1934, [*A*], **144**, 452.
FROST and ALYEA. *J. Amer. Chem. Soc.*, 1934, **56**, 1251.
GLASSTONE. *Ann. Reports Chem. Soc.*, 1935, **32**, 40.*
GOULD, BLEAKNEY and TAYLOR. *J. Chem. Physics*, 1934, **2**, 362.
GROSS and HALPERN. *Ibid.*, 1935, **3**, 452.
GROSS and STEINER. *Ibid.*, 1936, **4**, 165.
HARNWELL, SMYTH, VAN VOORHIS and KUPER. *Physical Rev.*, 1934, **45**, 655.
HINSHELWOOD, WILLIAMSON and WOLFENDEN. *Proc. Roy. Soc.*, 1934, [*A*], **147**, 48 ; *Nature*, 1934, **133**, 836.
HORIUTI and POLANYI. *Ibid.*, 1933, **132**, 819 ; 1934, **133**, 142 ; **134**, 377.
HUGHES, INGOLD and WILSON. *J. Chem. Soc.*, 1934, 493.
JOHNSTON. *J. Amer. Chem. Soc.*, 1931, **53**, 2866.
JOHNSTON and LONG. *J. Chem. Physics*, 1934, **2**, 389.
KEESOM *et al.* *Proc. K. Akad. Wetensch. Amsterdam*, 1933, **36**, 248.
KING, JAMES, LAWSON and BRISCOE. *J. Chem. Soc.*, 1935, 1545.
LEWIS and MACDONALD. *J. Chem. Physics*, 1933, **1**, 341.
LEWIS *et al.* *J. Amer. Chem. Soc.*, 1933, **55**, 2616, 3057, 3504, 4370, 4731, 5061 ; 1934, **56**, 493, 1000, 1001, 1002, 1913.
LOZIER, SMITH and BLEAKNEY. *Physical Rev.*, 1934, **45**, 655.
MELVILLE. *J. Chem. Soc.*, 1934, 797, 1243.

MELVILLE and RIDEAL. *Proc. Roy. Soc.*, 1935, [*A*], **153**, 77, 89.
MOTZ and PATAT. *Monatsh.*, 1934, **64**, 17.
MURPHY and JOHNSTON. *Physical Rev.*, 1934, **45**, 500, 761 ; **46**, 95.
OGDEN. *Nature*, 1935, **136**, 912.
RITTENBERG, BLEAKNEY and UREY. *J. Chem. Physics*, 1934, **2**, 48.
RITTENBERG and UREY. *Ibid.*, p. 106.
ROLLEFSON. *Ibid.*, p. 144.
SELWOOD, TAYLOR, LOZIER and BLEAKNEY. *J. Amer. Chem. Soc.*, 1935, **57**, 780.
STERN and VOLMER. *Ann. Physik*, 1919, **59**, 225.
SUTHERLAND. *Ann. Reports Chem. Soc.*, 1935, **32**, 53.*
TAYLOR *et al.* *J. Chem. Physics*, 1934, **2**, 373, 452 ; 1935, **3**, 338 ; *J. Amer. Chem. Soc.*, 1933, **55**, 5057 ; 1934, **56**, 998 ; 1935, **57**, 383, 679.
TAYLOR, EYRING and FROST. *J. Chem. Physics*, 1933, **1**, 823.
TOPLEY and EYRING. *Ibid.*, 1934, **2**, 217.
TUVE, HAFSTAD and DAHL. *Physical Rev.*, 1934, **45**, 840.
UREY. *J. Amer. Chem. Soc.*, 1931, **53**, 2872.
UREY, BRICKWEDDE and MURPHY. *Physical Rev.*, 1932, **39**, 164, 864 ; **40**, 1464 ; *J. Chem. Physics*, 1933, **1**, 513.
UREY and GRIEFF. *J. Amer. Chem. Soc.*, 1935, **57**, 321.
UREY and RITTENBERG. *J. Chem. Physics*, 1933, **1**, 137.
UREY and TEAL. *Rev. Mod. Physics*, 1935, **7**, 34.*
WASHBURN and SMITH. *J. Chem. Physics*, 1933, **1**, 426.
WEBSTER, WAHL and UREY. *Ibid.*, 1935, **3**, 129.
WOLFENDEN. *Ann. Reports Chem. Soc.*, 1933, **30**, 28.*
WYNNE-JONES. *J. Chem. Physics*, 1934, **2**, 381 ; *Chem. Reviews*, 1935, **17**, 115.*

* Review papers and books, wherein further references can be found, are marked with an asterisk.

CHAPTER V

ELECTRON DIFFRACTION BY GASES AND VAPOURS

The Scattering of X-rays. The regular arrangement of atoms and molecules in a crystal leads to the production of X-ray diffraction patterns which, for simple molecules at least, are relatively easy to interpret, since the distance apart of successive reflecting planes of the same type is constant and definite. The results, as is well known, permit of the interpretation of the structures of the molecules constituting the crystal and provide information concerning inter-atomic distances. Liquids are also able to diffract X-rays, but the patterns are somewhat more difficult to understand : interference results not only from scattering by the atoms within an individual molecule, that is, on account of intra-molecular effects, but inter-molecular effects, due to interference between rays scattered by two or more molecules in close proximity, are superimposed. When a gas, or vapour, under relatively low pressure is considered, however, the molecules are so far apart that inter-molecular effects are negligible, and the observed X-ray pattern is due to the scattering of separate atoms within each molecule. Since the molecules of a gas are in continual motion there is no definite orientation of the molecules with respect to the X-ray beam, and so, as in the powder method for studying crystals, rays are reflected over a series of solid angles, which produce a number of concentric rings on a photographic plate inserted across their path. From the positions of these diffraction rings it should be possible to obtain information concerning the distances apart of the atoms in the gas molecule.

X-Rays and Electron Waves. The mathematical treatment of the scattering of X-rays by gases was first developed independently by Debye and by Ehrenfest in 1915, but it was not until 1929 that the experimental applications of the concept were made by Debye,

Bewilogua and Ehrhardt. A number of substances, as for example, the four chloromethanes, *cis*- and *trans*-dichloroethylene, carbon dioxide and disulphide, were studied by these authors, and also by Gajewski (1931, 1932), Bewilogua (1932) and Ehrhardt (1932), and interesting results were obtained. It seemed, at one time, as if the X-ray method for the study of the structure of gas molecules was likely to prove a valuable means of investigation, but in the meantime the analogous application of electron waves has proved to be very much simpler, and has become of considerable importance. It is now a familiar fact, following on the early discoveries of Davisson and Germer, and of G. P. Thomson and others, that electrons can behave as waves, and can be scattered and show diffraction effects similar to those exhibited by X-rays. The wavelength of the electron waves is given, apart from the relativity correction, by the de Broglie equation $\lambda = h/mv$, where h is the Planck constant, and m the mass and v the velocity of the electron. This equation may be written in the form $\lambda = \sqrt{150/V} \times 10^{-8}$ cm., where V is the potential in volts by which the electrons are accelerated, so that with a voltage of about 60,000 across a discharge tube a beam of electrons with an effective wavelength of 0·05 Å. is produced.

The shortness of the wavelength of electron waves, as compared with a value of about 1 Å. for normal X-rays, means that the diffraction rings produced by a given substance, as for example a gas, in the manner already considered, will be much closer together when electrons are employed than with X-rays. Theoretically, therefore, it should be possible to get more accurate results from measurements with the latter, but there are at least two factors which compensate for the apparent advantage of X-rays in this work. The possibility of obtaining, without great difficulty, intense electron beams which have a strong photographic effect, has meant that very satisfactory diffraction photographs of gases can be obtained in a few seconds instead of the many hours required by X-rays. Further, the maximum value for the function $(\sin \theta/2)/\lambda$ obtained in this kind of work with X-rays is about 0·65, whereas values of 1·9 or more have been reported for electrons: this means that a larger number of rings can be

observed with the latter, a fact of a great importance since the intensities of the first few rings are often obscured by extraneous effects, as will be seen later. For these reasons, and because of the relative simplicity of the apparatus required, the electron-diffraction method has attracted greater attention, and it has, in practice, proved possible to obtain more accurate results in this way than when X-rays were employed. The principles involved in the use of X-rays and of electrons are fundamentally the same, and so in the present chapter these principles will be considered only as far as they affect the application of the electron-diffraction method to the study of the structures of gaseous molecules.

Coherent Scattering. The scattering of electrons, like that of X-rays, is of two types : these are coherent, or elastic, scattering which is the most important, and the incoherent, or inelastic, scattering due to the change of wavelength of the scattered radiation as a result of the Compton effect. The incoherent scattering is generally only important at small scattering angles and, as will be seen later, is frequently neglected. Mark and Wierl (1930) showed that the variation of the intensity of the coherent scattering of high-velocity electrons with the scattering angle could be represented by an equation similar to those deduced by Debye and by Ehrenfest for X-rays ; thus, when the scattering angle, that is, the angle between the primary and the scattered electron beam, is θ, then the intensity of the latter is given by the expression

$$I = k\Sigma_i\Sigma_j\psi_i\psi_j \frac{\sin x_{ij}}{x_{ij}} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

where k is a constant, ψ is the scattering factor of the particular atom for electrons, and

$$x_{ij} = \frac{\sin \theta/2}{\lambda} 4\pi l_{ij} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

the term l_{ij} being the distance between the centres of the atoms designated by i and j, and λ is the equivalent wavelength of the electrons, which may be evaluated by means of the de Broglie equation given above, or in other ways. Equation (i.) may be interpreted as meaning that the scattering intensity is determined

by the sum of all the $\psi_i\psi_j (\sin x_{ij})/x_{ij}$ terms for every possible pair of atoms in the molecule, the scattering due to individual atoms being included: its application may best be understood by considering one or two examples. For a diatomic molecule AB, there are four possible terms, involving atom-pairs, included in the equation: these pairs are A and A, A and B, B and A, which are identical, and B and B, the corresponding x terms being $x_{A\text{-}A}$, $x_{A\text{-}B}$, $x_{A\text{-}B}$ and $x_{B\text{-}B}$, respectively, so that equation (i.) becomes

$$I/k = \psi_A\psi_A \frac{\sin x_{A\text{-}A}}{x_{A\text{-}A}} + 2\psi_A\psi_B \frac{\sin x_{A\text{-}B}}{x_{A\text{-}B}} + \psi_B\psi_B \frac{\sin x_{B\text{-}B}}{x_{B\text{-}B}} . \quad \text{(iii.)}$$

In the atomic scattering terms, that is for A–A and B–B, the distance l included in the quantity x in equation (ii.) is zero, so that $(\sin x)/x$ under these conditions becomes equal to unity: it follows, then, that equation (iii.) can be reduced to

$$I/k = \psi_A{}^2 + 2\psi_A\psi_B \frac{\sin x_{A\text{-}B}}{x_{A\text{-}B}} + \psi_B{}^2 \quad . \quad . \quad . \quad \text{(iv.)}$$

The scattering intensity of each atom is, therefore, given by the square of its scattering factor, and this result is always applicable.

A slightly more complex case is that of the symmetrical molecule, carbon tetrachloride; here there are one carbon and four chlorine atom terms, twelve identical chlorine–chlorine terms, since there are four chlorine atoms each of which can be taken in pairs with three others, and eight carbon–chlorine terms, consisting of the carbon atom with each chlorine atom, and *vice versâ*. The complete scattering equation is thus

$$I/k = \psi_C{}^2 + 4\psi_{Cl}{}^2 + 12\psi_{Cl}{}^2 \frac{\sin x_{Cl\text{-}Cl}}{x_{Cl\text{-}Cl}} + 8\psi_C\psi_{Cl} \frac{\sin x_{C\text{-}Cl}}{x_{C\text{-}Cl}} . \quad \text{(v.)}$$

In this equation it is tacitly assumed that the molecule is tetrahedral, for if not, the distance apart of every pair of chlorine atoms, that is $l_{Cl\text{-}Cl}$, would not necessarily be the same, and instead of having twelve identical terms some would differ from the others. For a symmetrical molecule, which is of course to be expected in any case, the carbon–chlorine distances would be constant, and so the eight carbon–chlorine terms would all be the

same. Since a tetrahedral configuration has been assumed the consequences may be pursued a stage further: the distance apart of the carbon and a chlorine atom is $\sqrt{3/8}$ times the distance between two chlorine atoms, and so $x_{C\text{-}Cl}$ is equal to $x_{Cl\text{-}Cl}\cdot\sqrt{3/8}$, for a given value of the scattering angle. Equation (v.) thus becomes

$$I/k = \psi_C^2 + 4\psi_{Cl}^2 + 12\psi_{Cl}^2 \frac{\sin x}{x} + 8\psi_C\psi_{Cl} \frac{\sin(\sqrt{3/8}x)}{\sqrt{3/8}x} \quad . \quad \text{(vi.)}$$

where the value of x is the same in the last two scattering terms, and is the value for the chlorine–chlorine scattering. The coherent scattering is thus expressed in terms of only one parameter of the carbon tetrachloride molecule, namely, the distance apart of any two chlorine atoms. This is a matter of some importance, as will be seen later.

Approximate Scattering Equation. The scattering factor ψ_i, for any atom i, is given by the equation

$$\psi_i = \frac{Z_i - F_i}{[(\sin\theta/2)/\lambda]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii.)}$$

$$= \frac{Z_i(1 - F_i/Z_i)}{[(\sin\theta/2)/\lambda]^2} \quad . \quad . \quad . \quad . \quad . \quad \text{(vii}a\text{.)}$$

where Z_i is the atomic number of the atom, and F_i is its scattering, or "form," factor for X-rays, values of which have been calculated and are tabulated in the literature of X-ray crystallography. The form factor F_i is generally small in comparison with the atomic number, especially when the scattering angle is appreciable, as it decreases with increasing values of θ, and so it is possible to simplify the equations for the angular scattering intensity by replacing ψ with the atomic number Z; that is

$$I/k' \approx \Sigma_i\Sigma_j Z_i Z_j \frac{\sin x_{ij}}{x_{ij}} \quad . \quad . \quad . \quad . \quad . \quad \text{(viii.)}$$

This approximation is frequently employed, and is quite accurate enough for most purposes for atoms having fairly high atomic numbers, especially with the experimental methods generally used. Now that the scattering factor has been replaced

by the atomic number a further simplification is possible and is often made : the scattering due to light atoms can be neglected in comparison with that due to atoms of higher atomic number. For example, in the halogenobenzenes, the total scattering is made up of terms for the hydrogen, carbon and halogen atoms, and also for the hydrogen–hydrogen, carbon–carbon, hydrogen–carbon, halogen–halogen and carbon–halogen atom pairs ; of these the first six types of scattering are relatively small, and so can be neglected, in comparison with the others, and quite accurate results are obtained by considering the halogen–halogen and carbon–halogen scatterings only. In 2 : 4 : 6-trichlorobenzene, for example, assuming a regular plane, hexagonal structure, there would be, in addition to the three halogen-atom terms, six identical halogen–halogen terms and thirty-six carbon–halogen terms, falling into four groups, according to the four possible carbon–halogen distances in the molecule ; in comparison with these the scattering due to hydrogen and carbon, more especially if the halogen is bromine or iodine, may be ignored without serious error.

Incoherent Scattering. Brief mention must now be made of the incoherent scattering which is an additive quantity, the contribution of each atom in the molecule being given by the relationship

$$I_{\text{inco.}} = \frac{Z_i S_i}{[(\sin \theta/2)/\lambda]^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix.)}$$

where S_i is a quantity which is itself dependent on the atomic number Z_i and on the scattering angle θ ; it has been evaluated by Bewilogua (1931, 1932) and tabulated by him. From the results it is evident that the incoherent scattering due to any atom is appreciable only at small scattering angles and then falls off rapidly, but steadily, at increasing angles. The incoherent scattering should thus produce a rapidly falling background, from the centre outwards, upon which is superimposed the effect of the coherent scattering.

Maxima and Minima of Intensity. From equation (i) it is seen that since the expression for the coherent scattering intensity contains the quantity $(\sin x)/x$, the values of I must pass through a series of maxima and minima as the scattering angle θ increases.

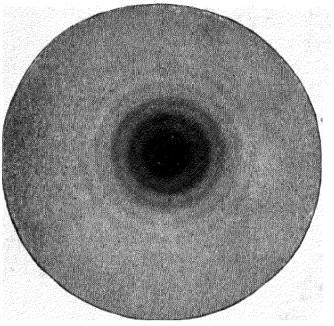


FIG. 13.—Electron-diffraction pattern given by carbon tetrachloride vapour. (After Wierl.)

When a beam of high-velocity electrons is passed through a gas at low pressure, therefore, and then allowed to fall on a photographic plate, the latter on development should show the falling background due to incoherent scattering, as well as to scattering within the body of the apparatus used, and to other causes, with occasional increases and decreases of intensity, corresponding to the maxima and minima of the coherent scattering, superimposed upon it. Actual examination of the photographic plate apparently shows, in practice, a central spot, caused by the unscattered electron beam, surrounded by a series of concentric rings, which appear to be alternately light and dark, suggesting a series of maxima and minima of scattering without a falling background intensity (Fig. 13). It seems, however, that this appearance is merely a psychological effect, since when the photographic plate is examined by means of a photometer there is no doubt that the intensity curve is of the type expected from the theoretical considerations described above. The positions of apparent maximum intensity, as they appear to the eye, in the photographic plate, correspond approximately to the inflexions in the photometer curve.

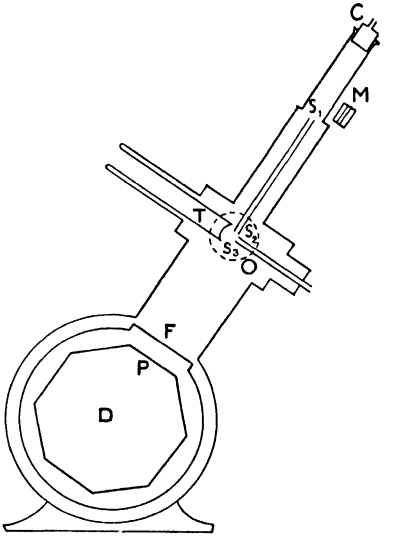


FIG. 14.—Diagrammatic representation of apparatus for studying electron diffraction by gases and vapours. (After Cosslett.)

Experimental Procedure. The experimental method in general use follows closely that first devised by Wierl (1931): the apparatus is shown diagrammatically in Fig. 14. A stream of electrons from the cathode *C*, accelerated by an applied potential of about 50,000 volts, passes through the slits S_1 and S_2, and

emerges from the latter in the form of a fine beam. It then meets at right-angles a stream of the gas or vapour under examination emerging from the slit S_3 : a minute oven, which can be heated electrically, is generally built into the apparatus to the right of S_3, so that substances which do not vaporise at relatively low temperatures may be volatilised. In order to prevent the accumulation of vapour in the apparatus, liquid air is placed inside the vessel T, so that the substance is condensed on the outer surface. A pressure as low as 10^{-5} mm. of mercury is maintained, if possible, by means of a vacuum pump which is connected to the apparatus by a side connection at the position O, marked by a dotted circle. The beam of electrons after passage through the vapour falls on to a fluorescent screen F, where the diffraction pattern may be observed through a suitably placed window. If the pattern appears satisfactory, the screen is moved from outside by a gastight device and the electrons allowed to fall on the photographic plate P, held on the drum D. The latter can have as many as eight plates fixed to it, and by rotating the drum the various plates can be exposed in turn without opening the apparatus. In between the exposures the electron beam is deflected by switching on a small electromagnet at M : this is also adjusted so as to give automatically any desired length of exposure from 0·5 to 6 seconds. At the conclusion of the exposure the photographic plates are removed, developed and the positions of the maxima, and minima if distinct, of scattering determined. This may be done either visually, by holding the plate up to a light and marking the positions where the fogging density appears to be high and low ; or the plate may be put through a photometer and the positions of inflexion on the curve noted.

The positions of maximum and minimum scattering must now be expressed in terms of $(\sin \theta/2)/\lambda$, and this is done in the following manner. If d_1 is *half* the distance between the maximum (or minimum) of a particular diffraction ring and the spot due to the undeflected beam in the centre of the ring, *i.e.*, one-quarter of the diameter of the ring, and d_2 is the distance from the photographic plate to the point at which the electron beam first meets the stream of vapour, then

$$\sin \theta/2 = d_1/\sqrt{d_1^2 + d_2^2}$$
$$\approx d_1/d_2$$

since d_1 is small in comparison with d_2. As d_1 is obtained from measurements on the photographic plate or its photometric record, and d_2 from the dimensions of the apparatus, the value of $\sin \theta/2$ for each maximum and minimum of diffraction is quite readily obtained. The wavelength λ of the electron waves is calculated, from the known applied voltage V, by means of the appropriate form of the de Broglie equation given above p. 190), there sult being multiplied by the relativity correction $1/(1 + 4{\cdot}95 \times 10^{-7}V)$. The voltage is measured on some form of voltmeter, standardised with the aid of the diffraction pattern obtained from gold foil, for which the spacings are known very accurately from X-ray measurements.

Calculation of Scattering Intensity Curves. The next stage in the investigation, after having obtained the experimental $(\sin \theta/2)/\lambda$ values for the diffraction maxima and minima, is to calculate a theoretical intensity curve, for coherent and incoherent scattering, by means of equations (i.) and (ix.). In order to do this it is necessary in the first place to assume a definite configuration for the molecule and in the simplest case only one parameter, as in equation (vi.), should be involved. The scattering intensity equation is then expressed in its simplest form, using atomic numbers (equation viii.) instead of the correct scattering factors; with carbon tetrachloride, for example, assuming the tetrahedral structure, this becomes

$$I/k' \approx 6^2 + 4 \times 17^2 + 12 \times 17^2 \frac{\sin x}{x} + 8 \times 6 \times 17 \frac{\sin \sqrt{3/8}x}{\sqrt{3/8}x} \quad \text{(x.)}$$

where 6 and 17 are the atomic numbers of carbon and chlorine, respectively, and x is the parameter involving the chlorine–chlorine distance, as in equation (vi.). By taking a series of arbitrary numerical values of x, for example, from 0 to 50, a curve can be plotted of the intensity I (or I/k') against x: this is shown in Fig. 15, the first three maxima in the curve being for x values of 7·75, 13·9 and 20·6, respectively. Turning now to the results obtained from the examination of the experimental photographic

plates it is found that the first three maxima appear in positions corresponding to (sin $\theta/2)/\lambda$ values of 0·217, 0·380 and 0·555 $\times$ 10^8, respectively. Inserting these calculated and observed results in equation (ii.) it is seen that

$$(a)\quad 7{\cdot}75 = 0{\cdot}217 \times 10^8 \times 4\pi l \quad \therefore l = 2{\cdot}81 \times 10^{-8}\ \text{cm.}$$

$$(b)\quad 13{\cdot}9 = 0{\cdot}380 \times 10^8 \times 4\pi l \quad \therefore l = 2{\cdot}91 \times 10^{-8}$$

and $$(c)\quad 20{\cdot}6 = 0{\cdot}555 \times 10^8 \times 4\pi l \quad \therefore l = 2{\cdot}95 \times 10^{-8}$$

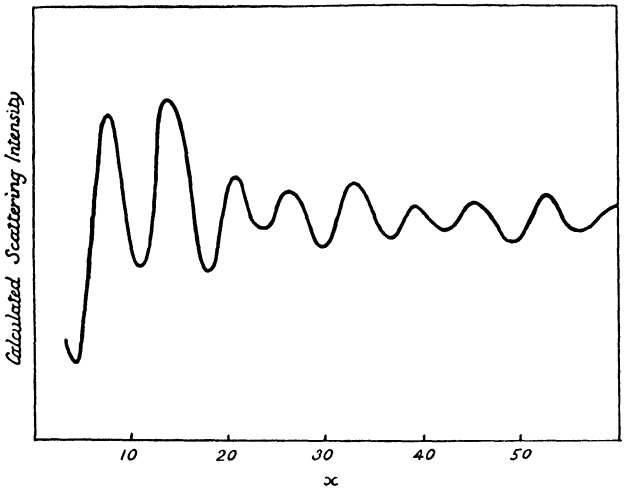


FIG. 15.—Simplified calculated curve for the intensity of coherent electron-scattering by carbon tetrachloride vapour. (After Wierl.)

Taking as an average of these three results the figure $l = 2{\cdot}9 \times 10^{-8}$, equation (ii.) for carbon tetrachloride may be written in the form

$$\frac{\sin \theta/2}{\lambda} = \frac{x}{4\pi \times 2{\cdot}9 \times 10^{-8}} \quad \text{. . . . . (xi.)}$$

as a first approximation.

It is now possible to apply the correction for the use of atomic number instead of the correct scattering factor ψ: this could not be done until an expression of the form of equation (xi.), relating (sin $\theta/2)/\lambda$ to x, was available. According to equation (viia.) the intensity calculated by the use of Z for the scattering factor should

be multiplied by $(1 - F_i/Z_i)/[(\sin\theta/2)/\lambda]^2$, and since this can now be expressed in terms of F_i, Z_i and x, it can be calculated for each atom over a series of arbitrary x values. Each scattering term in equation (x.) must be multiplied by the appropriate correction at each point: the sum of these terms can then be plotted against x to give a corrected coherent scattering intensity curve. Actually this only differs in form from the curve in Fig. 15 at small values of the scattering angle (*cf.* Table XXVII.). Finally, the connection between $(\sin\theta/2)/\lambda$ and x permits the calculation of the incoherent scattering for various values of x, by means of equation (ix.) and Bewilogua's data, which is added to the corrected coherent scattering, and the result gives the complete calculated scattering intensity curve. The maxima above a smooth curve give the exact positions of the diffraction maxima in terms of x: these are now once more related to the corresponding $(\sin\theta/2)/\lambda$ values, by means of equation (ii.), and more exact values of l calculated. The data in Table XXVII., taken from the accurate work of Cosslett (1934) on carbon tetrachloride, indicate the nature of the results obtained.

TABLE XXVII

Electron-diffraction Measurements on Carbon Tetrachloride Vapour.

No. of Maximum	1	2	3	4	5	6	7
	Values of x from Curves.						
Uncorrected .	7·75	13·9	20·6	26·5	33·0	39·4	45·3
Corrected for scattering factor . .	7·45	13·1	20·1	25·9	32·6	39·2	45·2
With incoherent correction .	7·43	13·1	20·0	25·8	32·6	39·3	45·2
Experimental $(\sin\theta/2)/10^8\lambda$ positions .	0·218	0·380	0·555	0·727	0·909	1·104	1·261
l in Å units .	2·71	2·74	2·87	2·83	2·85	2·83	2·85

Neglecting the results for the first two maxima, the exact positions of which are always difficult to determine because of their closeness to the dark central spot, it is evident that the value of l,

representing the distance apart of two chlorine atoms in carbon tetrachloride, may be taken as 2·85 ± 0·02 Å. The corresponding carbon–chlorine distance is consequently 1·74 Å. The constancy of the values of l obtained in Table XXVII. incidentally provides definite confirmation of the tetrahedral structure of carbon tetrachloride, for if it had any other structure there would be some variation in the results.

Visual Identification of Maxima and Minima. A further examination reveals a number of interesting and important points. In the first place it is evident that the incoherent scattering correction has very little influence on the positions of the maxima. In actual practice it is found, in fact, that because of the rapidly falling value of the incoherent scattering there is a tendency for the maxima to be somewhat suppressed, so that their identification is difficult. For these reasons the incoherent contribution is generally neglected : very little, if any, error is introduced as a result of this simplification. Further, it is seen that, apart from the first two, the values of x corresponding to the maxima on the approximate curve, obtained by assuming the scattering factor to be equal to the atomic number, are very close to those obtained by applying the laborious correction for the true scattering factor ψ. In his original work, Wierl (1931, 1932) had shown that quite satisfactory results are obtained by the use of the approximate equation (viii.) to calculate the scattering intensities, and after a comprehensive investigation Pauling and Brockway (1934) have concluded that this equation, in conjunction with the *visual* method for identifying the positions of maxima and minima on the photographic plate, gives results as satisfactory as those obtained by the more tedious, but highly accurate, procedure outlined above. The value for the C–Cl distance in carbon tetrachloride obtained in this way was 1·76 Å., compared with 1·74 ± 0·02 Å. given by Cosslett, provided the first one or two diffraction rings were ignored.

According to Pauling and Brockway there is some reason for believing that because of the nature of the background scattering, which falls from the centre outwards, the eye automatically corrects, at least approximately, for the difference between the

atomic number and the true scattering factor. If this is so, the visual method of identifying the maxima should not be used in conjunction with corrected curves, and the photometric method should not be employed if the approximate equation (viii.) only is used to calculate the scattering intensities. The use of the eye to find the diffraction maxima on the photographic plate goes hand in hand, therefore, with the advantage of the use of the simplified method of calculation. Another, somewhat surprising, advantage of the visual method is that the eye is more sensitive than a mechanical photometer, and by its aid it is possible to detect ten or more diffraction maxima and several minima, whereas the photometer rarely indicates more than about seven maxima, and very few, if any, minima.

The St. John Effect. As a result of the intense blackening of the central spot, caused by unscattered electrons and other effects, the positions of the first one or two maxima cannot, as a rule, be estimated exactly : this is mainly due to what is known as the St. John effect, discovered by St. John and Ware (1916), a physiological phenomenon which militates against the accurate determination of the position of maximum density of a photographic plate when the rate of decline of the background intensity is different on the two sides of the maximum. For this reason, as well as for those given above, the first one or two diffraction rings should always be ignored when using electron-diffraction measurements to evaluate inter-atomic distances; they may, however, be used for purposes of general comparison in order to determine whether an assumed configuration is correct or not. The St. John effect is also operative when two rings are close together, since the background intensity on one side of each is much greater than that on the other. A pair of rings of this type generally show a " shelf " in the calculated intensity curve, representing two maxima, one more intense than the other, so close together that there is no definite minimum between them. The positions of maxima of the shelf type, determined visually, should consequently also not be used in the final evaluation of inter-atomic distances, although they may be used for qualitative comparison to verify, or disprove, any particular configuration.

Omission of Atomic Scattering. A further simplification in the calculation is possible by the use of the visual method in conjunction with equation (viii.): it is evident from an application of the latter, as in equation (x.), that the scattering contributions of individual atoms, viz., 6^2 for carbon and 4×17^2 for the four

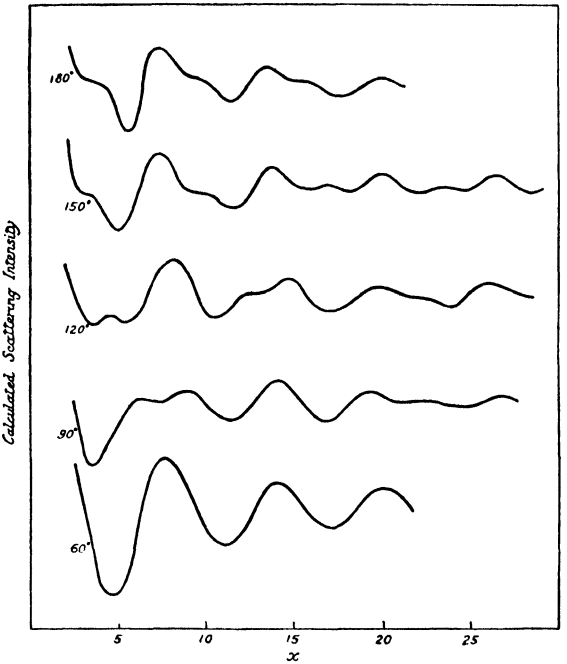
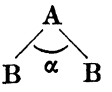


FIG. 16.—Calculated electron-diffraction scattering intensity curves for chlorine monoxide, assuming different valency angles for oxygen. (After Sutton and Brockway.)

chlorine atoms in carbon tetrachloride, are constant. Since they are *added* to the variable scattering of pairs of atoms, the atom scattering cannot affect the positions of the maxima and minima, and so may be omitted entirely from the calculations. This simplification, as with the others, is only justifiable if the scattering angle is not very small, that is to say, provided the first one or two rings are not taken into consideration in the final computations.

Two Independent Parameters. So far it has been assumed that the configuration of the molecule can be expressed in terms of one parameter, but this is only possible in a limited number of cases. In substances of the type AB_2, where the angle between the two A—B valency bonds, as well as the actual bond distance is unknown, the configuration of the molecule is then expressed in terms of two parameters, namely, the valency angle α,



and the distance l_{A-B} between the A and B atoms. The simplified scattering equation (viii.) for this molecule, excluding the atomic scattering which may be regarded as constant, then takes the form :

$$I/k' \approx 4Z_AZ_B \frac{\sin x_{A-B}}{x_{A-B}} + 2Z_BZ_B \frac{\sin x_{B-B}}{x_{B-B}} . \quad . \quad . \quad \text{(xii.)}$$

The distance l_{B-B}, which is involved in x_{B-B} is equal to $2l_{A-B} \sin \alpha$; hence x_{B-B} is equal to $2x_{A-B} \sin \alpha$. Substituting in equation (xii.), and omitting the suffixes, it follows that

$$I/k' \approx 4Z_AZ_B \frac{\sin x}{x} + 2Z_B{}^2 \frac{\sin (2x \sin \alpha)}{2x \sin \alpha} \quad . \quad . \quad \text{(xiii.)}$$

where the x term includes the inter-atomic distance l_{A-B}. The method of calculation adopted with a compound of this type is to evaluate the scattering intensity curves from equation (xiii.) for a number of different arbitrary values of the angle α. For example, in Fig. 16 is shown a series of simplified theoretical scattering intensity curves for chlorine monoxide, obtained by Sutton and Brockway (1935), assuming α to have values of 60°, 90°, 120°, 150° and 180°, respectively. These curves were then compared with the electron-diffraction photographs : for chlorine monoxide these show a weak first maximum, a weak second minimum, a strong broad second maximum, a strong third minimum, a medium strong third maximum followed by a broad shelf, and so on. This information is sufficient to show that the angle α must be in the

vicinity of 120°, since none of the other theoretical curves satisfies the requirements of the experimental diffraction pattern. The intensity curves were now calculated for a series of angles in the vicinity of 120° and more precise comparison made with the photographs : as a result it was found that a value of α of 111 $\pm$ 2° gave the best agreement. Having decided on the correct angle, the true intensity curve is consequently fixed, and by comparing the x values corresponding to maxima and minima on this curve with the $(\sin \theta/2)/\lambda$ values for the maxima and minima of intensity on the photographic plate, the distance l, between the centres of the A and B atoms, can be determined by equation (ii.) The results for chlorine monoxide, taken from the work of Sutton and Brockway, are quoted in Table XXVIII.; the x terms for five maxima and four minima, and the l values, representing the Cl–O distances derived from them, are given for the angles 110° and 112°.

The calculated distances in brackets are excluded from the final mean by the fact that the St. John effect is operative, so that

TABLE XXVIII

Electron-diffraction Measurements with Chlorine Monoxide.

Max.	Min.	Experimental $(\sin \theta/2)/10^8$Å.	Value of x from Curve.		Cl–O Distance (l).	
			110°	112°	110°	112°
1		0·2230	4·98	4·90	(1·778) Å.	(1·749) Å.
	2	0·3024	6·00	5·90	(1·579)	(1·553)
2		0·3847	8·25	8·20	1·706	1·696
	3	0·5013	10·65	10·60	1·692	1·684
3		0·5829	12·95	13·00	(1·767)	(1·774)
	4	0·6656	—	14·30	- -	(1·710)
4		0·7274	—	15·50	—	(1·695)
	5	0·8275	17·85	17·70	1·717	1·702
5		0·9111	· 20·20	20·05	1·750	1·737

they cannot be relied upon ; apart from these the weighted mean of the results gives a chlorine–oxygen distance of 1·71 $\pm$ 0·02 Å., with the valency angle of 111 $\pm$ 2°.

Several Parameters. When more than two parameters are

required to determine the configuration of a molecule, as for example with carbonyl chloride where three are necessary, then a valency angle, one bond distance and the ratio of one to another may be chosen as the parameters in terms of which the theoretical scattering intensity is to be calculated. The method is essentially the same as that described above, except that a larger number of theoretical curves for different values of the angle and of the ratio of bond distances, corresponding to different possible configurations, may have to be drawn before the one which agrees best with the electron-diffraction photograph is found. This gives the appropriate valency angle and the bond-distance ratio, leaving only one other parameter to be evaluated from a comparison of the experimental $(\sin \theta/2)/\lambda$ values for maxima and minima with the corresponding x terms on the chosen curve. With benzene derivatives the calculations are considerably simplified by assuming a plane, regular hexagonal structure : there is no doubt that such a configuration gives the best agreement between the calculated curves and the electron-diffraction photographs. In a halogeno-benzene, for example, the number of parameters is thus reduced to three, namely, the C–H, C–C and C–X bond distances, where X is the halogen ; if the effect of the hydrogen atoms is neglected, as is often the case (*vide supra*), only two parameters remain, and the calculations become much less complicated.

The Radial Distribution Method. A new procedure, called the "radial distribution method," has been recently introduced by Pauling and Brockway (1935) for the analysis of electron-diffraction photographs, which is likely to prove a useful adjunct to the method already described, although it is improbable, as will be seen later, that it will replace it altogether. The radial distribution method has the great advantage that it leads directly to the value for the principal inter-atomic distances in a molecule without the necessity of having to assume any particular configuration, or to find by calculation which of a number of arrangements is the most probable. The method has its limitations, however, when there are several different distances between important scattering centres in the molecule.

The principle of the radial distribution method is related to that

developed by Zernike and Prins (1927) for the interpretation of X-ray diffraction data obtained with liquids: an expression is deduced which gives the product of the scattering powers of all volume elements at any distance l apart, in terms of l. This has been called the distribution function for scattering power, and by the equations given below it can be computed for a number of arbitrary l values and plotted on a graph. The maxima in the curve must correspond to distances separating important scattering

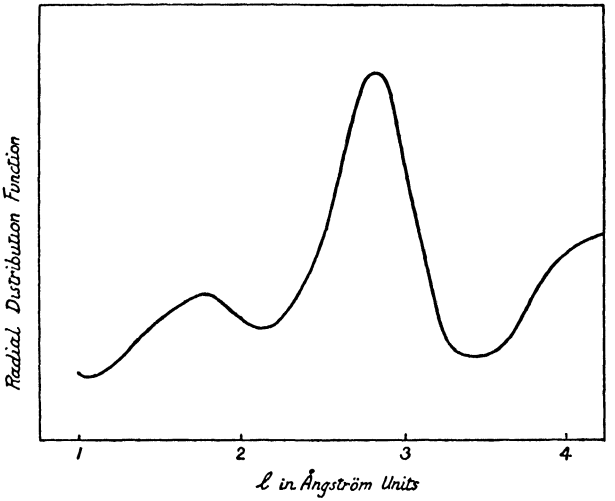


FIG. 17.—Curve of radial distribution function for electron diffraction by carbon tetrachloride. (After Pauling and Brockway.)

centres, that is, at which atoms are situated. In other words, the l values for which the distribution function of the product of the scattering powers shows maxima are the distances apart of atoms. The higher the atomic numbers of the atoms concerned the greater will be the scattering power and consequently the more marked will be the maximum in the distribution curve. Pauling and Brockway have shown that the distribution of the scattering product D for different distances l is given *very approximately* by the relationship

$$D = \Sigma I_k \frac{\sin s_k l}{s_k l} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv.)}$$

in which s_k is defined by

$$s_k = \frac{4\pi \sin \theta_k/2}{\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xv.)}$$

where θ_k is the scattering angle for the kth diffraction ring, as obtained experimentally in the manner already described (p. 196), and I_k is a relative value for the intensity of this ring, which may be estimated visually. The value of D for a series of distances l, generally at intervals of 0·1 Å. between 0 and 4 Å., is obtained by summing the appropriate I (sin sl)/sl terms for as many diffraction rings as can be observed in the photographs, although since the intensity falls off with the increasing order of the rings the omission of those of higher order does not result in the introduction of any serious error. Strictly speaking, the scattering product should fall off asymptotically to zero as the distance l increases, but when the approximate equation (xiv.) is used this does not occur : for this reason the curves of l values greater than about 4 Å. have no significance and need not be plotted. The results given by Pauling and Brockway for the intensities and s functions obtained from an examination of the electron-diffraction photographs of carbon tetrachloride are recorded in Table XXIX.

TABLE XXIX

Electron-diffraction Data for Carbon Tetrachloride.

No. of Ring (k).	Rel. Intensity (I_k).	s_k
1	20	2·93
2	30	4·91
3	15	7·13
4	10	9·23
5	10	11·34
6	5	13·54
7	4	15·79
8	2	17·82
9	1	19·98
10	1	22·34

From these data the scattering products have been obtained for a series of distances and plotted in Fig. 17; in this curve two

maxima are clearly seen. The larger of these must be due to scattering by the pairs of chlorine atoms and the smaller to that from the carbon and chlorine atom-pairs. The carbon–chlorine distance is thus obtained directly from the graph as 1·74 Å., and the chlorine–chlorine distance as 2·856 Å. The former of these values is not reliable as it is somewhat sensitive to the number of diffraction rings included in the summation of equation (xiv.), but the latter figure is hardly changed by increasing the number of rings above six. From the distance apart of two chlorine atoms the carbon–chlorine distance, assuming a tetrahedral configuration, is calculated as 1·75 Å., in excellent agreement with the value recorded previously (p. 200).

Comparison of Methods of Calculation. For some molecules, as, for example, sulphur dioxide, the usual method of calculating the scattering intensity curve and comparing the positions of the maxima with the $(\sin \theta/2)/\lambda$ values obtained from the visual examination of the diffraction photographs, fails to give a definite value of the valency angle: the variation in the curves for different angles is not sufficiently marked to permit of a choice being made between them (Cross and Brockway, 1935). In such cases the radial distribution method gives directly the distances apart of the various atoms so that the angle can be evaluated without difficulty: thus, for sulphur dioxide, the S–O distance is found to be $1{\cdot}43 \pm 0{\cdot}02$ Å. and the O–O distance is $2{\cdot}56 \pm 0{\cdot}15$ Å., giving a sulphur valency angle of $124 \pm 15°$ (Pauling and Brockway), which may be compared with the value of $122 \pm 5°$ derived from spectroscopic data (Bailey and Cassie, 1933). The radial distribution method is also of special value when the molecule contains rotating groups, or when exact formulation of the configuration is difficult, as, for example, with sulphur monochloride. On the other hand, the ordinary visual method is to be preferred, firstly, when there are simple geometrical relations between the inter-atomic distances, as in benzene; secondly, when the molecule contains two or more important inter-atomic distances with values near to one another, and the corresponding maxima in the scattering distribution curve are so close that only a broad maximum appears instead of two peaks; and thirdly, when the

diffraction photograph shows certain features, such as very sharp rings, capable of exact measurement. Further, if there are a number of maxima in the curve, even if they are clearly defined, it may not always be possible to allocate them correctly to the corresponding inter-atomic distances. It may be concluded, therefore, as Pauling and Brockway have done, that both the ordinary visual method and the radial distribution method have their uses, and they may be regarded as complementary : sometimes one gives more reliable results, and sometimes the other.

APPLICATIONS

It is hoped that sufficient has been said concerning the methods employed in the interpretation of electron-diffraction photographs and of their use for the determination of molecular configurations, valency angles and inter-atomic distances for the underlying principles to be clear. The actual calculations, of course, become more lengthy the more complex the molecule and the less that can be assumed about its structure. In any case the number of trial curves is reduced by previous approximate knowledge of bond distances and valency angles, but it appears that up to the present only molecules having not more than three independent unknown parameters have been treated. A number of illustrations of the types of information that can be obtained by the electron-diffraction method will now be given and discussed : the results are not always conclusive, as will appear in due course.

Inter-atomic Distances. Confidence in the electron-diffraction method as a means of investigation has been established by the fact that with many simple molecules, such as the halogens, the results obtained are in excellent agreement with those arrived at from the study of band spectra. The data recorded in Table XXX. permit of a comparison of inter-atomic distances, that is, of the distances between the nuclei, for some diatomic molecules obtained by the two methods.

The results, in general, agree to within 1 or 2 per cent., and this is the order of accuracy usually ascribed to the electron-diffraction method.

TABLE XXX

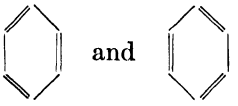
Inter-atomic Distances.

Molecule.	Electron Diffraction.	Band Spectra.
Cl–Cl . .	2·01 Å.	1·99 Å.
Br–Br . .	2·29	2·28
I–I . .	2·64	2·66
I–Cl . .	2·30	2·31

The carbon–carbon distance in aliphatic compounds, such as paraffins and *cyclo*-paraffins, obtained by electron diffraction, is about 1·52 Å., which compares well with the value of 1·54 Å. from X-ray measurements on crystals of diamond and a number of organic compounds. Similarly, there is satisfactory agreement for the distance between aromatic carbon nuclei, which is found to be 1·39 to 1·42 Å. by electron diffraction, whereas the study of crystals of aromatic compounds by X-rays gives 1·41 Å.

Resonance. It should be noted that the results of both X-ray diffraction by crystals and electron diffraction by vapours lead to the conclusion that all the aromatic carbon–carbon distances, in benzene and its derivatives are the same, whereas if the Kekulé structure of alternating single and double bonds were applicable, analysis of the diffraction patterns should give two characteristic distances. This apparent anomaly is explained by the concept of wave-mechanical " resonance " (see " Recent Advances in Physical Chemistry," Chapter I.), according to which it is supposed that when a molecule can exist in two, or more, structural forms having the same, or similar, potential energy then the actual state will be a linear combination of the possible forms with a lower energy. The two or more forms must not differ as regards the arrangement of the atoms, but only as far as the distribution of the valency electrons is concerned. As a consequence of resonance the effective configuration of the molecule corresponds to something between the possible arrangements of the bonds ; actually, as will be seen shortly, it tends to approach one of these preferentially. Benzene provides one of the best examples of resonance : although

five different configurations of similar energies are theoretically possible, the two alternative Kekulé structures

 and

are the most important resonating states. In benzene, therefore, the effective configuration of the molecule may be regarded as being made up of both forms, so that all the bonds are virtually equivalent, and they each possess equal parts of single- and double-bond character. The distance between the centres of two singly-linked carbon atoms is 1·54 Å., as already seen, but that between two doubly-bound atoms is not more than 1·38 Å., from spectroscopic data. The actual bond dimensions in benzene and its derivatives are all constant at about 1·40 Å., and so it follows that in this instance the resonance results in all the bonds having lengths approximating to those to be expected for double-bonded atoms. As a result of observations such as these, Pauling (1932) has suggested that whenever resonance occurs between different possible structures of a molecule, the actual configuration tends to approach more closely that of the form having the greater radial force constants : that is to say, the molecular dimensions tend towards the values for multiple bonds, double being preferred to single bonds, and triple to double bonds. This conclusion is of considerable importance in connection with the problems of molecular structure, as will be seen below.

Effective Atomic Radii. So far reference has been made only to bond dimensions between two identical atoms, and now bonds involving different atoms must be considered. In this connection Sidgwick (1931) and Pauling (1932) have independently proposed, as a first approximation, the concept of the additivity of covalent bond distances : the suggestion has received support from other workers and, as will be seen, is in general harmony with the results of electron-diffraction measurements. It is considered that to each atom taking part in a covalent linkage there can be ascribed an apparent effective radius, which represents the contribution the atom makes towards the length of the covalent bond between it

and another atom, no matter what the nature of the latter. If r_A represents the effective atomic radius of an atom A, and r_B that of any atom B, then in the molecule AB or in any molecule containing the covalent A—B link, the distance between the centres of the atoms, that is to say, the bond distance, as given by the electron-diffraction method, for example, should be equal to $r_A + r_B$. When an atom is involved in a double or a triple bond its effective radius is decreased, and it is generally agreed that the double-bonded radius is about 0·90, and the triple-bond distance about 0·79, times that of the corresponding single bond value.

From a consideration of various data, based chiefly on X-ray measurements and band spectra, and to some extent on electron-diffraction observations, it has been found possible to ascribe effective radii to a number of atoms, and a selection of these, which are of particular interest for the present chapter, are quoted in Table XXXI.: the values are mainly those given by Pauling and Huggins (1934).

TABLE XXXI

Covalent Single-Bond (Tetrahedral) Radii in Ångström Units.

Carbon	Nitrogen	Oxygen	Fluorine
0·77	0·70	0·66	0·64
Silicon	Phosphorus	Sulphur	Chlorine
1·17	1·10	1·04	0·99
Germanium	Arsenic	Selenium	Bromine
1·22	1·18	1·14	1·14
Tin	Antimony	Tellurium	Iodine
1·40	1·36	1·32	1·33

The sum of the radii for iodine and chlorine is seen to be 2·32 Å., and this may be compared with the measured bond distance of 2·31 Å., in iodine monochloride, as recorded in Table XXX.: many similar instances may be quoted in which the Sidgwick-Pauling rule of the additivity of bond distances is applicable. The measured values quoted in Table XXXII., which are for singly-linked atoms only, were all obtained by the electron-diffraction method.

TABLE XXXII

Comparison of Measured and Additive Bond Distances.

Compound.	Bond.	Measured.	Additive.
Carbon tetrachloride .	C—Cl	1·76 Å.	1·76 Å.
Carbon tetrabromide .	C—Br	1·93	1·91
Dimethyl ether Dioxan . .	C—O	1·45	1·43
Methyl azide . Nitromethane .	C—N	1·47	1·47
Methyl hydroxylamine	N—O	1·37	1·36

Such excellent agreement as that shown in the above table is, however, not always found, and when there are discrepancies the results may often have important significance, although there is reason to believe that the effective bond distances are influenced to some extent by factors not completely understood. For example, the C–F bond distance in carbon tetrafluoride is 1·36 Å., that is, 0·05 Å. less than the additive value, whereas that of the O–F bond in oxygen fluoride, given by different authors as 1·36 or 1·41 Å., is greater than the additive distance of 1·30 Å. These discrepancies are not easy to explain: it has been suggested (Brockway and Wall, 1934) that the shortening of the bond between carbon and fluorine is due to the partially ionic character of the C—F linkage, resulting from the difference in the electronegativities of the two elements. A completely ionic link, $C^+—F^-$, would mean a distance between the centres of the atoms, or ions, of about 1·53 Å., which is actually greater than the covalent bond length, so that a value *smaller* than that anticipated cannot be accounted for in this manner. It may also be noted in this connection that steric considerations are against the formation of ionic linkages between carbon and fluorine: the radius of the C^{4+} ion is about 0·2 Å., and so four fluorine ions of radius 1·33 Å. could not accommodate themselves closely round it. The oxygen–chlorine distance in chlorine monoxide appears to be 1·68 Å., instead of the expected value of 1·65 Å.; the difference here is so small that it may well be due to experimental error.

Structures of Halides. An interesting problem is presented by

the hexafluorides of sulphur, selenium and tellurium, which have been studied by Brockway and Pauling (1933) and by Braune and Knoke (1933) using the electron-diffraction method. There is no doubt concerning the regular octahedral structure of these molecules and of the fact that all the bond distances in each molecule are constant : the observed values, and those calculated on the assumption of bond additivity are given in Table XXXIII.

TABLE XXXIII

Observed and Additive Bond Distances in Hexafluorides.

Compound.	Bond.	Measured.	Additive.
Sulphur hexafluoride .	S—F	1·58 Å.	1·68 Å.
Selenium hexafluoride .	Se—F	1·70	1·81
Tellurium hexafluoride .	Te—F	1·84	2·01

In these cases also, the marked discrepancies between observed and calculated bond distances, which are quite beyond the limits of experimental error, have been attributed to the tendency to form ionic linkages between the central atom and the fluorine. It is true that in these fluorides the ionic bond radii might be somewhat shorter than the lengths of the corresponding covalent links, but sterically the arrangement seems unlikely. For example, in sulphur hexafluoride it would be necessary for six fluorine ions of radius 1·33 Å. to be accommodated round a S^{6+} ion of radius 0·3 Å., but this is impossible : the radius of the central ion would have to be increased to at least 0·55 Å., when the S^{+}–F^{-} distance would be 1·88 Å., which is much greater than the observed value. It may be noted, further, that similar discrepancies, of the order of 0·1 to 0·2 Å., are found between the additive and experimental distances from electron-diffraction measurements with the tetrachlorides of silicon (2·00 Å.), germanium (2·08 Å.) and tin (2·30 Å.), and also with the trifluorides (1·52 Å. and 1·72 Å.) and trichlorides (2·00 Å. and 2·16 Å.) of phosphorus and arsenic. (The observed values given in brackets may be compared with the additive results obtained from Table XXXI.) It is highly improbable that

the tendency to form ionic linkages is operative in all these instances. On the whole it must be concluded, therefore, that departure from exact bond additivity may occur in certain instances as a result of factors not clearly understood. One final point in connection with the bond distances in the hexafluorides is worthy of mention: the results appear to dispose of the suggestion that single-electron linkages are present in these molecules. Although nothing is known definitely of the length of such bonds, it may be argued by analogy, at least, that they should be greater than the corresponding single-bond distances, involving electron pairs.

Carbon–Halogen Distances. It has been seen in Table XXXII. that the carbon–chlorine and the carbon–bromine bond distances in the tetrahalides are additive, and it is of interest to inquire if this agreement extends to other halides. Unfortunately there is in this connection considerable disagreement between the results of different authors, and so the conclusions drawn may have to be regarded as speculative. There is little doubt, in the first place, that in all four chloromethanes, viz., methyl chloride, methylene chloride, chloroform and carbon tetrachloride, the carbon–chlorine bond distance has the constant value of 1·75 to 1·77 Å. (Sutton and Brockway, 1935), but when the molecule contains a double bond the carbon–chlorine distance is shorter. Brockway, Beach and Pauling (1935) have made a study of all six chloroethylenes, and found the C–Cl dimensions to vary from 1·67 to 1·73 Å.; de Laszlo (1935) has also recorded distances shorter than the normal value, but none less than 1·74 Å. The former authors have ascribed the shortening of the bond to resonance between structures of the types >C=C—Cl and >C—C=Cl, so that the carbon–chlorine bond will show some tendency towards the double-link value, which is only nine-tenths of the corresponding single-bond distance. In general, the more chlorine atoms substituted in the ethylene molecule the larger the observed C–Cl distance: thus, with tetrachloroethylene it is 1·73 Å., but only 1·67 Å. in vinyl chloride. In the latter the double-bond resonance can occur only with one chlorine atom, but in the former four atoms can share in it, so that the double-bond character of the carbon–chlorine

link should be greater with vinyl chloride than with the tetrachloro-compound. It must be pointed out that the results of Brockway, Beach and Pauling were obtained on the assumption that the C=C bond length in the various chloroethylenes had the constant value of 1·38 Å., which is the " theoretical " value, that is, nine-tenths of the additive single-bonded carbon–carbon distance : this is not necessarily correct and it is not certain how far the results may be affected by any variation in this bond length.

A somewhat analogous problem is raised by a consideration of the carbon–halogen distances in aromatic compounds : these have been determined by electron diffraction in hexachloro-, hexabromo-, 2 : 4 : 6-tribromo-, 2 : 4 : 6-tri-iodo-, *p*-dibromo- and *p*-di-iodo-benzenes. The results obtained by de Laszlo (1934) are recorded in Table XXXIV. : the values appear to be the same for each kind of carbon–halogen bond, irrespective of the number of halogen atoms substituted in the benzene nucleus.

TABLE XXXIV

Observed and Additive Bond Distances in Aromatic Compounds.

Bond.	Measured.	Additive.
C—Cl . .	1·69 Å.	1·76 Å.
C—Br . .	1·88	1·91
C—I . .	2·05	2·10

Here again the observed values are slightly smaller than those to be expected from the additivity rule, assuming that the carbon atom contributes its full *aliphatic* bond radius of 0·77 Å. The difference has been attributed to resonance between alternative structures of the type $>C_{ar.}—X$ and $>C_{ar.}=X$, so that the bond distances tend to approach the double-bond values (Pauling, Brockway and Beach, 1935). This explanation would, however, require different lengths for the carbon–halogen bonds in the different compounds, according to the number of halogen atoms

substituted in the ring, as with the chloroethylenes: such variations have not been observed, although it is not impossible that they may be revealed by further careful investigation. In the meantime attention may be called to the point that the discrepancies in Table XXXIV. are by no means large, especially when the differences between measured and additive bond lengths for other compounds are considered. Further, it should be noted that the distance between an aliphatic and an aromatic carbon atom, in compounds such as durene (tetramethylbenzene) and dibenzyl, has been found by X-ray measurements of the crystals to be 1·47 Å. (Robertson, 1933, 1934), as compared with the normal carbon–carbon distance of 1·54 Å. Electron-diffraction measurements have given 1·50 Å. for the aliphatic–aromatic carbon distance in methyl benzenes (P. L. F. Jones, 1935), and although this is not as small as the value from the X-ray work it is definitely less than the expected distance. In these compounds resonance of the type suggested for the halogen derivatives is impossible, yet there is a definite shortening of the bond: this may well be attributed to a tightening effect in the linkage joining the aromatic carbon to an external atom, brought about by the resonating system of single and double bonds in the benzene nucleus. The shortening of the carbon–halogen bonds, as shown in Table XXXIV., may be due to the same cause.

It is a well-known fact (see "Recent Advances in Physical Chemistry," Chapter IV.) that the fundamental vibration frequency of a bond, *e.g.*, the carbon–hydrogen linkage, as determined by the Raman effect, is influenced by the nature of the groups attached to the carbon atom, and it would not be surprising if there were a corresponding change in the bond distance. Variations of the order of 10 per cent. in the Raman displacement are not uncommon, and this may possibly be related to analogous alterations in the equilibrium distance between the two atoms taking part in the vibration, even where resonance effects are not operative. It would appear advisable to exercise caution in the interpretation of the results of electron-diffraction measurements before resorting to the postulation of the existence of resonance in the molecule.

Double and Triple Bonds. Mention has been already made of the generally accepted, although probably approximate, relationship between the length of a single and that of a double or a triple bond, between the same two atoms : some examples may be quoted from electron-diffraction measurements to show how far the observed results agree with expectation. Very few data are available from measurements with ethylene compounds concerning the C=C distance, but these indicate a value of 1·32 Å., instead of 1·38 Å., which is nine-tenths of the distance between two singly-bonded carbon atoms ; experimental errors and uncertainties in the interpretation of the observations might easily account for the discrepancy. The triple bond C≡C distance appears to be known more definitely, and it is given as 1·20 to 1·22 Å. from electron-diffraction measurements with acetylene and with di-acetylene : this result agrees well with the expected value, that is, 0·79 × 1·54, which is 1·22 Å. It is not certain how far the recorded bond distances are influenced by those anticipated, especially when several parameters have to be taken into consideration in calculating the theoretical intensity curve. Some writers admit having assumed a particular value, as for example Brockway, Beach and Pauling (1935), who used 1·38 Å. for the double-bonded carbon distance, but in other cases the final choice, apparently reached from the experimental results, may have been determined, to some extent, by preconceived notions, especially where there is no clear differentiation between the intensity curves for different distances.

The C=O distance in carbonyl and acetyl chlorides and bromides was at one time given as 1·13 Å. (Dornte, 1933), which was surprisingly small, but newer measurements by Brockway, Beach and Pauling (1935) indicate a value of 1·28 ± 0·02 Å. in carbonyl chloride ; this figure is in excellent agreement with the additive value based on the usual assumption concerning the ratio of single- and double-bond distances. A similar result, 1·29 Å., has been reported as derived from electron-diffraction measurements with the dimeric form of formic acid as vapour (Pauling and Brockway, 1934), and also from the X-ray study of various crystals.

Carbon Dioxide and Disulphide. In carbon dioxide the distance

between the carbon atom and each of the oxygen atoms has been given as 1·13 Å. (Wierl, 1932), which is much lower than expected : this low value is not due to experimental error, as a similar figure has been obtained for the carbon–oxygen distance in carbonyl sulphide. The result is of fundamental importance as it appears to indicate that in the carbon dioxide molecule there is resonance between the normal form, with two double-bonded carbon and oxygen linkages, and two excited states, each of which contains a triple bond ; thus

$$\overset{-}{\mathrm{O}}\!-\!\mathrm{C}\equiv\overset{+}{\mathrm{O}} \qquad \mathrm{O}=\mathrm{C}=\mathrm{O} \qquad \overset{+}{\mathrm{O}}\equiv\mathrm{C}\!-\!\overset{-}{\mathrm{O}}.$$

Since each of the measured inter-atomic dimensions would tend to approach that corresponding to the largest number of bonds, both carbon–oxygen distances will approximate to the value for a triple bond, which may be expected to be about 1·13 Å. Similar resonance should occur in carbon disulphide and in carbonyl sulphide, and in fact in both cases the carbon–sulphur bond lengths are about 1·55 Å. (Boersch, 1935 ; Cross and Brockway, 1935), whereas the additive value expected for a C=S bond would be approximately 1·63 Å. The triple-bond distance between carbon and sulphur should be about 1·43 Å., and so there is evidently less tendency to form excited structures with triple bonds than is the case with carbon and oxygen, where the measured distances, in carbon dioxide and carbonyl sulphide, approach very closely the triple-bond values.

Carbon Suboxide. Electron-diffraction measurements of inter-atomic distances have also thrown light on the structure of carbon suboxide, C_3O_2. The results definitely exclude any cyclic configuration for this molecule, and according to the usual linear formula, viz., O=C=C=C=O, the carbon–oxygen distances should be about 1·28 Å., and the carbon–carbon distances about 1·38 Å., whereas in actual fact they were found to be 1·18 to 1·20 Å., and 1·27 to 1·30 Å., respectively (Brockway and Pauling, 1933 ; Boersch, 1935). This means that there is a considerable shortening of the bonds below the values to be expected for double linkages, and the interpretation of the results that has been proposed is that in addition to the normal state of carbon suboxide,

there can exist two excited states of similar energy with which it can enter into resonance. These two alternative states may be represented as

$$\overset{+}{O}\equiv C-C\equiv C-\overset{-}{O} \quad \text{and} \quad \overset{-}{O}-C\equiv C-C\equiv\overset{+}{O},$$

so that both the carbon–oxygen and the carbon–carbon distances will tend to approach the triple-bond values, which are 1·13 and 1·22 Å., respectively.

Cyanogen. Resonance of a similar type has been postulated to account for the carbon–carbon bond distance in cyanogen, $N\equiv C-C\equiv N$, which should be 1·54 Å., the single-bond value, but is actually only 1·43 Å. The carbon–nitrogen inter-atomic distance is, however, equal to the expected triple-bond dimension, namely, 1·16 Å. (Wierl, 1931; Brockway, 1933). The shortness of the carbon–carbon linkage is attributed to resonance between the normal form of cyanogen, depicted above, and two excited states, present to some extent, viz.,

$$\overset{-}{N}=C=C=\overset{+}{N} \quad \text{and} \quad \overset{+}{N}=C=C=\overset{-}{N},$$

so that the double-bond distance is approached for the carbon atoms, whilst retaining the triple-bond distance for the carbon–nitrogen linkage existing in the normal structure.

Oxides of Nitrogen. Electron-diffraction measurements with nitrous oxide have shown that in this compound resonance probably also occurs. Since the scattering powers of oxygen and nitrogen are very much the same it is impossible to distinguish between the arrangements NNO and NON, but the first of these is generally favoured from other considerations, and so is adopted as a basis for the interpretation of the electron-diffraction measurements. If this structure is assumed, the distance between the extreme nitrogen and oxygen atoms is $2{\cdot}38 \pm 0{\cdot}06$ Å. (Maxwell, Mosley and Deming, 1934), which agrees reasonably well with the sum of the distances for $N\equiv N$, that is, 1·10 Å., and for $N=O$, that is, 1·22 Å. This result implies that in nitrous oxide resonance occurs between two states of similar potential energy, viz.,

$$\overset{-}{N}=\overset{+}{N}=O \quad \text{and} \quad N\equiv\overset{+}{N}-\overset{-}{O},$$

so that the nitrogen–nitrogen distance approaches the value for a triple bond, and the nitrogen–oxygen distance that of a double bond. A third possible state, in which the two nitrogen atoms are singly linked, and the nitrogen and oxygen joined by a triple bond, is excluded, as this would tend to make the smaller nitrogen–oxygen distance 1·07 Å., which is the triple-link value, and the distance between the extreme nitrogen and oxygen atoms should then be 2·17 Å., instead of the observed value of 2·38 Å. Observations have also been made of the electron diffraction of nitrogen dioxide, tetroxide and pentoxide, but the results are not sufficiently clear to permit of any definite interpretation. It does seem certain, however, that nitrogen dioxide, unlike carbon dioxide, is not a linear molecule, the valency angle of the nitrogen atom being somewhere between 90° and 120°.

Boron Amide. The compound $B_3N_3H_6$, generally known as boron amide, has been examined by Stock and Wierl (1931), and found to give an electron-diffraction pattern very similar to that of benzene: the molecule is evidently a flat, regular hexagon, with alternate boron and nitrogen atoms round the ring. The boron–nitrogen distance was found to have a constant value of 1·47 $\pm$ 0·07 Å., which is much smaller than the value for singly-linked atoms, viz., 1·59 Å., but little different from the additive double-bond value, namely, 1·43 Å. The conclusion appears inevitable, therefore, that there is resonance in boron amide between two alternative structures of the Kekulé type, so that each boron–nitrogen linkage has 50 per cent. double-bond character; the inter-atomic dimensions are, therefore, all the same and approach that to be expected for a double bond.

MOLECULAR CONFIGURATIONS

In addition to the information concerning molecular structure obtained from a consideration of bond distances, described above, electron-diffraction measurements often permit of a definite decision being made between a number of possible configurations of different types. As a general rule only one of these gives a theoretical scattering curve which reproduces closely the features

of the experimental diffraction pattern, both as regards intensities and positions of the rings. Mention has been made of the fact that only a planar configuration, in the form of a regular hexagon, complies with the requirements of the observations with benzene and its derivatives, and of the necessity of postulating a regular octahedral structure for the hexafluorides of sulphur, selenium and tellurium. Further, the tetrahalides of carbon, silicon, germanium and tin must be tetrahedral, whereas carbon dioxide and disulphide and carbonyl sulphide must be linear; nitrogen dioxide and sulphur dioxide, on the other hand, have angular configurations. As might be expected, *cyclo*hexane is not planar, and neither is dioxan; the observations with the latter substance show clearly that in the vapour state, at least, the molecules are mainly in the **Z-**, or *trans-*, form (Sutton and Brockway, 1935). This result agrees with the fact that the liquid has a dipole moment of almost zero.

The Triazo-group. The structure of the triazo-group has long been a matter for discussion, and parachor and other measurements indicated that the familiar cyclic structure was correct (" Recent Advances in Physical Chemistry," Chapter II.); dipole-moment studies cast some doubt on this conclusion, and now electron-diffraction observations with methyl azide indicate clearly that for the vapour the three-membered ring is quite out of the question (Brockway and Pauling, 1933). The results are, however, compatible with a linear arrangement of the three nitrogen atoms, although the distances between the two pairs of atoms is not the same: the actual dimensions are represented by

$$\overset{1\cdot26}{\text{—N—}}\overset{1\cdot10}{\text{N—N.}}$$

The simplest way of interpreting these facts is to suppose that resonance occurs between the two possible linear structures of the azide group, viz.,

$$\text{—N}=\overset{+}{\text{N}}=\overset{-}{\text{N}} \quad \text{and} \quad \text{—}\overset{-}{\text{N}}\text{—}\overset{+}{\text{N}}\equiv\text{N},$$

so that the two nitrogen–nitrogen bond lengths will tend to approach the values for N=N, which is 1·26 Å., and for N≡N, which is 1·10 Å., respectively. The proposed linear arrangement of the nitrogen atoms in azides is in agreement with the results

obtained from the X-ray study of crystals of cyanuric azide (Knaggs, 1935) and of various alkali azides.

Diazo- and Azo-Groups. Electron-diffraction measurements have also resulted in the rejection of the familiar ring structure for the aliphatic diazo-group, which was apparently supported by the parachors and boiling points of aliphatic diazo-compounds. The work of Boersch (1935) on diazomethane vapour shows that the molecule as a whole is linear, the carbon–nitrogen distance being $1{\cdot}34 \pm 0{\cdot}05$ Å., and that between the two nitrogen atoms $1{\cdot}13 \pm 0{\cdot}04$ Å. These measurements suggest resonance between the two structures

$$H_2C{=}\overset{+}{N}{=}\overset{-}{N} \quad \text{and} \quad H_2C{-}\overset{-}{N}{\equiv}\overset{+}{N},$$

which should lead to distances approaching 1·32 and 1·10 Å., respectively.

Azomethane, as is to be expected, has the structure of a conventional azo-compound, viz., $CH_3{\cdot}N{=}N{\cdot}CH_3$ (Boersch, 1935); the carbon–nitrogen and nitrogen–nitrogen distances are $1{\cdot}47 \pm 0{\cdot}06$ and $1{\cdot}24 \pm 0{\cdot}05$ Å., respectively, and these are very close to the additive values for C—N and N=N, which should be 1·47 and 1·26 Å., respectively. Theoretically azo-compounds might be expected to exist in both *cis-* and *trans*-forms, although it is well known that no such isomerism has been detected. It is of interest, therefore, to record that the electron-diffraction patterns of azomethane show that in the vapour state the molecule exists almost entirely in the *trans*-form; this conclusion is in harmony with the very small dipole moments of other azo-compounds.

***Cis-* and *Trans*-Compounds.** The *cis-* and *trans*-modifications of dichloro- and of dibromo-ethylene give distinctly different maxima and minima in the diffraction of electrons (Wierl, 1932; Dornte, 1933; Brockway, *et al.*, 1935): the dimensions of the molecules agree very closely with those to be expected from the accepted configurations, so that the electron-diffraction method might be used in certain cases to distinguish between two isomeric forms. It is of interest that the dimensions of ethylene dichloride and dibromide, in both of which free rotation about the C—C

bond is possible, indicate that the molecule takes up a preferential configuration analogous to a *trans-* arrangement, that is, with the halogen atoms tending to repel one another (Wierl, 1932). This result is in harmony with the conclusions from the measurement of dipole moments; according to these it appears that the moments of $X{\cdot}CH_2{\cdot}CH_2X$ are smaller than would be expected if rotation of the $—CH_2X$ groups were completely free, so that the halogen atoms spend more time in the distant than in the closer positions.

Nickel Carbonyl. The structure of nickel carbonyl, $Ni(CO)_4$, presents an interesting problem which has been answered by the application of electron-diffraction methods: the dipole moment of this compound is zero, and so it must have either a tetrahedral or a square-planar arrangement with the nickel atom in the centre; the cyclic structure, at one time considered, is definitely eliminated. According to Pauling's wave-mechanical theory of valency ("Recent Advances in Physical Chemistry," Chapter I.) *quadri*-valent nickel, as in the tetra-carbonyl, should have a tetrahedral structure, and this has in fact been proved to be the case by a comparison of the calculated electron-scattering intensity curves for the two configurations with the actual diffraction rings (Brockway and Cross, 1935). The C—O distance in nickel carbonyl is $1{\cdot}15 \pm 0{\cdot}02$ Å., which is close to the normal value for carbon monoxide as obtained from spectroscopic data. The length of the Ni—C linkage, $1{\cdot}82 \pm 0{\cdot}03$ Å., is considered to be 0·18 Å. less than the covalent single-bond value, and consequently a certain degree of resonance between the structures

$$Ni(—C{\equiv}O)_4 \quad \text{and} \quad Ni(=C=O)_4$$

is possible. This would not be surprising as the same type of resonance probably occurs in carbon monoxide itself.

VALENCY ANGLES

Carbon. Although there has never been any doubt concerning the regular tetrahedral arrangement of the chlorine atoms in carbon tetrachloride, it is satisfactory to know that electron-

diffraction measurements are in conformity with this structure; it appeared at one time, however, that in methylene chloride and in chloroform the angles between the carbon–chlorine bonds were greater than the tetrahedral value of 109° 28′. This conclusion appeared to obtain support from the observed dipole moments, since that for chloroform, $1{\cdot}05 \times 10^{-18}$, was much less than the moment of methyl chloride, $1{\cdot}8 \times 10^{-18}$, with which it should have been identical, had the angles all been tetrahedral. New electron-diffraction measurements have now shown that the Cl—C—Cl angles in both chloroform and methylene chloride are $111 \pm 2°$, and so are very close to the tetrahedral value (Sutton and Brockway, 1935). The discrepancy in the dipole moments must evidently be due to the induced effect of one C—Cl bond on another.

When a carbon atom is joined to other atoms by one double and two single bonds, and the angle between the two latter remains at the tetrahedral value, then the angle between the double bond and either of the single ones, represented by =C—, should be $\frac{1}{2}$ (360°—109° 28′), that is, 125° 44′. Electron-diffraction studies have given $121{\cdot}5 \pm 1°$ for the =C— angle in carbonyl chloride and in thiocarbonyl chloride (Brockway, *et al.*, 1935), and less reliable measurements indicate values of $125 \pm 10°$ in acetyl chloride and bromide (Dornte, 1933). A series of figures from 122 to $124 \pm 2°$ have also been reported for the =C—Cl angle in the six chloroethylenes (Brockway, *et al.*, 1935). The actual angles appear to be slightly less than the theoretical, but it would not be at all unexpected if the presence of a double bond on a carbon atom resulted in the increase of the angle between the two single linkages, so that the latter was somewhat greater than the tetrahedral amount.

Oxygen. The valency angle of oxygen has been a subject of interest since Debye showed from dipole moment considerations that water could not have the linear structure which had been tacitly assumed for it. Pauling (1931) had shown, with the aid of wave mechanics, that the valency angle of oxygen should be 90°, but there was considerable evidence in favour of the view that in water the value was about 105°, and that it might be larger

still in diphenyl ethers. Some definite and important information is now available from a study of the electron diffraction of chlorine monoxide, dimethyl ether, dioxan and α-methylhydroxylamine : in these four substances the angle is found to be approximately 111 ± 4° (Sutton and Brockway, 1935 ; Brockway, *et al.*, 1935). A somewhat smaller value, although this is not known with certainty, is recorded for oxygen fluoride (Boersch, 1935). Owing to the small scattering power of the hydrogen atom, water vapour does not lend itself readily to study by the electron-diffraction method. On reviewing the results given, it might appear at first sight that the natural valency angle of oxygen approached the tetrahedral value, rather than the 90° proposed by Pauling : this conclusion may, however, not be entirely justified. The distance between the chlorine atoms in chlorine monoxide was found to be 2·82 Å., but this is appreciably less than the distance of closest approach of two non-bonded chlorine atoms, that is, chlorine atoms not joined to one another, as found in crystals. Similarly, in dimethyl ether the two non-bonded carbon atoms are only 2·39 Å. from centre to centre, whereas the minimum distance of closest approach is normally about 3·4 Å. It is apparent, therefore, that in these substances there is a force operative bringing the two atoms, joined to the oxygen, closer together than they would prefer to be : that is to say, the actual oxygen valency angle of about 111° is a compromise between the natural angle, which is smaller, and the tendency for the non-bonded atoms to keep apart. Even in water the observed angle of 105°, from spectroscopic data, may be due to repulsion between the hydrogen atoms, for it is significant that in hydrogen sulphide the valency angle of sulphur, which being a larger atom would keep the hydrogen atoms further apart, is little more than 90°. It may be noted that in diphenyl ethers, and related substances, the oxygen valency angle is definitely larger than tetrahedral, as shown both by electron-diffraction and dipole moment studies : there are here special circumstances operative connected with the properties of the phenyl group.

Elements of Group V. According to Pauling's calculations the bond angles of nitrogen and the allied elements, phosphorus and arsenic, should lie between 90° and 109° 28′, the value being

smaller the larger the atomic number. There is very little definite information as to the angle between two single bonds attached to nitrogen, but from the limited number of electron-diffraction measurements it appears that this must be approximately equal to the tetrahedral value. In nitromethane, for example, the nitrogen angle, which would probably be O—N=O, is 127 ± 3° (Brockway, *et al.*, 1935), so that the O—N—O angle, with single bonds, may be expected to be about 105°. The measurements with phosphorus trichloride and trifluoride, and with arsenic trichloride, are reasonably precise, and they indicate valency angles of 101°, 104° and 103°, all ± about 3° (Brockway and Wall, 1934; Pauling and Brockway, 1935), so that the results are in harmony with the theoretical considerations.

The electron-diffraction method of investigating intra-molecular dimensions is only in its infancy, but it should be apparent from what has been written in this chapter that it is likely to prove a weapon of great value to the chemist. It must be admitted, however, that the technique of the method will have to be advanced considerably before it can be applied to relatively complicated compounds, or to cases where different configurations do not produce any important changes in the calculated scattering curves.

REFERENCES

Bewilogua. *Physikal. Z.*, 1931, **32**, 740; 1932, **33**, 688.
Boersch. *Monatsh.*, 1935, **65**, 311.
Braune and Knoke. *Z. physikal. Chem.*, 1933, [*B*], **21**, 297.
Brockway. *J. Amer. Chem. Soc.*, 1935, **57**, 958.
Brockway and Pauling. *Proc. Nat. Acad. Sci.*, 1933, **19**, 68, 860, 868.
Brockway, Beach and Pauling. *J. Amer. Chem. Soc.*, 1935, **57**, 2693.
Brockway and Wall. *Ibid.*, 1934, **56**, 2373.
Cosslett. *Trans. Faraday Soc.*, 1934, **30**, 981.
Cross and Brockway. *J. Chem. Physics*, 1935, **3**, 821.
Debye. *Ann. Physik*, 1915, **46**, 809.
Dornte. *J. Chem. Physics*, 1933, **1**, 566, 630; *J. Amer. Chem. Soc.*, 1933, **55**, 4126.
Ehrenfest. *Vers. K. Akad. Amsterdam*, 1915, **23**, 1132.
Jones. *Trans. Faraday Soc.*, 1935, **31**, 1036.
de Laszlo. *Proc. Roy. Soc.*, 1934, [*A*], **146**, 672, 690.
Mark and Wierl. *Z. Physik*, 1930, **60**, 741; *Z. Elektrochem.*, 1930, **36**, 675.
Maxwell, Hendricks *et al.* *J. Chem. Physics*, 1933, **1**, 549; 1934, **2**, 331; 1935, **3**, 699.

PAULING. *Proc. Nat. Acad. Sci.*, 1932, **18**, 293, 498.
PAULING and BROCKWAY. *J. Chem. Physics*, 1934, **2**, 867 ; *J. Amer. Chem. Soc.*, 1935, **57**, 2684.
PAULING, BROCKWAY and BEACH. *Ibid.*, 2705.
PAULING and HUGGINS. *Z. Kristallog.*, 1934, **87**, 205.
RANDALL. " The Diffraction of X-rays and Electrons," 1934.
SIDGWICK. *Ann. Reports Chem. Soc.*, 1931, **28**, 385 ; 1933, **30**, 118 ; " The Covalent Link in Chemistry," 1933.
STOCK and WIERL. *Z. anorg. Chem.*, 1931, **203**, 228.
SUTTON and BROCKWAY. *J. Amer. Chem. Soc.*, 1935, **57**, 473.
WIERL. *Physikal. Z.*, 1930, **31**, 366, 1028 ; *Ann. Physik*, 1931, **8**, 521 ; 1932, **13**, 453.

CHAPTER VI

SOLUBILITY

Solubility and Vapour Pressure. The phenomena of solubility have for many years presented some of the most perplexing problems of physical chemistry, and various investigators have attempted, from time to time, to find a unifying principle which will permit the known facts to be fitted into a simple system. Even to-day the problem is far from being solved completely, but the recent work of Hildebrand and of Kendall, and their co-workers following on that of Dolezalek, van Laar, Rothmund and others, has opened up a viewpoint which is not only of great theoretical interest, but has also considerable practical importance. Before giving an outline of recent developments in connection with the theory of solubility of *non-electrolytes*, mention must be made of a fact, which a brief consideration shows to be obvious, but which does not seem to be widely realised. The vapour pressure of any component of a solution represents the pressure under which the concentration of that component is the saturation value, and *vice versâ*. For example, at 100° C. the vapour pressures of carbon tetrachloride and tin tetrachloride, over a mixture in which the respective molar fractions are 0·274 and 0·726, are 1450 mm. and 499 mm. respectively ; hence at 100° C. and a pressure of 1450 mm. the molar fraction of carbon tetrachloride in the saturated solution in tin tetrachloride is 0·274. An important consequence of this relationship is that solubility may be treated from the standpoint of vapour pressures.

In his treatment of the problem of solutions, Hildebrand (1916) accepts the Raoult vapour pressure equation as the definition for ideal solutions. It is true that at infinite dilution the Raoult formula and the gas law equation ($PV = RT$) are identical, but at appreciable concentrations the results obtained diverge very

markedly, and it is essential to choose one only of these equations as the basis of subsequent treatment. It does not seem possible to decide between them on purely theoretical grounds, but it is an undoubted fact that although no known solutions obey the van't Hoff gas law equation at appreciable concentrations, there are a number of mixtures of two components to which the Raoult relationship is applicable over the whole range of concentrations. For this and other reasons, Hildebrand has chosen the latter as his fundamental equation to represent the behaviour of an ideal solution ; this choice is by no means universal, but for the present it may be taken as justified by the success of the theory of solubility based on the Raoult equation.

The Raoult Equation. If two liquids are chosen such that the attractive forces between the molecules of each are almost the same, then on mixing these liquids the forces acting on a given molecule will be very little different from those operating in the pure liquid. The tendency of that molecule to escape from the liquid into the vapour phase, as measured by the partial vapour pressure, will then be the same in the mixture as in the pure state. The partial vapour pressure of any component of a mixture is determined by the product of the " escaping tendency " of a single molecule and the number of molecules of that component present ; since the escaping tendency remains unchanged, therefore, the ratio of the partial vapour pressure of a given component in a mixture to that in the pure liquid is equal to the ratio of the number of molecules of this component to the total number in the mixture. If n_1 and n_2 are the numbers of molecules of the two components present in the mixture, and p_1 and p_2 are the respective partial vapour pressures, whereas p_1° and p_2° are the vapour pressures of the pure liquids, then

$$\frac{p_1}{p_1^\circ} = \frac{n_1}{n_1 + n_2} \text{ and } \frac{p_2}{p_2^\circ} = \frac{n_2}{n_1 + n_2} \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

If N_1 and N_2 represent the respective molar fractions of the two species, then

$$\frac{p_1}{p_1^\circ} = N_1 \text{ and } \frac{p_2}{p_2^\circ} = N_2 \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

This is the form of Raoult's law used in connection with the discussion of solubility.

In this deduction two assumptions have been made : firstly that the tendency of a molecule to escape from a liquid is measured by the pressure it exerts in the vapour phase, and secondly that the inter-molecular forces are the same in both components of the mixture. Any deviation from Raoult's law must, therefore, be ascribed to deviations from accuracy of either or both of these assumptions. The first assumption can be shown to involve the supposition that the vapour behaves as a perfect gas ; this is never actually the case, although for small pressures the deviations are not very considerable. It is the second assumption, therefore, which is in most cases responsible for the fact that actual solutions do not obey Raoult's law. As already indicated, the vapour pressure–concentration equation may also represent a solubility–pressure relationship, and so these mixtures, which deviate from Raoult's law, will also have mutual solubilities departing from the ideal. The factors responsible for the vapour pressure deviations, *e.g.*, variations in inter-molecular forces, will therefore be the cause of abnormal solubilities ; this is the basis of Hildebrand's treatment of the solubility problem.

THE SOLUBILITY OF GASES

Calculation of Ideal Solubility. By assuming the accuracy of the Raoult equation, it is possible to determine the solubility of a gas *below its critical temperature :* the latter proviso is essential, since the equation involves a knowledge of the vapour pressure of the pure liquid, and this can only exist below the critical temperature. For example, the critical temperature of ethane is 34° C., but at 25° C. the pure liquid has a vapour pressure of about 42 atms. ; by means of the Raoult equation it follows that the molar fraction (N_2) of ethane in a solution over which the partial pressure of this component is 1 atm., is given by the relationship

$$\frac{1}{42} = N_2 = 0{\cdot}024 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

since p_2 is 1 and p_2° is 42 atms. Hence in an *ideal solution* of ethane its partial vapour pressure would be 1 atm. when its molar fraction was 0·024; consequently at a pressure of 1 atm. the solubility of ethane in an *ideal* solution should be 0·024 molar fraction, *irrespective of the nature of the solvent.* The actual solubility in *n*-hexane at 25° C. and 1 atm. pressure is 0·0171 molar fraction, and hence in this solvent the behaviour is not quite ideal; this is not surprising since the deviations of the vapour from the perfect gas laws at a pressure of 42 atms. must be very considerable. The agreement between observed and calculated values is, however, sufficiently close to justify the application of the Raoult equation to solubility problems.

The method used here for calculating the solubility of a gas may be extended to temperatures above the critical value by extrapolating the vapour pressures of the pure liquid solute measured below the critical temperature. For vapours obeying the gas laws the Clausius-Clapeyron equation may be written

$$\frac{d \ln p^\circ}{dT} = \frac{L}{RT^2} \quad \text{(iv.)}$$

or

$$\frac{d \ln p^\circ}{d(1/T)} = -\frac{L}{R} \quad \text{(v.)}$$

where L is the molar heat of vaporisation of the liquid and p° its vapour pressure at the temperature T. If L may be regarded as constant over a range of temperature, then the plot of $\ln p^\circ$ (or $\log p^\circ$) against $1/T$ should be a straight line; this may be obtained from measurements of the vapour pressure of the liquid at various temperatures, and may be easily extrapolated to give the hypothetical value of p° at temperatures above the critical point. Methane, for example, has a critical temperature of $-95{\cdot}5^\circ$ C., but by extrapolating the straight line plot of $\ln p^\circ$ against $1/T$ the imaginary value of p° at 25° is found to be 370 atms. The ideal solubility of methane at 25°, and under a partial pressure of 1 atm., should then be $1/370 = 0{\cdot}0027$ molar fraction; from actual measurements the solubility at this temperature and pressure has been found to be 0·0031 molar fraction in hexane, and

0·0026 in xylene. The agreement is almost better than might have been expected.

Solubility and Critical Temperature. In general, it follows from the application of Raoult's law that the solubility (N) of a gas, expressed in molar fractions, at a partial pressure of 1 atm. is given by the expression

$$N = \frac{1}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi.)}$$

where p is the saturated vapour pressure of the pure solute at the same temperature. The higher the boiling point, and the critical temperature, of the substance the lower will be the vapour pressure p at a given temperature, and so the higher the solubility. The connection between critical temperature and solubility, based on the Raoult equation, is in general agreement with observation; this may be seen from an examination of the results, calculated by Hildebrand from the measurements of Just (1901), quoted in Table XXXV.

TABLE XXXV

Solubilities of Various Gases in Different Solvents (Molar Fractions).

Gas.	Crit. Temp.	Solvent.		
		Benzene.	Chloroform.	Carbon Disulphide.
Hydrogen . .	− 235° C.	0·00026	—	—
Nitrogen . . .	− 146°	0·00041	0·00043	0·00013
Carbon monoxide .	− 141°	0·00061	0·00063	0·00020
Carbon dioxide . .	+ 31°	0·0094	0·0123	0·0023

Although the general agreement with the requirements of Raoult's equation is satisfactory, it is seen that the solutions are by no means ideal, since the solubility is not independent of the nature of the solvent.

Solubility and Temperature. Another general conclusion concerning the solubility of gases relates to the variation with temperature: since the value of $p_1°$, the vapour pressure of the pure solute in the liquid form, increases with temperature, the

solubility, according to equation (vi.), must decrease. This is, of course, in agreement with experimental observation. The variation of the vapour pressure is given by the Clausius-Clapeyron equation (iv.), and so this relationship may be used for ideal solutions to determine the change of solubility with temperature.

Deviations from the Raoult Equation. It has been seen that in practice solutions do not always behave in an ideal manner, and a study of the vapour pressures of a large number of mixtures has shown that the deviations from Raoult's law may be divided into two main types. In the first case the partial vapour pressure of

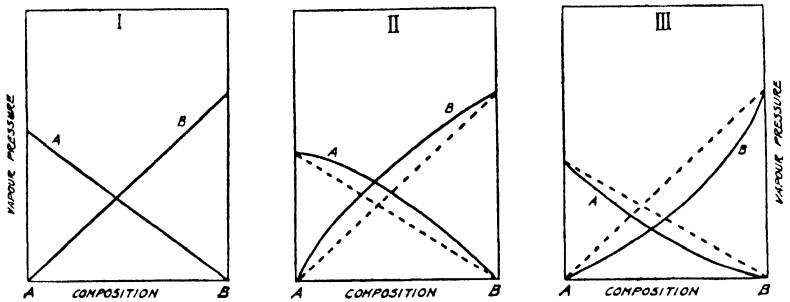


FIG. 18.—Variation of the *partial* vapour pressure of each component (A and B) of a binary mixture with the composition in molar fractions. The ideal curve, according to the Raoult equation, is shown in I. (also by broken lines in II. and III.); the full curves in II. indicate positive deviations, and in III. negative deviations from the ideal equation.

each component may be greater than the theoretical (ideal) value; the deviations are then said to be positive (Fig. 18, II.). On the other hand, the partial vapour pressure may be less than the value given by the Raoult equation, and the deviation is then negative (Fig. 18, III.). It should be mentioned that the deviations shown by each component of a mixture may be different in value, but they are almost invariably in the same direction. Without entering, for the present, into a discussion of the causes of departure from ideal behaviour, certain consequences of the divergence may be noted. If the deviation from Raoult's law is positive, it may be seen from Fig. 18, II., that for a given partial pressure, *e.g.*, 1 atm., of the component A, the mixture will contain a smaller

proportion of A than would have been the case had the solution been ideal. A positive deviation implies, therefore, that the solubility of the gas will be lower than the ideal value. In the same way it may be shown from an examination of Fig. 18, III., that when a solute shows a negative deviation from the requirements of Raoult's equation, the solubility will be greater than the calculated amount. Liquids in which this type of divergence occurs are commonly called " good solvents." The deviations of any system from Raoult's law decrease as the temperature is raised, and so the higher the temperature the more closely does the behaviour of any solution approach the ideal.

The solubility of a gas decreases with increasing temperature, and since at the same time the deviations from Raoult's equation diminish, it follows that for solutions in which the deviations are negative, *i.e.*, in good solvents, the decrease of solubility as the temperature is raised must be more marked than in a solution showing positive deviations ; in the latter the solubility is below the ideal value, and the difference becomes less as the temperature is increased. Hildebrand has generalised this in the statement that " the solubility of a given gas will usually decrease with temperature more rapidly in a good solvent for it than in a poor one."

MUTUAL SOLUBILITY OF LIQUIDS

Ideal Solutions. For a system containing two liquid components it is known that two liquid phases are possible ; if such layers are formed, then at equilibrium the vapour pressure of either component will be the same in both layers. If this were not so, the phases would not be in equilibrium, and the components would tend to distil from one phase to the other until this condition was attained. If Raoult's law applies to the system, then it follows that the molar fraction of either component is the same in both phases, or, in other words, both layers have exactly the same composition, and so must be one layer. It may be concluded, therefore, that in a system of two liquids obeying the ideal solution law, it is not possible for two layers to form, and the two liquids must be miscible in all proportions. When a solution shows

positive deviations from Raoult's law, the vapour pressure is greater than the ideal value, and if the divergence is sufficiently large it may be possible to have two solutions of different compositions yet having the same partial pressures of the two components. Two layers can then form, and the liquids are said to be partially miscible with one another; incomplete miscibility is therefore a consequence of positive deviations from the ideal.

Partial Miscibility. The same conclusion may be reached in a more definite manner: it can be shown that when a mixture does not obey Raoult's law the actual vapour pressures may be represented by the relation

$$\frac{p_1}{p_1^\circ} = N_1 e^{\beta N_2^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii.)}$$

or

$$\ln \frac{p_1}{p_1^\circ} = \ln N_1 + \beta N_2^2 \quad . \quad . \quad . \quad . \quad . \quad \text{(vii}a\text{.)}$$

where β represents the extent of the deviation from ideal behaviour. From these equations it may be seen that for a system showing positive deviations β is positive, and the variation of p_1, the partial vapour pressure, with N_1, the molar fraction, of a particular component will be represented by a series of curves such as those shown in Fig. 19. As a result of lowering the temperature, the deviation from Raoult's law, and hence the value of β, increases, and so the curves I., II. and III., which may be taken as representing the behaviour at three temperatures *decreasing* in the order given, show increasing positive deviations. At sufficiently low temperatures, the actual value depending on the magnitude of the divergence of the particular system from ideal behaviour, curves of the type of III. are obtained; the S-shaped portion of this curve implies that there should be three different solutions, represented in composition by *a*, *b* and *c*, having the same vapour pressure. This would imply that the three liquid layers *a*, *b* and *c* should be capable of existing in equilibrium with one another at the given temperature; from the Phase Rule this is known to be impossible, and in actual practice it is found that the phase *b* does not exist, but only those corresponding to *a* and *c* can be obtained. (The significance of the curve between *a*, *b* and *c* is similar to that

of the S-shaped portion of the van der Waals curves: only the extreme values of the volume for any given pressure can be realised experimentally.) It is clear, therefore, that when the positive deviation from Raoult's law is sufficiently great, two liquids can form two layers, and so become partially miscible. As the temperature is lowered, the distance between *a* and *c* (Fig. 19)

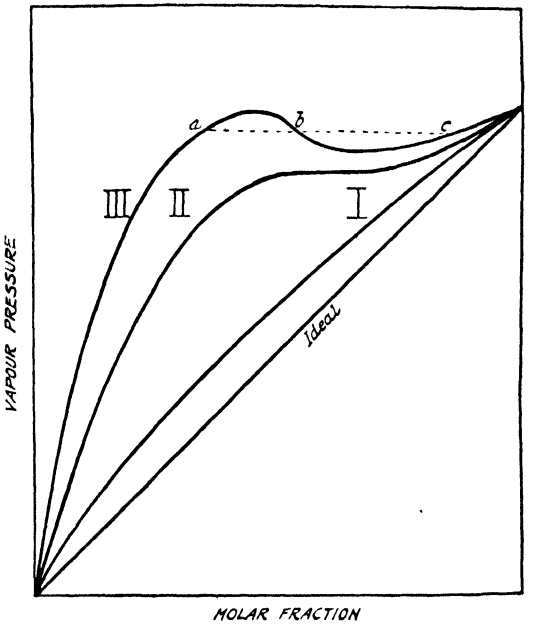


FIG. 19.—Partial vapour pressure curves for one of the components in a mixture of two liquids showing positive deviations from Raoult's equation. The extent of the deviations increases in passing from I. to II. to III., as the temperature is lowered. (After Hildebrand.)

becomes greater, and the mutual solubility of the liquids decreases, but if the temperature is raised so that the deviations from ideal behaviour diminish, *a* and *c* approach one another and become identical at the critical solution temperature. This temperature is actually represented by a curve such as II. in Fig. 19, with a point of inflexion, that is, with a horizontal tangent at one point only; the curve is in fact similar to the critical temperature curve

obtained from the van der Waals equation. It must be mentioned here that not all partially miscible liquids have their mutual solubilities increased as the temperature is raised; in some cases complete miscibility is attained as a result of lowering the temperature. The cause of this abnormality will be discussed later.

SOLUBILITY OF SOLIDS IN LIQUIDS

The Ideal Solubility. Raoult's law, in the form $N = p/p^\circ$, may be used to calculate the ideal solubility of a solid in a liquid; here p represents the partial vapour pressure of the solid solute over the solution, and p° is the vapour pressure of the pure solute in the *liquid* state at the same temperature. When a solution is saturated with solid, the vapour pressure of the latter (p^s) must be identical with its partial vapour pressure (p) over the solution, otherwise equilibrium between solid and solution would not be possible. The solubility (N) of a solid, in molar fractions, at a given temperature may consequently be represented by the equation

$$N = p^s/p^\circ \quad . \quad . \quad . \quad . \quad . \quad . \text{(viii.)}$$

where p^s and p° represent the vapour pressures of the solid and the supercooled liquid, respectively, at the particular temperature chosen. When the solid solute is capable of existence, the liquid form must be metastable, and have a higher vapour pressure; that is, p° is greater than p^s, and so the value of N, the solubility, is a *finite fraction* varying with temperature. The solubility of a solid in a liquid therefore is *limited* and depends on the temperature.

In order to utilise the solubility form of the Raoult equation practically, it is necessary to introduce the Clausius-Clapeyron relationship as applied to the liquid–vapour transformation

$$\frac{d \ln p^\circ}{dT} = \frac{L_V}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix}a\text{.)}$$

where L_V is the latent heat of vaporisation per gm.-mol. of liquid. Similarly for the solid–vapour system, the equation takes the form

$$\frac{d \ln p^s}{dT} = \frac{L_S}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix}b\text{.)}$$

where L_S is the latent heat of sublimation per gm.-mol. Subtracting these two equations, it follows that

$$\frac{d \ln (p^s/p^\circ)}{dT} = \frac{L_S - L_V}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad \text{(x.)}$$

and

$$\frac{d \ln N}{dT} = \frac{L_F}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xi.)}$$

since N, the solubility, is equal to p^s/p° (equation (viii.)) and L_F, the latent heat of fusion, is equal to the difference between the heats of sublimation and vaporisation. Integrating this equation between the temperature limits of T and T', the corresponding solubilities, in molar fractions, being N and N', there results

$$\ln \frac{N}{N'} = \frac{L_F}{R}\left(\frac{1}{T'} - \frac{1}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad \text{(xii.)}$$

assuming the latent heat of fusion to remain constant. At the melting point (T_m) the vapour pressures of the solid and liquid states are identical, that is, $p^s = p^\circ$, and so N is unity ; substituting T_m for T' and 1 for N', the equation reduces to

$$\ln N = \frac{L_F}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad \text{(xiii.)}$$

or

$$\log N = \frac{L_F}{4{\cdot}57}\left(\frac{1}{T_m} - \frac{1}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv.)}$$

replacing natural logarithms by those to the base of 10, and putting R equal to 1·985 cals. This relationship may be used to determine the *ideal* solubility of a solute in the following manner : with naphthalene as solute, for example, the latent heat of fusion per gm.-mol. (L_F) is known to be 4400 cals., and the melting point is 80° C., and so T_m is 353° ; hence at 25° C. ($T = 298°$) $\log N$ is calculated as $-0{\cdot}507$ and N is therefore 0·311 molar fraction. For an ideal solution this value would be independent of the nature of the solvent, but in actual practice it does depend on the latter ; in benzene at 25° the saturated solution contains 0·29 molar fraction of naphthalene, and similar values have been observed in toluene, chlorobenzene, ethylene dichloride and chloroform, but in aniline, acetone and hexane the solubility is

appreciably lower than the ideal value, especially at low temperatures.

Since T_m is a constant for a given solute, and L_F has been assumed to be independent of temperature, equation (xiv.) may be written in the form

$$\log N = a + \frac{b}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xv.)}$$

where $a = L_F/4{\cdot}57T_m$ and $b = -L_F/4{\cdot}57$ are constants. The plot of log N against $1/T$ should consequently be a straight line when the Raoult equation is obeyed; the slope of this line is equal to $-L_F/4{\cdot}57$, and when N is unity—that is, for the pure solute—log N is zero and T is equal, as it should be, to T_m. The curve under discussion gives the variation of solubility (N) with the temperature, and the ideal form can be obtained in two ways: if the melting point is known, T ($= T_m$) is known for $N = 1$, and so one determination of the (ideal) solubility is sufficient to fix the ideal curve; alternatively the slope of the curve may be calculated if the latent heat of fusion is known, and its position fixed either by the melting point or by one solubility determination. The negative value for the slope ($-L_F/4{\cdot}57$) implies, as is well known, that the solubility N must increase as the temperature increases, or as $1/T$ decreases.

Solubility and Melting Point. Two general deductions may be made from equation (xiv.); firstly, if the latent heats of fusion of two substances are of the same order, then it follows that the larger the value of T_m, the smaller is $1/T_m$, and the smaller the solubility (N). It will be seen, therefore, that providing the heats of fusion do not differ considerably, the solid with the higher melting point will have a lower solubility than the solid with the lower melting point. This connection between solubility and melting point has been known empirically for many years, and is borne out, approximately at least, by the results in Table XXXVI., taken from Hildebrand's book on Solubility.

The second deduction is not so useful on account of the lack of the necessary data: if two solids have similar melting points, the value of $\frac{1}{T_m} - \frac{1}{T}$ will be a constant negative quantity ($= -k$);

TABLE XXXVI.—*Solubility and Melting Point.*

Solute.	Melting Point.	Molar Fractions at 25° in	
		Ether.	Benzene.
Anthraquinone . .	282°	0·00037	0·0013
Anthracene . .	217°	0·0059	0·0063
Phenanthrene . .	100°	0·151	0·186
Naphthalene . .	80°	*ca.* 0·27	0·290

hence log N will be equal to $-kL_F$, and N will increase as L_F decreases. It follows that for such solids the one with the higher latent heat of fusion will be the less soluble at a given temperature.

Deviations from Ideal Behaviour. Actually it appears that there are very few solid–liquid systems for which Raoult's law applies exactly, and deviations lead to the departure of the observed solubilities from the calculated values. If the deviations are positive, the partial vapour pressure of the solute over the solution will attain the value for the pure solid at a smaller concentration than would have been the case had the Raoult equation been obeyed. The saturation solubility for positive deviations from the law will thus be less than the ideal value, calculated in the manner described. Similarly, if the deviations are negative, the solubility of the solid will be greater than the calculated value. The fact that Raoult's law is approached more closely as the temperature is raised, whereas at the same time the ideal solubility increases, leads to the conclusion that for poor solvents, namely, those in which the deviations are positive, the temperature coefficient must be greater than for good solvents. This conclusion is the reverse of that reached in connection with the solubility of gases, but it must be remembered that for the latter solutes the solubility generally decreases with increasing temperature.

If the positive deviation from ideal behavour is small, the curve of log N against $1/T$ may be of the type of I., Fig. 20 ; although the slope is not that of the ideal curve, it approaches the latter as

the temperature is raised. For larger deviations the curve may be of type II. (Fig. 20), the solubility approaching the ideal value only at the melting point of the solute. If the positive deviations are very considerable, however, the plot of log N against $1/T$ does not continue directly to the melting point as log N approaches zero, and a curve of type III. (Fig. 20) is obtained. Even at the melting point the solubility of the solid, in the particular solvent,

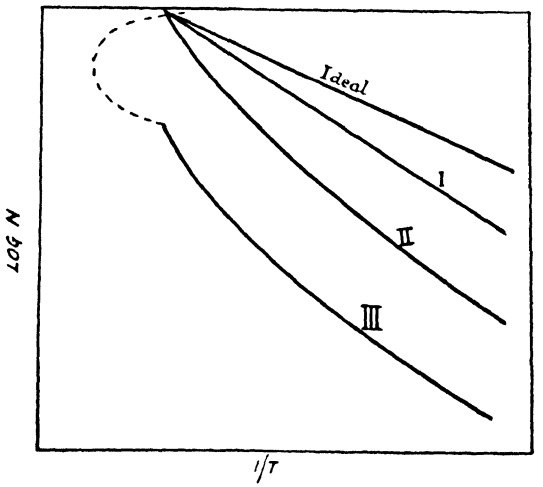


FIG. 20.—Variation with temperature of the solubility (N) of a solid in a liquid. Curves I., II. and III. indicate increasing positive deviations; the broken portion of III. shows that two liquid layers are formed above the melting point of the solute. (After Hildebrand.)

is very much less than the ideal value, and in the vicinity of the melting point of the solute two liquid layers are formed; the temperature–composition curve of the conjugate binary liquid layers is shown by the usual " parabolic " type of curve, which is dotted in Fig. 20.

CAUSE OF DEVIATIONS FROM RAOULT'S LAW

In attempting to find the cause of deviations from ideal behaviour thermodynamic methods have been used to discover the conditions under which the Raoult equation is obeyed. It appears

that for systems which obey Raoult's law there is no heat or volume change on mixing, and the heat of solution of a solid is the same as its latent heat of fusion. Although the converse of this statement cannot be taken as necessarily true it may be assumed that, in general, when there is an absorption of heat on mixing two liquids, or when the heat of solution of a solid is greater than the latent heat of fusion, there is a positive deviation from Raoult's law; if heat is evolved on mixing, or the heat of solution is less than the latent heat of fusion, the deviations from Raoult's law are negative. Further, if there is an increase of volume on mixing, the deviations are generally positive, but a decrease of volume generally implies negative deviations from ideal behaviour.

Internal Pressure. In the further development of the theory of solubility, however, the important conclusion has been reached that only those liquids having identical values of $(dp/dT)_v$ can obey Raoult's law at all temperatures and pressures. That is, the variation of pressure with temperature, at constant volume, for two substances must be exactly the same for the mixture to obey Raoult's law exactly. Provided certain disturbing factors, to be discussed later, do not operate, the deviations from the ideal law resulting from differences in the $(dp/dT)_v$ term will be *positive*. According to Hildebrand, it seems reasonable to expect that " since differences in the values of $(dp/dT)_v$ for two liquids lead to deviations from the ideal behaviour, the amount of the deviation will be determined, at least partly, by the magnitude of the difference between the values of this important quantity for the two liquids." This is only approximately true, but is close enough for the treatment of the solubility problem.

It can be shown by means of the second law of thermodynamics, that for any homogeneous substance the equation

$$p + \left(\frac{du}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v \quad . \quad . \quad . \quad . \quad \text{(xvi.)}$$

applies, where u is the total energy of the substance. This equation may be correlated with the van der Waals equation of state in the form

$$p + \frac{a}{v^2} = T\,\frac{R}{v - b} \quad . \quad . \quad . \quad . \quad . \quad \text{(xvii.)}$$

which on differentiation with respect to T, at constant volume, gives

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b} \quad \ldots\ldots \text{(xviii.)}$$

$$\therefore p + \frac{a}{v^2} = T\left(\frac{dp}{dT}\right)_v \quad \ldots\ldots \text{(xix.)}$$

On comparing equations (xvi.) and (xix.) it is seen that the term a/v^2, which attempts to represent the attractive force of the molecules, may be put as approximately equal to $(du/dv)_T$.* It is probably more accurate to say that $(du/dv)_T$ is exactly equal to the attractive force of the molecules, since this differential term is the mathematical expression of the energy absorbed in expansion at constant temperature, when the kinetic energy of the molecules is constant, and so is presumably equal to the work done against the attraction of the molecules. Hence $(du/dv)_T$ may be regarded as a measure of the " internal pressure " of the substance under consideration. For a liquid the " external pressure " (p), which is generally of the order of one atmosphere or less, is negligible in comparison with the internal pressure ; it is, therefore, possible to write *for a liquid*

$$\left(\frac{du}{dv}\right)_T \approx T\left(\frac{dp}{dT}\right)_v \quad \ldots\ldots \text{(xx.)}$$

and so the right-hand side of this equation may be regarded as approximately equal to the internal pressure.

In a previous paragraph it was stated that systems consisting only of liquids having the same value of $(dp/dT)_v$ would be expected to obey Raoult's law, and presumably this condition applies to the term $T\,(dp/dT)_v$, which is equal to the internal pressure. It may be concluded that a mixture of two liquids can only be expected to show no deviations from the ideal behaviour required by Raoult's law provided they have the same internal pressures. Any difference in the internal pressures will mean, as a general rule, positive deviations from the ideal equation, so that vapour pressures will be greater and solubilities less than the ideal values. It may be recalled that in the deduction of the Raoult equation

* This is only approximate since equation (xvi.) is exact, but not (xix.).

(p. 230), it was assumed that the attractive forces between the molecules of each of the components of the mixture are almost the same; any deviations from equality must result in the equation not being strictly obeyed. This view is in harmony with the conclusion reached by Hildebrand, and described here, from thermodynamic reasoning, since the internal pressure may be identified with the attractive force between the molecules. If, as already assumed, the deviations from Raoult's law are proportional to the differences in the $(dp/dT)_v$ terms for the two components of the mixture, it follows that the deviations are proportional to the differences in the internal pressures.

MEASUREMENT OF INTERNAL PRESSURE

The internal pressure of a liquid may be determined approximately by a number of methods, some of which, however, give only relative values; the results, although not identical, are in general agreement and give a satisfactory indication of the differences in the internal pressures of various liquids.

The coefficient of expansion (α) may be represented by the equation

$$\alpha = \frac{1}{v}\left(\frac{dv}{dT}\right)_p \quad \ldots\ldots\ldots \text{(xxi.)}$$

whereas the coefficient of compressibility (β) is given by the expression

$$\beta = -\frac{1}{v}\left(\frac{dv}{dp}\right)_T \quad \ldots\ldots\ldots \text{(xxii.)}$$

Dividing equation (xxi.) by (xxii.) it follows that

$$-\frac{\alpha}{\beta} = \left(\frac{dv}{dT}\right)_p \left(\frac{dp}{dv}\right)_T = -\left(\frac{dp}{dT}\right)_v \quad \ldots \text{(xxiii.)}$$

$$\therefore T\frac{\alpha}{\beta} = T\left(\frac{dp}{dT}\right)_v = \text{Internal Pressure} \quad \ldots \text{(xxiv.)}$$

The internal pressure may thus be calculated from the coefficients of expansion and compressibility of the liquid.

It has been stated that a/v^2 of van der Waals' equation may be

taken as a measure of the internal pressure, and so also may the term $RT/(v - b)$, which is almost equal to a/v^2 for a liquid (equation xvii.), when the external pressure is small compared with the internal pressure. It is thus possible to determine the latter if either a or b for the particular substance is known. Van Laar (1916) has shown that $\sqrt{a}$ for a molecule may be regarded as approximately equal to the sum of the $\sqrt{a}$ values attributed to its constituent atoms; from the compilation made by van Laar it is possible to obtain a value of a which may be used when a more direct determination cannot be carried out. An alternative method of evaluating a/v^2 is to differentiate the van der Waals equation with respect to v, at constant pressure, when the following equation is obtained:

$$-\frac{2a}{v^3}(v - b) + \frac{a}{v^2} = R\left(\frac{dT}{dv}\right)_p \quad . \quad . \quad . \quad \text{(xxv.)}$$

Replacing $(v - b)$ by $RT\Big/\left(p + \frac{a}{v^2}\right)$, to which it is equal by the van der Waals equation, it follows that

$$\frac{a}{v^2} - \frac{2a}{v^3} \cdot \frac{RT}{\left(p + \frac{a}{v^2}\right)} = R\left(\frac{dT}{dv}\right)_p \quad . \quad . \quad . \quad \text{(xxvi.)}$$

Since $(dv/dT)_p = \alpha v$ (equation xxi.) then by neglecting p in comparison with a/v^2 it may be deduced that

$$\frac{a}{v^2} = \frac{R}{v}\left(\frac{1}{\alpha} + 2T\right) \quad . \quad . \quad . \quad . \quad . \quad \text{(xxvii.)}$$

and so the internal pressure may once more be calculated from the coefficient of expansion; v is the molecular volume of the liquid at the temperature T, generally 293° K. (20° C.).

If a gm.-mol. of a liquid, occupying a volume v, could be expanded isothermally until it attained the volume v' of the saturated vapour, the work done against the molecular attraction, that is, the cohesive energy, could be identified with the *internal*

molar heat of vaporisation (E), which is RT less than the total heat of vaporisation. It follows, therefore, that

$$E = \int_{v}^{v'} \frac{a}{v^2}\, dv = -a\left(\frac{1}{v'} - \frac{1}{v}\right) \quad . \quad . \qquad \text{(xxviii.)}$$

Since the volume of the vapour (v') is large compared with that of the liquid (v) it is possible to neglect $1/v'$, and so

$$E = \frac{a}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(xxix.)}$$

$$\therefore \frac{a}{v^2} = \frac{E}{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(xxx.)}$$

The internal pressure may thus be determined from the heat of vaporisation and the molecular volume of the liquid. Hildebrand has shown that E may be approximately related to the boiling point of the liquid, on the Centigrade scale, by the formula

$$E = 5280 + 24{\cdot}5t$$

$$\therefore \text{Internal pressure} = \frac{5280 + 24{\cdot}5t}{v} \quad . \quad . \quad . \qquad \text{(xxxi.)}$$

It should be noted that E is here expressed in *calories* and the result should be multiplied by the mechanical equivalent of heat in order to obtain the internal pressure in dynes per sq. cm.; the same warning as to correction for units applies to the value of R in equation (xxvii.).

Finally, the relative internal pressure may be calculated from the total surface energy S, by the relationship

$$\text{Internal Pressure} \propto \frac{S}{\sqrt[3]{v}} \quad . \quad . \quad . \quad . \qquad \text{(xxxii.)}$$

where

$$S = \gamma - T\left(\frac{d\gamma}{dT}\right),$$

γ being the surface tension, and v the molecular volume of the liquid.

All these methods for determining absolute or relative internal

pressures yield results in close agreement; in Table XXXVII. are given some relative values, with the internal pressure of naphthalene as unity, compiled mainly from the results quoted by Mortimer (1923).

TABLE XXXVII.—*Relative Internal Pressures.*

Substance.	Rel. Int. Pressure.	Substance.	Rel. Int. Pressure.
Hexane	0·56	Naphthalene	1·00
Ethyl ether	0·62	*p*-Dibromobenzene	1·09
Ethyl acetate	0·73	Ethylene dibromide	1·13
Carbon tetrachloride	0·81	Pyridine	1·17
Toluene	0·84	Carbon disulphide	1·18
Chloroform	0·90	Phenol	1·4
Benzene	0·96	Iodine	1·82
Bromobenzene	0·96	Phosphorus	2·5
Chlorobenzene	0·96	Water	4·55

REGULAR SOLUTIONS

Provided there are no deviations caused by polarity, molecular association or compound formation, such as are considered in the next section, the curves representing the variation of solubility with temperature show a definite regularity (see Fig. 20), even when departure from ideal behaviour is large. Such systems have been called "regular solutions" (Hildebrand, 1929), and consideration of their properties has produced results of importance. Hitherto the relation between the departure of solubility from the ideal and the difference in internal pressure of solvent and solute has only been a qualitative one, but by applying the theory of the structure of liquids, suggested by Menke (1932) as a result of X-ray studies, to the concept of regular solutions, in which the molecules are assumed to be arranged in a completely random manner, a quantitative connection has been deduced (Hildebrand and Wood, 1933). In the theoretical treatment a number of approximations had to be made and finally an equation, identical with one previously deduced by Scatchard (1931) by

making assumptions concerning the energy of mixing, was developed : this may be written in the form

$$RT\ln\frac{N_2^{\,i}}{N_2} = V_1^2 v_2\left\{\left(\frac{E_2}{v_2}\right)^{1/2} - \left(\frac{E_1}{v_1}\right)^{1/2}\right\}^2 \quad . \quad . \quad \text{(xxxiii.)}$$

where N_2 is the observed solubility, in molar fractions, and $N_2^{\,i}$ is the ideal value ; v_1 and v_2 are the molecular volumes, and E_1 and E_2 the cohesive energies of the two constituents of the solution ; V_1 is the volume fraction of the solvent, defined by the relationship

$$V_1 = \frac{n_1 v_1}{n_1 v_1 + n_2 v_2} \quad . \quad . \quad . \quad . \quad \text{(xxxiv.)}$$

where n_1 and n_2 are the number of gm.-mols. of the two components, in this case solvent and solute, respectively. The cohesive energies may be taken as equal to the corresponding internal molar heats of vaporisation, and so E/v is an approximate measure of the internal pressure of a liquid (see equation xxx.) to which the van der Waals equation is applicable. When solvent and solute have the same internal pressure the right-hand side of equation (xxxiii.) is zero, and so the actual solubility is then equal to the ideal value. If the internal pressures are different there will be departure from ideal behaviour, the extent of which can be calculated from the equation. If the solvent and the solute have the same molecular volume, that is, v_1 and v_2 are equal, equation (xxxiii.) reduces to

$$RT\ln\frac{N_2^{\,i}}{N_2} = N_1^2(E_1^{1/2} - E_2^{1/2})^2 \quad . \quad . \quad \text{(xxxv.)}$$

which is identical in form with equation (vii*a*.), already considered in connection with two-liquid systems.

In order to test the applicability of equation (xxxiii.) two methods may be employed. From a knowledge of the molecular volumes, the latent heats of vaporisation and the ideal solubility, obtained as already described, it is possible to calculate the actual solubility, at least approximately (Scatchard, 1931) ; alternatively, from the measured solubility, the ideal value and the latent heat of the solvent, it is possible to calculate that of the solute. The values obtained in this way should be constant for the same

solute in a series of solvents; this method has been used by Hildebrand (1935) and will be considered later in connection with the solubility of solids for which the data are available. In the meantime mention may be made of a simple verification of equation (xxxv.): the molecular volumes of iodine and carbon disulphide are 59·0 and 60·7 c.c., respectively, at 25°, and so this equation may be regarded as being applicable. The molar internal heats of vaporisation at 25° are 11,300 cals. and 5970 cals., respectively, and so $(E_1^{1/2} - E_2^{1/2})^2$ is equal to 840 cals. The ideal solubility of iodine is 0·212 molar fraction, whereas the actual value in carbon disulphide is 0·0576; the left-hand side of equation (xxxv.) is thus 771 cals., whereas the right-hand side is 746 cals. The agreement between these two values is quite satisfactory.

IRREGULAR SOLUTIONS

Association and Deviations from Raoult's Law. Before proceeding to discuss the applications of the internal pressure concept to the theory of solutions, mention may be made of certain other factors liable to cause deviations from the ideal vapour pressure equation. Such factors have an influence on solubility which is in addition to that resulting from differences in internal pressures: they result in departure from regular behaviour, and the systems in which they are operative have been called "irregular" solutions. Consider a mixture of two components A and B: if the forces between molecules of A are almost the same as those between molecules of B, and neither type of molecule has any polarity resulting in an external electrical field, then it is reasonable to suppose that the forces between A and B will also be the same. Under these conditions the average force acting on any molecule will be independent of the composition, and, from what has already been said, it is clear that the mixture will obey Raoult's law.

If, on the other hand, the forces between the molecules A are greater than those between B, the former will tend to aggregate together so that the latter are squeezed out; in other words, the high internal pressure of one of the components of the mixture

increases the escaping tendency, and hence the vapour pressure of the other. As already seen, therefore, a difference in internal pressure of the two components of a mixture results in positive deviations from Raoult's law. If the compound A is polar, that is, it has an unsymmetrical field of force and contains a grouping possessing an appreciable dipole moment, then there is a specific attraction between the molecules which tends to decrease their external electrostatic field ("Recent Advances in Physical Chemistry," Chapter III.). Under these conditions it appears that the positive deviations from the ideal behaviour are more than the direct proportionality to differences in the internal pressures would indicate. A non-polar substance will then, as a general rule, be particularly insoluble in a polar solvent; for example, non-polar substances like hydrocarbons, carbon tetrachloride and carbon disulphide, are almost insoluble in the highly polar liquid water. For the same reason a polar compound is usually only very sparingly soluble in a non-polar solvent.

In the extreme case of attraction between polar molecules definite association into complex molecules results; this will have the effect of increasing the positive deviations from Raoult's equation still further. In a mixture consisting of n_1 gm.-mols. of A and n_2 gm.-mols. of B, in which x gm.-mols. of the latter have associated to form double molecules, the number of gm.-mols. of single molecules of B remaining is $n_2 - 2x$, and the total number of gm.-mols. in the mixture is $n_1 + n_2 - x$, made up of n_1 of A, $n_2 - 2x$ of B, and x of B_2. It follows, therefore, that if there were no other factors operative causing deviations from the ideal equation, then

$$\frac{p_1}{p_1^\circ} = \frac{n_1}{n_1 + n_2 - x} \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxvi.)}$$

The value of the vapour pressure p_1 of A is clearly greater than would have been the case had no association of B occurred, and so this factor introduces positive deviations, apart from those due to other influences. The effect of association in the liquid B is, therefore, to cause the solubility of A to decrease; similarly the solubility of B in A will be lowered as a result of the association.

Dolezalek (1908, 1918) has attempted to account for the

deviations from Raoult's law in a number of instances by attributing them entirely to association, and sometimes also to compound formation between the components (*vide infra*), without making any allowance for the effect of internal pressure differences. This view involves the necessity of assuming that such symmetrical molecules as carbon tetrachloride and stannic chloride, and even argon, form double molecules in the liquid phase, and that three molecules of ethyl iodide are associated together in a complex. The improbability of these suggestions is sufficient to show that association cannot account for the whole of the observed vapour pressure deviations.

Compound Formation. There is still the possibility that the force of molecular attraction between A and B will be abnormally large : in this case the escaping tendency of each molecular species is considerably reduced, so that the vapour pressures are less than the ideal values ; the system then shows negative deviations from the ideal behaviour, and the mutual solubilities are greater than might be expected from the Raoult equation. This exceptional molecular attraction is found when both components of the mixture are polar ; for example, pyridine and water have rather different internal pressures, and so might be expected to show positive deviations from Raoult's law, and hence a limited mutual solubility. Both liquids are, however, polar, and presumably on account of the attraction between the two kinds of molecules the deviations are reduced to such an extent that mutual solubility, in all proportions, becomes possible. In the limiting case, the attraction between the different molecules, although not necessarily due to polarity, results in compound formation, and this can be readily shown to cause negative deviations from the ideal law. If in a mixture consisting of n_1 gm.-mols. of A and n_2 gm.-mols. of B, x gm.-mols. of each are used up in the formation of x gm.-mols. of a compound AB, then the total number of gm.-mols. present is $(n_1 - x) + (n_2 - x) + x$, that is, $n_1 + n_2 - x$; if Raoult's equation is assumed to be obeyed by the molecules present, then

$$\frac{p_1}{p_1^\circ} = \frac{n_1 - x}{n_1 + n_2 - x} \quad . \quad . \quad . \quad . \quad . \text{(xxxvii.)}$$

It may be deduced from this equation that p_1, the vapour pressure of the compound A, is *less* than would have been the case had no compound formation occurred; this factor, therefore, causes negative deviations from Raoult's law, and hence increased mutual solubility. Kendall and his co-workers (1921) have made comprehensive studies of compound formation and solubility in systems involving both polar and non-polar constituents, and from their results there is very little doubt that the tendency to compound formation between the components of a mixture and mutual solubility are definitely parallel.

It is interesting to mention in connection with the subject of compound formation that a number of systems consisting of two partially miscible liquids, *e.g.*, water and methyl ethyl ketone, show a *lower* critical solution temperature. In the ordinary way increase of temperature decreases the deviation from Raoult's law, so that the mutual solubility of two liquids would be expected to increase as the temperature is raised (p. 238); there should thus be an *upper* critical solution temperature. If combination between the components is possible, however, the extent to which this occurs increases with decreasing temperature, so that the mutual solubility in such cases will also increase as the temperature falls. The oxygen atom in the carbonyl group of a ketone has a lone pair of electrons which may take part in the formation of a resonance bond with one of the hydrogen atoms of water, so that compound formation between methyl ethyl ketone and water is possible (see "Recent Advances in Physical Chemistry," Chapter I.). The same factor is undoubtedly responsible for the increase observed in the solubility of many ethers and esters in water as the temperature is lowered; these substances all contain an oxygen atom with a lone pair of electrons, and so tend to form compounds with water. In each case a lower critical solution temperature should exist theoretically, although the hypothetical temperature is generally well below the freezing point of water. Since the deviations from Raoult's law in any case decrease with increasing temperature, all such systems should show an upper, as well as a lower, critical solution temperature.

The relatively high solubilities of phenol and aniline in water is

probably also to be ascribed to compound formation, the oxygen and nitrogen atoms, respectively, providing the pair of electrons for co-ordination with one of the hydrogen atoms of water; in neither instance, however, has any tendency been observed towards increased solubility on lowering the temperature.

Pseudo-Ideal Systems. Kendall (1925) has shown that a binary system, *e.g.*, ethyl acetate and water, may sometimes behave as "pseudo-ideal"; since the two liquids are partially miscible, the system cannot obey Raoult's law over the whole range of concentrations, yet the freezing-point depressions of dilute solutions of ethyl acetate in water indicate that the mixture behaves ideally. The internal pressures of the two liquids are very different, and in addition water is polar and associated, whereas ethyl acetate is non-associated; the mutual solubilities would therefore be expected to be very small, and the positive deviations from ideal behaviour very marked. Actually, although ethyl acetate is by no means completely miscible with water, its solubility in the latter is quite appreciable, and hence a factor is operative which counteracts the large positive deviation from Raoult's law. Kendall considers that this is the tendency to compound formation between the ester and the water; a view borne out by the fact, already mentioned, that the solubility of ethyl acetate increases with decreasing temperature.

It may be pointed out here that freezing-point measurements, especially in solutions having concentrations less than molar, do not always give a clear indication of departure from ideal behaviour. Hildebrand (1936) has shown that it is possible for regular solutions to give accurate molecular weights by the freezing-point method even when the internal pressures of solvent and solute differ appreciably. For this reason the conclusions of Bury and Jenkins (1934), who determined the freezing points of a number of benzene solutions, and found no correlation to exist between the results and the internal pressures of the components, must be accepted with reserve.

GASES AND THE SOLUBILITY THEORY

Having described the internal pressure theory of solubility and the factors causing positive and negative deviations from ideal

behaviour, some experimental results will be discussed in the light of the theory. In the first place, the solubility of non-polar gases will be considered; in Table XXXVIII. are given the solubilities of hydrogen, nitrogen and methane, expressed in molar fractions, in a series of solvents of increasing internal pressures. For nitrogen and methane the ideal solubilities, calculated by the method described on p. 231, are quoted, but for hydrogen the necessary extrapolation would be so prolonged as to make the result valueless.

TABLE XXXVIII

Solubilities of Gases at 1 *Atm. in Molar Fractions at* 20° *C.*

Solvent.	Hydrogen.	Nitrogen.	Methane.
Ideal	—	$0{\cdot}10 \times 10^{-2}$	$0{\cdot}32 \times 10^{-2}$
Hexane	—	—	0·31
Ethyl acetate	0·032	0·068	—
m-Xylene	0·040	0·061	0·26
Toluene	0·037	0·053	0·21
Benzene	0·025	0·043	0·18
Ethyl alcohol	0·021	0·033	0·11
Methyl alcohol	0·015	0·022	0·074
Water	0·0015	0·0013	0·024

The internal pressure of liquid nitrogen is approximately the same as that of hexane, and it is probable that the values for hydrogen and methane are not very different. These gases might therefore be expected to have solubilities approaching the ideal value in the solvents of low internal pressure at the head of Table XXXVIII., and this is undoubtedly the case. The solubility, expressed in molar fractions, decreases down the table as the internal pressure of the solvent, and hence the difference between it and that of the solute, increases; this result is in harmony with the theory developed. The solubility of the gases in water is perhaps unusually low, and this may be attributed to the polarity and association of this liquid. It is significant in this connection that the solubility of chlorine, the liquid form of which has an internal pressure close to that of benzene, is only $0{\cdot}75 \times 10^{-2}$ molar

fraction in water, whereas the ideal value is $27{\cdot}3 \times 10^{-2}$ at 0°; this low solubility, in spite of the reaction occurring between water and chlorine, illustrates the marked influence of polarity and association. The effect of the tendency to compound formation between solvent and solute is observed in connection with the solubility of carbon dioxide in water; the experimental value 7×10^{-4} molar fraction is much below the ideal value, allowing for deviations from the gas laws, of 254×10^{-4} molar fraction, but even then it is still greater than would have been anticipated had there been no compound formation. This may be inferred from the results in Table XXXIX. for the ratio of the solubility in two solvents of hydrogen, nitrogen, carbon monoxide, oxygen and carbon dioxide, all of which have almost the same internal pressures.

TABLE XXXIX

Ratio of Solubilities in Two Solvents.

	Hydrogen.	Nitrogen.	Carbon Monoxide.	Oxygen.	Carbon Dioxide.
$\frac{\text{Solubility in water}}{\text{Solubility in benzene}}$	0·058	0·032	0·031	0·031	0·077
$\frac{\text{Solubility in water}}{\text{Solubility in carbon disulphide}}$	—	0·10	0·095	—	0·32

The solubility of carbon dioxide in water is actually nearly three times as great as would have been the case had no compound formation occurred.

The solubility of ammonia is interesting as illustrating the behaviour of a highly polar gas. The internal pressure of ammonia is comparatively high, the estimated value being of the same order as that of iodine, and so the solubility of the gas in solvents of low internal pressure, *e.g.*, toluene and ether, would be expected to be lower than the ideal value. In polar solvents, however, the solubility should be high, and even in excess of the calculated amount, since compound formation is often possible. The literature contains only limited data on the solubility of ammonia gas, but

Hildebrand quotes the results in Table XL., which are in excellent agreement with the extended theory of solubility.

TABLE XL

Molar Fractions of Ammonia Gas at 1 *Atm. and* 0° *C.*

Ideal.	Toluene.	Ether.	Ethyl Alcohol.	Methyl Alcohol.	Water.
0·238	0·0026	0·079	0·398	0·439	0·481

LIQUIDS AND THE SOLUBILITY THEORY

Water and the lower alcohols are polar substances with high internal pressures, and so are miscible in all proportions under normal conditions. With increasing length of hydrocarbon chain the internal pressure of the alcohols, and the intensity of the electrostatic field in the vicinity of the molecules, become less, so that their solubilities in water decrease with increasing molecular weight. At the same time it may be observed, in agreement with anticipation, that the solubilities in non-polar solvents of low internal pressure, *e.g.*, hydrocarbons, definitely increase. The same general conclusion applies to the fatty acid series; the tendency to association and the high internal pressure of the lower members diminish steadily as the hydrocarbon chain is lengthened.

On the whole, it may be stated, although the fact is quite well known empirically, that polar liquids are miscible with polar liquids and non-polar with non-polar, but polar and non-polar liquids are generally immiscible. This probably accounts for the fact that liquid phosphorus, in spite of its high internal pressure, is almost insoluble in water, whereas it is very soluble in carbon disulphide; the same applies to sulphur, the internal pressure of which is of the same order as that of iodine. Hildebrand (1920) has determined the critical solution temperatures of liquid (white) phosphorus in various liquids: the higher this temperature the less, of course, is the tendency for the phosphorus to dissolve; the

results are given in Table XLI., together with the approximate relative internal pressures of the various liquids (naphthalene 1·0).

TABLE XLI

Critical Solution Temperature with Liquid Phosphorus (Internal Pressure, 2·5).

Liquid.	C.S.T.	Int. Press.	Liquid.	C.S.T.	Int. Press.
Decane . .	>390° C.	0·55	Ethylene dibromide	165° C.	1·13
Chlorobenzene .	264°	0·96	*p*-Dibromobenzene	163°	1·09
Naphthalene .	202°	1·0	Carbon disulphide	−6·5°	1·18
Phenanthrene .	200°	1·09	Bromoform	<0°	1·25
Anthracene .	198°	1·1 ?			

None of the substances is highly polar, and so the order of decreasing temperatures should be in the order of increasing internal pressures, since that of phosphorus is higher than for any of the other liquids. The results are in general agreement with this view ; small deviations may be attributed to the fact that the internal pressures are approximate, and in any case are only strictly applicable at about 20° C. Very similar results have been obtained for the critical solution temperatures of liquid sulphur, stannic iodide and various other liquids.

Reference has been made (p. 254) to the question of the miscibility of esters with water ; the differences in internal pressure and association are marked, so that the mutual solubility should be small. It is difficult to understand, however, why ethyl acetate should be five times as soluble in water as is ethyl propionate at 20° C. There is no doubt that compound formation is an important factor to be taken into consideration. Solubility variations of a similar type are noted with ethyl bromide and iodide ; the molar solubility of the former in water is about three times as great as that of the latter, but differences in internal pressure, polarity, or compound formation do not seem sufficient to account for the discrepancy. In addition to water the alcohols are sufficiently polar to form two layers with non-polar and slightly polar liquids, *e.g.*, methyl alcohol and hexane, methyl alcohol and

carbon disulphide. When two non-polar or slightly polar liquids have internal pressures which are sufficiently different, partial miscibility generally results; thus Keyes and Hildebrand (1917) found that aniline (internal pressure 1·46) and hexane (internal pressure 0·56) form a system of two liquid layers with a critical solution temperature of 59·6° C. The system of nitrobenzene (internal pressure 1·07) and hexane has a critical solution temperature of 21° C. in spite of the high polarity of the former; the decreased difference in the internal pressures is evidently sufficient to counteract this factor.

NON-ELECTROLYTE SOLIDS IN LIQUIDS

The solubilities of solid non-electrolytes in various liquids fall into general line with the theory considered in this chapter, and there are in a number of cases sufficient data available for the testing of equation (xxxiii.), which gives the quantitative relationship between the departure from ideal behaviour and the cohesive energies, or approximate internal pressures. An excellent illustration is to be found in connection with iodine solutions: these are generally brown or violet, and when the solubilities, expressed in molar fractions, are plotted against $1/T$ the violet solutions give a series of related lines, showing them to be regular solutions (p. 248). The solvents yielding brownish solutions are almost invariably polar, and so the latter fall into the irregular category. The results in Table XLII., collected by Hildebrand (1935), give the solubilities of iodine in a number of violet solutions at 25° C.; the values of E_1/v_1 for the various solvents were determined from the known molar heats of vaporisation and molar volumes, and for each solution E_2/v_2 for iodine was calculated by means of equation (xxxiii.) and the measured and ideal (0·212) solubilities.

The constancy of the figures in the last column, even for solutions in the polar solvents chloroform and bromoform, provides striking confirmation of equation (xxxiii.); the agreement between the results is perhaps better than would have been expected, but it may be connected in some manner with the fact that the internal pressure of iodine is markedly greater than that of any of the

solvents. The value of $(E_2/v_2)^{1/2}$ for iodine at 25° C., calculated from the latent heat of vaporisation at this temperature, derived from the application of the Clausius-Clapeyron equation to the known vapour pressures, is 13·6, which agrees remarkably well with the average of 13·67 from Table XLII. It will be observed from this table that all the experimental solubilities are much less than the ideal value, since none of the solvents has an internal pressure approaching that of iodine.

TABLE XLII

Solubility of Iodine in Regular Solutions at 25° C.

Solvent.	Solubility (Molar Fraction).	$\left(\frac{E_1}{v_1}\right)^{1/2}$	$\left(\frac{E_2}{v_2}\right)^{1/2}$
n-Hexane . . .	0·00456	7·44	13·67
Silicon tetrachloride .	0·00499	7·57	13·71
iso-Octane . . .	0·00592	7·50	13·51
n-Heptane . . .	0·00679	7·45	13·35
Carbon tetrachloride .	0·01147	8·54	13·99
Titanium tetrachloride .	0·0215	8·70	13·52
Chloroform . . .	0·0228	8·93	13·71
Carbon disulphide .	0·0576	9·98	13·82
Bromoform . . .	0·0616	10·1	13·78

A number of data are also available for sulphur which permit of similar calculations to those described above for iodine: it is unnecessary to give these in detail, for it is sufficient to state that the solubility measurements are in general agreement with the quantitative requirements of the internal pressure theory as expressed by equation (xxxiii.). The constancy of $(E_2/v_2)^{1/2}$ is perhaps not quite so good as for iodine, as recorded in Table XLII.; the average calculated value is 12·8, although that obtained from vapour-pressure data is 11·7. Sulphur has a high internal pressure and so ideal solubility should only be approached in solvents with similarly high values; these are, however, generally polar, and so it is only in liquid iodine that the solution does not deviate appreciably from Raoult's law; in other solvents the saturation molar fraction is less than the ideal value on account of positive deviations from the law. The order of solvents with decreasing

solubility is as follows: methylene iodide, carbon disulphide, sulphur monochloride, ethylene dibromide, iodobenzene, *m*-xylene, toluene, benzene, chloroform, carbon tetrachloride, tin tetrachloride, phenol, ethylene dichloride, ether and heptane (Hildebrand, 1921); with *m*-xylene, and the solvents which follow, the deviations from ideal behaviour are so marked that two liquid layers tend to form when the melting point of sulphur is approached. The order of solvents given corresponds almost exactly to the order of decreasing internal pressure, as required by the solubility theory. Hildebrand considers that there is a slight discrepancy in connection with *m*-xylene, toluene and benzene: the solubilities are in the reverse order of what would have been expected from the internal pressures. The partial molal volumes of S_8 in these three solvents have been measured at 25°, and found to be 123·6 c.c., 133·4 c.c. and 138·7 c.c., respectively; it appears, therefore, that sulphur molecules can pack more readily in *m*-xylene than in the other solvents, and this favours the solubility. The partial molal volume of the solute is consequently a factor which must be taken into consideration in a complete theory of solubility.

Naphthalene is a non-polar substance with an internal pressure which brings it to about the middle of Table XXXVII.; in solvents like chloroform, chlorobenzene, ethylene dichloride and benzene, the solubilities should therefore approach the ideal value calculated from the latent heat of fusion and the melting point. This is actually found to be the case; in all other solvents positive deviations occur, so that the solubilities are less than the ideal value. Consider firstly solvents of lower internal pressure: the solubility of naphthalene decreases in the order—toluene, carbon tetrachloride, ethyl acetate, ether and hexane; with solvents of internal pressures higher than that of naphthalene the order of decreasing solubility is carbon disulphide, acetone, aniline and phosphorus. These results are in agreement with the theory attributing positive deviations from Raoult's law to internal pressure differences. Scatchard (1931) has calculated the solubilities of naphthalene in various solvents by means of equation (xxxiii.), in the manner already explained. The agreement between

these and the observed values is by no means exact, but it is sufficient to show that the internal pressure theory of solubility is, at least, a satisfactory approximate generalisation.

The solubility of *p*-dibromobenzene in various solvents is also in harmony with the theory; the results quoted in Table XLIII. are taken from the compilations of Hildebrand (1917) and of Mortimer (1923). The relative internal pressure of *p*-dibromobenzene is 1·09, and so its solubility approaches the ideal value in solvents of the same order of internal pressure; the results in Table XLIII. show that the solubility falls off on either side of this pressure.

TABLE XLIII

Solubility of p-*Dibromobenzene at* 25° *C.* (*Molar Fractions*).

Solvent.	Internal Pressure.	Solubility.
Hexane . . .	0·56	$8·6 \times 10^{-2}$
Ethyl ether . .	0·62	18·3
Carbon tetrachloride .	0·81	19·3
Benzene . . .	0·96	21·7
Carbon disulphide .	1·18	22·4
Nitrobenzene . .	1·07 ?	17·4
Aniline . . .	1·4 ?	10·7
Phenol . . .	1·4	4·67 ?
Ethyl alcohol . .	2·9 ?	1·98
Ideal . . .		24·8

The solubility of benzoic acid, as a compound with a polar group, in various solvents, is of interest since a number of new points are brought out; some results are given in Table XLIV., the solvents being placed in order of increasing internal pressure.

The ideal solubility is only approached in alcohol and ether, and Hildebrand considers that in both cases this may be attributed to the fact that the solvent, like the solute, contains a polar and a non-polar portion. If this is so, then it is remarkable that the solubility should be so small in acetic acid; it is not unlikely that

TABLE XLIV

Solubility of Benzoic Acid at 25° C.

Solvent.	Molar Fraction.	Solvent.	Molar Fraction.
Ideal	0·38	Carbon disulphide	0·0302
Ether	0·347	Acetophenone	0·163
Xylene	0·0856	Acetone.	0·219
Toluene	0·0828	Acetic acid	0·096
Carbon tetrachloride	0·0518	Ethyl alcohol	0·346
Benzene	0·0816	Nitrobenzene	0·1012
Chloroform	0·149	Water	0·00055

other factors, *e.g.*, compound formation, are operating to increase the solubility at least in ether, and possibly in acetone. In non-polar solvents, *e.g.*, hydrocarbons, carbon tetrachloride and carbon disulphide, the solubility of benzoic acid is low, as is to be expected, but it is larger in the polar solvents, chloroform and nitrobenzene, although perhaps somewhat lower than would have been anticipated in the latter solvent. Water is a poor solvent in spite of its high polarity, presumably because the attraction between the water molecules is so great as to prevent penetration by the phenyl group of the benzoic acid ; the same factor is probably operative in causing the low solubility in water of other compounds containing long hydrocarbon chains or benzene nuclei. Hildebrand (1924) made the following predictions concerning the solubility of benzoic acid, which illustrate the practical value of the theory : since bromoform is less polar than chloroform and has a higher internal pressure, it should be a poorer solvent ; ethylene dibromide is even still less polar, and so should probably be very little better as a solvent than carbon disulphide ; aniline is slightly polar and basic, and so should be a better solvent than nitrobenzene ; hexane should be a very poor solvent, since it is non-polar and has a very low internal pressure.

SOLUBILITY PREDICTION

Mortimer (1923) has made use of the fact that the departure of the solubility from the ideal value is approximately proportional

to the difference in the internal pressures of the solvent and solute in order to calculate solubilities. If the system obeys Raoult's law exactly, it has been already seen (p. 240) that the plot of log N against $1/T$ should have a slope equal to $-L/4{\cdot}57$; if the solution is not ideal, however, the actual slope does not agree with this value. Mortimer supposes, although this is not strictly true, that the log N——$1/T$ curves are straight lines with a slope of $fL/4{\cdot}57$ according to the equation

$$\log N = \frac{fL}{4{\cdot}57}\left(\frac{1}{T_m} - \frac{1}{T}\right) \quad . \quad . \quad . \quad . \text{(xxxviii.)}$$

where f is a factor representing the difference in internal pressure of the two components of the solution. In order to determine f use is made of Table XLV. which purports to give the relative internal pressures of a number of substances (naphthalene = 1·00); these values have been determined mainly from solubility data, and so it is not improbable that they include an appropriate allowance for the polarity of the compound. Mortimer's figures are reproduced in Table XLV., and it is interesting to note that substances of similar constitution, *e.g.*, ketones, amines, nitro-compounds, halogen derivatives, appear close together in the table.

When both solvent and solute in the system under consideration have internal pressures which are greater than that of naphthalene, the value of f, which gives the ratio of the experimental to the ideal slope of the log N against $1/T$ curve, is obtained from the expression

$$f = \pi_1 - \pi_2 + 1 \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxix}a\text{.)}$$

where π_1 and π_2 are the relative internal pressures of the two components obtained from Table XLV. If both solvent and solute have internal pressures less than that of naphthalene, then

$$f = 1/\pi_1 - 1/\pi_2 + 1, \quad . \quad . \quad . \quad \text{(xxxix}b\text{.)}$$

but if one is greater, *e.g.*, π_1, and the other (π_2) less, then

$$f = \pi_1 - 1/\pi_2 + 3 \quad . \quad . \quad . \quad . \quad \text{(xxxix}c\text{.)}$$

Using this method, Mortimer has calculated the solubilities of

TABLE XLV

Relative Internal Pressures from Solubility Data.

Substance.	Relative Int. Pres.	Substance.	Relative Int. Pres.
Hexane	0·56	Carbazole	1·12
Ethyl ether	0·66	Carbon disulphide	1·13
Acetic anhydride	0·76	Trinitrophenol	1·14
Paraldehyde	0·77	Dinitrophenol	1·15
Menthol	0·78	*p*-Nitrophenol	1·17
Ethyl acetate	0·83	Benzanthrone	1·20
Carbon tetrachloride	0·84	Anthraquinone	1·22
Phthalic anhydride	0·91	Antimony trichloride	1·23
Bromotoluene	0·93	Antimony tribromide	1·25
Bromobenzene	0·94	Thymol	1·26
Benzene	0·94	Benzophenone	1·27
Toluene	0·93	Acetophenone	1·30
Ethylene dibromide	0·95	Benzil	1·30
p-Dichlorobenzene	0·95	Aluminium bromide	1·30
p-Dibromobenzene	0·95	Acetone	1·32
Chloroform	0·95	Naphthylamines	1·33
Chlorotoluene	0·97	Toluidines	1·35
Chlorobenzene	0·98	Benzoic acid	1·38
NAPHTHALENE	1·000	Trichloroacetic acid	1·42
Diphenylamine	1·00	Aniline	1·46
Phenanthrene	1·02	Nitranilines	1·65
Fluorene	1·04	Sulphur	1·70
Anthracene	1·05	Iodine	1·85
Diphenyl methane	1.06	*p*-Azoxyanisole	1·87
Triphenyl methane	1·07	Acetic acid	1·95
Nitrobenzene	1·07	Acetanilide	2·78
Nitronaphthalene	1·08	Ethyl alcohol	2·90
m-Dinitrobenzene	1·08	Hydroquinone	3·27
Other nitro-compounds	1·08	Methyl alcohol	3·35
p-Chloronitrobenzene	1·08	Urethane	3·50
Other nitro halides	1·08	Resorcinol	3·55
Pyridine	1·10	Acetamide	3·80
Pyrrole	1·10	Water	4·60

p-dibromobenzene and of acetanilide in a number of solvents at various temperatures; some of the results, together with the observed values, are given in Table XLVI.

TABLE XLVI

Calculated and Observed Solubilities (Molar Fractions) at 20° C.

Solvent.	Solute.	Calc.	Obs.
Benzene	*p*-Dibromobenzene	0·202	0·202
Toluene	,,	0·200	0·197
Carbon tetrachloride	,,	0·163	0·159
Nitrobenzene	,,	0·148	0·144
Aniline	,,	0·085	0·085
Ethyl alcohol	,,	0·008	0·028
Ethyl alcohol	Acetanilide	0·193	0·212
Methyl alcohol	,,	0·096	0·095
Toluene	,,	0·011	0·0037
Urethane (40°)	,,	0·160	0·148

The agreement between calculated and observed values is good, perhaps better than would have been anticipated, but the relative internal pressures in Table XLV. were probably, to some extent, based on solubility determinations with solutes similar to those in Table XLVI. There is no doubt, however, that the method of Mortimer may be used to give a satisfactory idea of the order of solubility of various substances. If the relative internal pressure of a substance is not given in Table XLV., a rough estimate of its value may be obtained either by one of the methods already described, or else by a comparison of its structure and polarity with those of substances mentioned in the table.

CHOICE OF SOLVENT

When a solid is to be recrystallised, it is desirable to choose a solvent in which it is appreciably more soluble at higher than at ordinary temperatures, so that a reasonable amount separates on cooling the hot saturated solution. It has been seen (p. 241) that the greater the deviations from ideal behaviour the larger will be the temperature coefficient of solubility, and so it would

seem desirable to choose as solvent a liquid with an internal pressure or polarity somewhat different from that of the solute. If the difference is too great, however, the solubility is, of course, so small as to be valueless. This criterion is satisfactory for solutes of low melting point, *e.g.*, below 100° C., since they should be appreciably soluble in most solvents (cf. p. 240), but with solutes of high melting point and low solubility a small difference of internal pressure or polarity may be sufficient to depress the solubility to almost useless limits. In such cases it may be necessary to use a solvent of similar internal pressure and polarity in order to secure the maximum solubility, and rely on the normal increase of solubility with temperature to permit recrystallisation to be carried out. Incidentally, it is important to remember that since the solubilities discussed here are expressed in molar fractions the solubility of a given solute expressed in *grams* will be greater in a solvent of low molecular weight than in one with a high value, although they may be the same in molar fractions. Other factors being equal, therefore, it is desirable to choose a solvent of low molecular weight.

CONCLUSION

In conclusion it may be stated that although the internal pressure theory of solubility cannot yet be regarded as a comprehensive theory, especially as so many other factors, *e.g.*, polarity, association, partial molal volume, and type of group present in the molecule, must be taken into consideration, it has at least helped very considerably to correlate many of the results of solubility measurements. In the course of time the theory will no doubt be improved, but even at the present it seems to be so interesting as to merit a place in this book.

REFERENCES

BELL. *Ann. Reports Chem. Soc.*, 1933, **30**, 13.*
BURY and JENKINS. *J. Chem. Soc.*, 1934, 688.
COATES. *Amer. Reports Chem. Soc.*, 1925, **22**, 38.*
GUGGENHEIM. *Proc. Roy. Soc.*, 1932, [*A*], **135**, 181 ; [1935, [*A*], **148**, 304.

HILDEBRAND *et al.* *J. Amer. Chem. Soc.*, 1916, **38**, 1452 ; 1917, **39**, 2126, 2297, 2301 ; 1919, **41**, 1067 ; 1920, **42**, 2180, 2213 ; 1921, **43**, 500, 2172 ; 1923, **45**, 682, 2828 ; 1927, **49**, 729 ; 1929, **51**, 66 ; 1935, 866 ; *Physical Rev.*, 1929, **34**, 984 ; *J. Chem. Physics*, 1933, **1**, 817 ; " Solubility," 1936.*
KENDALL *et al.* *J. Amer. Chem. Soc.*, 1921, **43**, 979, 1470, 1481, 1853 ; 1923, **45**, 963 ; *J. Chem. Soc.*, 1925, **127**, 1778.
MORTIMER. *J. Amer. Chem.*, 1922, **44**, 1416 ; 1923, **45**, 633.
SCATCHARD. *Chem. Reviews*, 1931, **8**, 321 ; *J. Amer. Chem. Soc.*, 1935, **57**, 1805.
SUNIER. *J. Physical Chem.*, 1930, **34**, 2582.
WARD. *Ibid.*, 1926, **30**, 1316.

* Review papers and books, wherein further references can be found, are marked with an asterisk.

CHAPTER VII

THE MECHANISM OF REACTIONS IN SOLUTION

The Activated-Collision Theory. When two substances, A and B, react the number of molecules decomposed in a given time is generally much less than the number of A and B colliding in that time: it is evident, therefore, that since reaction cannot take place without collision, only a limited number of these are effective. According to the theory which has been applied with some success in connection with the study of homogeneous gas reactions (see "Recent Advances in Physical Chemistry," Chapter V.), molecules will only react when they have a definite amount of energy, known as the heat, or energy, of activation. Reaction only takes place between molecules which have become activated by acquiring this energy. It is well known, following the work of Clerk Maxwell in the nineteenth century, that in any system of molecules there is a distribution of velocities as a result of the continued impact of the molecules upon one another; similarly there is distribution of the energies, some molecules having values greatly in excess of the average. The energy can, of course, be in different degrees of freedom, viz., internal, that is, rotational and vibrational, or external, that is, translational, but if in a bimolecular reaction the energy is restricted to translational energy for each molecule in one degree of freedom, presumably that in the direction of impact, then the probability of two molecules in a collision having energy E is given by the usual expression $e^{-E/RT}$. If z is the number of molecules of A and B colliding with one another in unit time, then the rate of reaction between them should be equal to $ze^{-E/RT}$, that is,

$$\text{rate of reaction} = ze^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

where E is the energy of activation necessary for this reaction. According to calculations based on the kinetic theory of gases

$$z = \sigma^2_{A,B} n_A n_B \left\{ 8\pi RT(M_A + M_B)/M_A M_B \right\}^{1/2} \quad . \quad . \quad \text{(ii.)}$$

where $\sigma_{A,B}$ is the average " collision " diameter of the two reacting molecules, n_A and n_B are the number of each in unit volume (1 c.c.), and M_A and M_B are the molecular weights. The rate of reaction for a bimolecular process can also be written in the form

$$\text{rate of reaction} = kn_An_B \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

where k is the velocity constant in appropriate units, and comparing equation (i.) and (iii.) it follows that

$$k = \sigma_{A,B}^2\{8\pi RT(M_A + M_B)/M_AM_B\}^{1/2}e^{-E/RT} \quad . \quad . \quad \text{(iv.)}*$$

This expression is often written in the form

$$k = Ze^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

where Z, called the " collision number ", is the number of collisions per sec. between one molecule of each reactant when present in unit volume. Taking logarithms and differentiating with respect to T, the equation

$$\frac{d\ln k}{dT} = \frac{E}{RT^2} + \frac{1}{2T} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vi.)}$$

is obtained, but since the term $1/2T$ is generally small it can be neglected, so that the familiar Arrhenius equation results :

$$\frac{d\ln k}{dT} = \frac{E_A}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii.)}$$

By means of this expression the energy of activation E can be determined by calculation from the value of the velocity constant k at two or more temperatures, or better from the slope of the straight line obtained by plotting $\ln k$ against $1/T$.

Calculation of Velocity Constant. Since E for any reaction is readily determined it is possible to calculate k for any temperature and compare it with the observed value ; the diameters of the molecules, if not known accurately from viscosity or other data, may be assessed from the parachors or the molecular volumes in the liquid or solid states. For a number of bimolecular reactions between simple compounds in the gas phase, the calculated values

* This and analogous collision equations give the velocity constant in c.c./molecule/sec. units, and in order to obtain the value in terms of the common litre/gm.-mol./sec. units it is necessary to multiply by $N/1000$, where N is the Avogadro number.

are sufficiently close to the experimental results to lead one to accept the theory of activation as a general basis for the study of reaction velocities. It is true, as will be seen later, there are many instances in which there is a very marked discrepancy between the two values, but these are regarded as exceptional and have to be accounted for in some manner. As a general rule, provided the process is not a chain reaction, the observed bimolecular velocity constant when abnormal is less than the calculated value, but should it be greater it is possible to explain the anomaly by the supposition that E includes energy from the internal degrees of freedom of the molecules, as will shortly be shown to be necessary for unimolecular reactions. There is some reason for believing, however, that for bimolecular reactions this assumption is not altogether justifiable. In general the velocity constant may be written as a modified form of equation (v.); thus

$$k = PZe^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(viii.)}$$

where P is called the "probability," or "steric," factor, which makes allowances for effects bringing about deviations from the ideal equation.

Unimolecular Reactions. It is now accepted that even unimolecular reactions involve collisions whereby the molecules acquire the necessary energy of activation: the essential difference between uni- and bi-molecular processes is that whereas in the latter a suitable collision is immediately followed by reaction, in the former a certain interval elapses, during which the energy apparently rearranges itself among different degrees of freedom, before it decomposes. The fact that the molecule may become deactivated by collision with another molecule during this interval is responsible for the reaction velocity being dependent on the concentration instead of on its square. At low pressures, when the average time between collisions becomes greater than the interval between activation and decomposition, the process should become kinetically bimolecular, and this has, in fact, been observed with a large number of so-called unimolecular gas reactions ("Recent Advances in Physical Chemistry," Chapter V.). When the equation $k = Ze^{-E/RT}$ is applied to first-order reactions, it is found

that the observed velocity constant is invariably greater than the calculated value, and this has been attributed to the fact that energy from a number of internal degrees of freedom contribute to the activation energy, in addition to the translational energy. If energy expressible in s "square terms," where $\frac{1}{2}s - 1$ is virtually equal to the number of internal degrees of freedom involved, contributes to the total E, then the number of collisions in which energy greater than E is involved is equal to

$$\frac{e^{-E/RT}(E/RT)^{\frac{1}{2}s-1}}{(\frac{1}{2}s - 1)!}$$

and this replaces $e^{-E/RT}$ in the simple expression for the velocity constant. If s is equal to 10, a relatively small value involving only four internal degrees of freedom, E is 50,000 cals,, and T is 1000° K., then it can be calculated that for the same collision number, Z, the velocity constant, is increased over 150,000 times. The assumption of reasonable values for s is invariably sufficient, therefore, to account for differences between observed and calculated reaction velocities. The equation for the variation of $\ln k$ with temperature now becomes

$$\frac{d\ln k}{dT} = \frac{E - (\frac{1}{2}s - 1)RT}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad \text{(ix.)}$$

neglecting the $1/2T$ term ; if E_A is the activation energy determined by the use of the simple Arrhenius expression (equation vii.), as already described, it is equivalent to $E - (\frac{1}{2}s - 1)RT$, and the true energy of activation is equal to $E_A + (\frac{1}{2}s - 1)RT$.

Reactions in Solution. When the equation (iv.) for the velocity constant of a bimolecular reaction was first applied to homogeneous reactions in solution, Christiansen (1924) found that the velocity of hydrolysis of various acid amides and esters in aqueous solution was only 10^{-1} to 10^{-5} times the value calculated. This result was attributed to de-activating collisions by the molecules of the solvent, since there are so many of the latter that a large proportion of the collisions between two reacting molecules will also involve a molecule of solvent. If it is able to deprive the activated molecules in the collision of some of their energy, then

it is clear that the actual rate of reaction, involving molecules possessing the necessary energy of activation, will be much less than the value calculated from the equation for collisions in the gas phase, where no such de-activation can occur. A few years later, Norrish and Smith (1928) made a study of the rate of quaternary ammonium salt formation between *m*- and *p*-nitrobenzyl chlorides and trimethylamine in benzene solution, and found that for these reactions, as well as for others of an analogous type in different solvents, the value of P, the probability factor representing the ratio of the observed to the calculated velocity constants, varied from 5×10^{-5} to 4×10^{-11}. These enormous discrepancies were not easy to understand, and de-activating collisions by the solvent molecules seemed the only reasonable explanation.

COMPARISON OF VELOCITIES IN GAS AND SOLUTION

Decomposition of Chlorine Monoxide. Following the success of the theory of kinetic activation as applied to gases, it was only natural that reaction velocities in soluton should attract some attention, and in 1931 Moelwyn-Hughes and Hinshelwood made a study of the decomposition of chlorine monoxide in carbon tetrachloride solution in order that the result might be compared with those previously obtained (Hinshelwood and others, 1923, 1924) for the same reaction in the gas phase. The decomposition is actually somewhat complicated, there being an initial period in which the process is slow, followed by a marked acceleration: probably a number of reactions proceed consecutively, and so it is not possible to determine the velocity constant, but the reaction behaves virtually as a bimolecular one, and the rate in the gas phase is given approximately, at least, by the equation $k = Ze^{-E/RT}$, where E is 21,000 cals. In carbon tetrachloride solution, the decomposition of chlorine monoxide was found to exhibit the same features as in the gas reaction, provided access of light and water was prevented. The two processes could be compared by determining the time intervals between 20 per cent. and 60 per cent. decomposition of the monoxide at the same temperature and

initial concentration in the gas and in solution. The results obtained are set out in Table XLVII. : the concentration of chlorine monoxide is expressed in gm.-mol. per litre, and $t_{sol.}$ and t_{gas} represent the time intervals for solution and gas, respectively, their ratios being given in the last column.

TABLE XLVII

Decomposition of Chlorine Monoxide in Gas Phase and in Carbon Tetrachloride Solution.

Conc.	Temp. °C.	$t_{sol.}$	$t_{gas.}$	$t_{sol.}/t_{gas.}$
0·224	70·7	50	47·5	1·05
0·115	71·0	105	90·5	1·16
0·095	69·7	100	122	0·82
0·120	80·1	55	44	1·25
0·120	60·1	200	211	0·95

It is very striking, as the results in the last column show, that the reaction velocity is almost the same in carbon tetrachloride solution as in the gas phase. The activation energy for the decomposition in solution is 20,300 cals., also in excellent agreement with the value for the gas reaction. Since in the latter case the calculated and observed velocities are of the same order, it follows that the same must apply to the process in carbon tetrachloride solution. There is consequently no evidence in this case for de-activation by collision with solvent molecules.

Decomposition of Ozone. Another reaction, in this case involving two substances, is the decomposition of ozone catalysed by chlorine : the process is undoubtedly a complex one, probably involving a chain mechanism, but the rate of disappearance of ozone as a result of catalytic decomposition can be written, approximately at least, as

$$-\frac{d[O_3]}{dt} = k[O_3]^{3/2}[Cl_2]^{1/2}$$

between temperatures of 35° and 50° C. If the conditions are such that the un-catalysed spontaneous decomposition of ozone occurs at the same time, allowance must be made from the

observations on the process in the absence of chlorine. Bodenstein, Padelt and Schumacher (1929) found k to have a value of $9{\cdot}50 \times 10^{-2}$ for the catalysed reaction in the gas phase at 50° C., whereas Bowen, Moelwyn-Hughes and Hinshelwood (1931) obtained, for the same process in carbon tetrachloride solution, k as $1{\cdot}45 \times 10^{-2}$, with concentrations expressed in gm.-mol. per litre and time in seconds. The ratio of the two velocity constants is 1·53, indicating that the decomposition takes place virtually at the same speed in the solution as in the gaseous system. The apparent energies of activation are 20,040 and 26,730 cals., respectively, but this difference may quite possibly be due to the complexity of the process and to experimental errors.

Decomposition of Ethylene Iodide. The thermal decomposition of ethylene di-iodide has been studied in the gas phase (Arnold and Kistiakowsky, 1933) and also in carbon tetrachloride solution (Polissar, 1930): the essential process is catalysis by iodine atoms; thus, the preliminary stages

$$C_2H_4I_2 = C_2H_4 + I_2$$

and

$$I_2 = 2I$$

occurring to a small extent, are followed by

$$C_2H_4I_2 + I = C_2H_4I + I_2,$$

which is the rate-determing step, and

$$C_2H_4I = C_2H_4 + I,$$

regenerating the iodine atoms. The velocity of the reaction in solution was measured over the temperature range of 40° to 152° C., and in the gas phase between 205° and 230° C., but if the values of $\log k$ for the different cases are plotted against the temperatures, all the results fall almost on the same straight line. This indicates that not only are the decomposition velocities the same for the gas and for the solution, but the energies of activation are also approximately equal. The measured activation energy of the whole process is 30,200 cals., but from this must be subtracted half the heat of dissociation of the iodine molecule, giving approximately 12,000 cals. for the heat of activation of the rate-determining stage. The use of this value in the equation $k = Ze^{-E/RT}$, the concentration of iodine atoms being calculated

from the known equilibrium constant of the dissociation process at various temperatures (*cf.* p. 93), gives values for k in very good agreement with those determined experimentally both for gas and solution. It is evident that the carbon tetrachloride employed as solvent has very little influence either on the number of collisions between the reacting species or on the requisite activation energy.

Unimolecular Reactions in Solution. The existence of these " bimolecular " reactions, in which the solvent plays no obvious part, suggests the possibility that there may be reactions of other orders exhibiting the same phenomenon ; this is, in fact, the case with at least two unimolecular processes. The thermal decomposition of nitrogen pentoxide has been studied in the gas phase and also when dissolved in a number of different solvents (Eyring and Daniels, 1930). In propylene dichloride and in nitric acid solution the reaction appears to be abnormally slow, and the energy of activation high, but in the solvents listed in Table XLVIII. it is seen that both the velocity constants (k) and the activation energies (E) are very close to the corresponding values for the homogeneous gas reaction.

TABLE XLVIII

Decomposition of Nitrogen Pentoxide in Various Solvents at 20° *C.*

Solvent.	$k \times 10^5$.	E (cals.).
(Gas phase) . . .	1·65	24,700
Nitromethane . . .	1·53	24,500
Bromine	2·15	24,000
Pentachloroethane . .	2·20	25,000
Carbon tetrachloride . .	2·35	24,200
Ethylene dichloride . .	2·38	24,400
Chloroform . . .	2·74	24,600
Ethylidine chloride . .	3·22	24,900
Nitrogen tetroxide . .	3·44	25,000

It is clear that whatever theoretical interpretation is given to the results with gaseous nitrogen pentoxide, it must apply equally to the decomposition in solution.

When *d*-pinene is heated it undergoes isomeric change to dipentene ; the process is homogeneous and unimolecular, and can be observed both with the gas and in certain high boiling-point solvents. The following results (D. F. Smith, 1927) for the velocity constant were obtained at temperatures between 217·5° and 218° C. in the three solutions mentioned :

Petrolatum.	Acetophenone.	α-Methylnaphthalene.
$7{\cdot}8 \times 10^{-4}$	$8{\cdot}0 \times 10^{-5}$	$8{\cdot}7 \times 10^{-5}$

These may be compared with $5{\cdot}1 \times 10^{-4}$ for the gas reaction at the same temperature. Here again, the similarity of the results is very striking.

Photochemical Reactions. In most photochemical reactions the initial process is brought about by the absorption of a quantum of radiation, but the subsequent stages, leading to the final products and accounting for the quantum efficiency invariably involve molecular collisions (" Recent Advances in Physical Chemistry," Chapter VI.). If the rates for a given photochemical decomposition are the same in the gas phase and in solution, it is evident that the solvent molecules cannot act as removers of energy ; this is particularly the case with a chain reaction, especially of the " hot-molecule " type. The decomposition of hydrogen iodide is a simple process in which the stages are

$$HI + h\nu \rightarrow H + I$$

followed by $H + HI = H_2 + I$ and $I + I = I_2$,

where $h\nu$ represents the quantum of radiation. The quantum efficiency is 2 in the gas phase ; that is, two molecules of hydrogen iodide are decomposed for every quantum of energy absorbed. In a molar solution of the iodide in hexane the quantum efficiency is the same, although it is somewhat less in more dilute solutions. Similarly the efficiencies in the photochemical decomposition of chlorine monoxide, of ozone sensitised by chlorine, and of nitrogen trichloride, are the same in the gas phase as in carbon tetrachloride solution. The solvent in all these instances plays the part of a completely inert gas.

Since in a number of different cases (see also p. 282) there is no doubt that the solvent does not interfere with the reaction

mechanism, it is reasonable to inquire whether some of the processes, which are so much slower in solution than is to be expected from the simple collision hypothesis, may not in fact be equally slow in the gas phase. If this is the case then the explanation of the low rate of reaction is to be sought in the nature of the reaction, and not in the influence of the solvent.

"Slow" Reactions. The formation of quaternary ammonium salts by the addition of an alkyl iodide to a tertiary amine was found by Norrish and Smith (p. 273) to take place relatively slowly, the P factor, in equation (viii.) having an average value of about 10^{-5}, and Moelwyn-Hughes and Hinshelwood (1932) studied the velocity of the reaction between triethylamine and ethyl iodide in the gaseous phase, and also in carbon tetrachloride and hexane solutions. The gas reaction is somewhat disturbed by the interference of catalysis by the walls of the containing vessel, and by adsorbed films formed whilst the reaction is proceeding, so the velocity constant determined may be regarded as probably in excess of the true value for the homogeneous reaction. The velocity constants at 140·6° C. were found to be as follows:

Gaseous phase	$1{\cdot}9 \times 10^{-4}$
n-Hexane solution . . .	$0{\cdot}35 \times 10^{-4}$
Carbon tetrachloride solution .	$0{\cdot}60 \times 10^{-4}$

These results show that the reaction velocity is of the same order in the gas as in solution, but the value in hexane is smaller than that calculated as $Ze^{-E/RT}$, E being 14,600 cals., by a factor of approximately 10^{-8}, and the same must apply to the combination taking place between the reactants as gases. The quaternary ammonium salt formation under consideration was studied, as is well known, by Menschutkin (1890), who used a number of solvents: the highest velocity was noted in benzyl alcohol solution, but as this was less than 800 times as great as the value in n-hexane, there still remains a P factor of the order of 10^{-5} to be explained. It will be noted that in this case the reaction velocity constant is greater than for the gas reaction, so that benzyl alcohol and other solvents, *e.g.*, acetone and ethyl alcohol, exert a positive catalytic effect. Solvents such as carbon tetrachloride or n-hexane

have been termed " normal " solvents, since they generally give velocity coefficients for a given reaction little different from those obtained for the same reaction in the gaseous phase.

The reaction between ethyl alcohol and acetic anhydride showed a behaviour similar to that just discussed. At 79·2° C. the velocity constant was $1{\cdot}5 \times 10^{-2}$ for the gas reaction and $1{\cdot}8 \times 10^{-3}$ for the process in carbon tetrachloride solution, a similar value being observed in *n*-hexane ; the gas reaction is apparently about eight times as fast as in solution, but since the former is undoubtedly catalysed by the walls of the vessel, the difference in the speeds of the corresponding homogeneous processes may not be so great. In any case the velocities are much lower than calculated, the value of the probability factor being about 10^{-6} or less.

Another slow reaction, which has been studied in the gaseous phase and in solution, is the hydrolysis of carbonyl sulphide : the speed in the former case is of the same order as that in ethyl alcohol solution, but the values are approximately 10^{-5} times those to be expected from the simple kinetic activation theory (Thompson, Kearton and Lamb, 1935). It is of some interest that this reaction and the one previously mentioned have been studied in the gaseous state, in solution, and also as quasi-unimolecular processes in which the solvent was one of the reactants, viz., carbonyl sulphide in water, and acetic anhydride in alcohol. Assuming that every collision between a solvent and a solute molecule, under the latter circumstances, leads to reaction, provided the energy of activation is available, the calculated values of the velocity constants are very much closer to the observed values than is the case for the normal second-order process in the gas phase or in solution (Moelwyn-Hughes and Rolfe, 1932). For the acetic anhydride in ethyl alcohol reaction there is still a discrepancy factor of 630 for the ratio of calculated to observed velocity constants, but this may be partly due to the uncertainty in computing the number of collisions between solvent and solute molecules, and partly to the doubt as to the correct value to be used for the energy of activation (see p. 289).

Cause of " Slow " Reactions. Neglecting for the present the relatively small variations resulting from the use of different

solvents, although this factor must not be completely ignored, it is quite evident that there are a number of reactions which may be classed as "slow," whether occurring in the gas phase or in solution, although there is in actual fact a continuous gradation of the P factor between 10^{-8} and unity (Hinshelwood and Winkler, 1936). Four possibilities may be considered as contributing to the discrepancy between the observed and calculated values of the velocity constant. In the first place, there is the de-activating effect of other molecules which might have some influence, but this can only be small in view of the almost inert nature of the solvent. Secondly, there may be the necessity that when two molecules, with the requisite energy of activation, collide reaction will only occur when they are suitably orientated or in an appropriate internal phase; this factor will certainly be operative in many cases, especially when the reactants are complex molecules, but it does not seem to be sufficient to account for P factors of the order of 10^{-8}. It is generally believed that most reactions between two ions take place very readily, and it will be seen later that many processes involving an ion as one of the reactants behave normally in so far as they have velocities of the expected order, consequently another possibility is the necessity that one or both of the reactants must ionise before combination can take place. This has been considered by Moelwyn-Hughes and Hinshelwood (1932) in connection with two of the slow reactions already mentioned: the quaternary ammonium salt formation may be regarded as requiring preliminary ionisation of the ethyl iodide; thus

$$C_2H_5I \rightleftharpoons C_2H_5^{\cdot} + I',$$

and then

$$(C_2H_5)_3N + C_2H_5^{\cdot} = (C_2H_5)_4N^{\cdot}.$$

Since the primary process is reversible, with the equilibrium well over to the left-hand side, it is clear that most of the ethyl ions are used up in combination with iodine ions, and relatively few are available for reaction with the tertiary amine. The observed velocity would then be much less than that calculated on the basis of collisions between the latter and normal ethyl iodide molecules. Although the necessity for ionisation may account in some cases

for the discrepancy, it does not appear to be generally applicable, and it is the fourth factor which is probably the major cause of the slowness of the reactions under consideration. There is little doubt that when the reacting molecules with the correct amount of energy collide in a bimolecular process, an intermediate " activated complex " must form before the reaction can occur, and it appears to be the nature of this complex which is the chief cause of the very small probability factors in many cases. The subject will be considered in some detail in later parts of this chapter.

BIMOLECULAR REACTIONS IN SOLUTION

Application of the Collision Theory Solutions. In reviewing the results described so far it is reasonably justifiable to assume that, provided an inert or " normal " solvent is used, the formula giving the number of collisions between two molecular species A and B is the same for a solution as that used for collisions between gas molecules (equation ii.). It is actually possible that the collision number in solution may be somewhat larger than for gases at the same apparent concentrations: since the molecules of solvent occupy an appreciable volume, the " free space " in which the dissolved molecules move is less than the whole volume of the solution, so that the true concentrations, that is, the actual n_A and n_B, are greater than the apparent values. It has been calculated (Jowett, 1929) that the free-space correction should make the collision number in solution from 6 to 16 times as great as that normally given by equation (ii.). Some objection has been raised to the application of this correction (Polissar, 1932) on the grounds that owing to the relative proximity of the solvent molecules, collisions in a solution are of a different kind from those occurring in the gas phase. On the whole it appears that until further information is available concerning the structure of liquids it would be best to use the simple collision formula as an approximation without correction. A number of different kinds of reaction will now be considered in an attempt to elucidate further the mechanism of processes in solution.

Bimolecular Reactions in Solution. Mention has been made of

some reactions involving simple substances, such as the thermal decomposition of chlorine monoxide and the catalysed decomposition of ethylene di-iodide by iodine atoms, in which the observed and calculated velocity constants are quite close in value, and it is of interest to inquire whether there are further examples of this type of behaviour. Moelwyn-Hughes (1932, 1933) has collected a very large amount of data from chemical literature and has found this to be the case for a number of reactions. For example, most processes involving interaction between an alkyl halide and an alkyloxide or a phenoxide :

$$R{\cdot}I + R'{\cdot}ONa = R{\cdot}O{\cdot}R' + NaI$$

have velocity constants which are within a factor of ten of the values calculated from the expression $Ze^{-E/RT}$; it is apparent that in these instances the simple collision hypothesis is applicable. The data in Table XLIX. have been calculated from the observations of Segaller (1914) on the reactions between alkyl iodides and sodium phenoxide in absolute ethyl alcohol solution at 42·5° C. Similar results with a xylyloxide were obtained by Hardwick (1935).

TABLE XLIX

Reactions between Alkyl Iodides and Sodium Phenoxide in Alcohol Solution at 42·5° C.

Alkyl Iodide.	E (cals.).	$k \times 10^5$ (obs.).	$k \times 10^5$ (calc.)	P.
CH_3I . . .	22,120	101·0	19·1	0·2
C_2H_5I . .	22,000	22·5	22·7	1·0
C_3H_7I . .	22,450	8·7	11·4	1·3
C_4H_9I (*n*) . .	22,090	8·1	21·0	2·6
C_4H_9I (*iso*) . .	21,790	3·22	33·3	10·3
C_4H_9I (*tert.*) .	22,110	202·0	20·2	0·1
$C_5H_{11}I$ . .	22,280	3·5	16·1	4·2
$C_6H_{13}I$ . .	22,000	7·7	26·2	3·4
$C_7H_{15}I$ . .	22,230	7·5	18·5	2·5
$C_8H_{17}I$ . .	22,500	7·2	12·5	1·7
$C_{16}H_{33}I$ . .	22,430	7·1	16·1	2·3

Other bimolecular reactions in which the ratios of observed to calculated values of the velocity constant are of the same order of magnitude are the interaction of *o*- and *p*-dinitrobenzene and sodium alkyloxides; thus,

$$C_6H_4(NO_2)_2 + NaOR = C_6H_4(NO_2)(OR) + NaNO_2;$$

and the formation of triethylsulphonium bromide from ethyl bromide and diethyl sulphide, viz.,

$$C_2H_5Br + (C_2H_5)_2S = (C_2H_5)_3S{\cdot}Br.$$

The fact that in the reactions tabulated by Moelwyn-Hughes the ratio of the highest to the lowest measured velocities is 10^9, and the energies of activation vary from 16,760 to 25,100 cals., shows that the agreement of the experimental with the kinetically calculated velocity constants cannot be mere chance.

Molecule–Ion Reactions. Grant and Hinshelwood (1933) suggested that reactions involving a molecule and an ion behave normally; most of the reactions considered above, involving sodium alkyloxide, will fall into this category if it is assumed, as is very probable, that in solution the alkyloxide is dissociated into ions to a considerable extent, and that the reaction actually involves the alkyloxy ions. The reactions between ethyl halides and potassium hydroxide, in ethyl alcohol solution in which one of the reactants is an ion, also have normal velocities similar to those calculated, and the same applies to a considerable number of processes taking place between a molecule and an ion in aqueous, alcoholic, or acetone solutions (Moelwyn-Hughes. 1933). Any discrepancies between observed and calculated velocity constants may possibly be due to errors in the determination of the collision number, as some approximation must undoubtedly be involved in applying the gas-collision formula when one of the colliding species is an ion, and also to uncertainties in the values of the energies of activation to be used in the formula.

"Slow" Reactions. The best known type of "slow" reaction is, as already indicated, that between a tertiary amine and an alkyl halide leading to quaternary salt formation; a number of cases were studied by Norrish and Smith (1928), by Thompson and Blandon (1933), and by Winkler and Hinshelwood (1935), and in

every instance the calculated velocity coefficient is from 2 to 9 powers of ten greater than the observed value. The results in Table L. are taken from those quoted by Thompson and Blandon ; they show the general order of the discrepancies found.

TABLE L

Rates of Formation of Quaternary Ammonium Salts.

Tertiary Amine.	Alkyl Halide.	Solvent.	E (cals.).	$P = k_{obs.}/k_{calc.}$
Pyridine	Ethyl iodide	Benzophenone	14,300	$1{\cdot}1 \times 10^{-3}$
,,	,,	Nitrobenzene	15,000	$1{\cdot}7 \times 10^{-2}$
,,	Methyl iodide	Tetrachloroethane	13,220	$2{\cdot}0 \times 10^{-4}$
,,	,,	Chloroform	14,200	$4{\cdot}5 \times 10^{-4}$
Triethylamine	Ethyl bromide	Benzene	11,190	$5{\cdot}3 \times 10^{-8}$
,,	,,	Acetone	11,710	$1{\cdot}6 \times 10^{-6}$
Dimethylaniline	Ethyl iodide	Tetrachloroethane	11,680	$4{\cdot}8 \times 10^{-6}$
,,	,,	Nitrobenzene	13,020	$5{\cdot}3 \times 10^{-6}$
,,	,,	Acetone	13,680	$6{\cdot}2 \times 10^{-6}$
,,	,,	Benzyl alcohol	14,400	$1{\cdot}7 \times 10^{-3}$

Another definitely slow type of reaction is the benzoylation of amines, a number of examples of which have been studied in benzene solution and in other solvents by Hinshelwood and Grant (1933) and by Williams (1934) ; both substituted benzoyl chlorides and anilines have been used, and in every case the P factor, which gives the ratio of the observed to the calculated velocity constant, is about 10^{-7}.

Catalysed Bimolecular Reactions. When the decomposition of one molecule is catalysed by a molecule or an ion of another substance, the concentration of which remains constant, the velocity coefficient corresponds to that for a unimolecular process, but since the reaction actually involves a collision between two species the constant should be calculable by the application of the usual collision formula, equation (iv.). An example of this type of reaction is the mutarotation of beryllium benzoyl-camphor catalysed by pyridine or by alcohol, investigated by Lowry and Traill (1931), the results of which in carbon tetrachloride solution were first analysed in terms of the kinetic-activation theory by Traill (1932) and subsequently by Moelwyn-Hughes (1932), on

the assumption that the rate-determining stage in the mutarotation involves a collision between the beryllium compound and the catalyst. Instead of calculating the velocity constant from the measured energy of activation, an alternative procedure often adopted is to find the value of E required to give a velocity constant (k) equal to the experimental result in the equation $k = Ze^{-E/RT}$, and to compare this value of E with that found experimentally. Such a comparison is given in Table LI.; the agreement is seen to be very striking.

TABLE LI

Mutarotation of Beryllium Benzoyl-camphor in Carbon Tetrachloride Solution.

Catalyst.	E (obs.).	E (calc.).
Pyridine . .	18,850 cals.	18,840 cals.
Alcohol . .	18,410	18,690

In other instances there is, however, a somewhat greater difference between the observed and calculated values of the energy of activation or of the velocity constant; for example, the mutarotation of glucose in water is catalysed by a number of ions and molecules, and by the use of certain methods, described in Chapter VIII., it is possible to calculate the catalytic coefficients for the various substances present, *i.e.*, the velocity constants for the respective processes in which they are involved. The comparison recorded in Table LII. is given by Moelwyn-Hughes, based on the measurements of Kilpatrick and Kilpatrick (1931).

TABLE LII

Mutarotation of Glucose in Aqueous Solution at 18° *C.*

Catalyst.	k	E (obs.).	E (calc.).
Hydrogen ion .	$1{\cdot}27 \times 10^{-3}$	19,300 cals.	20,860 cals.
Pyridine . .	$7{\cdot}37 \times 10^{-3}$	18,000	17,980
Acetate ion . .	$2{\cdot}61 \times 10^{-3}$	19,100	19,570

The calculated values of E are of the right order, but the discrepancy in the case of the hydrogen ion is larger than might be anticipated. In this case the observed energy of activation is smaller, and hence the velocity constant is *greater*, than the calculated value ; if one internal degree of freedom contributes to the activation energy, the discrepancy could be accounted for, but it is not certain how far the calculated reaction constant involves errors in the application of the equation for the collision frequency. The mutarotation of glucose is also catalysed by water molecules, but since the process occurs in aqueous solution the collision number cannot be calculated in the way already described ; by using an equation to be given subsequently (p. 292), however, the observed and calculated values of the activation energy are found to be in good agreement.

The simple collision hypothesis can also be applied to a catalytic reaction of an entirely different type, namely, the Beckmann rearrangement of benzophenoneoxime picryl ether, $(C_6H_5)_2C{:}N{\cdot}OPic$, in carbon tetrachloride when accelerated by compounds containing polar groups (Chapman, 1934). The reaction is somewhat complicated by the spontaneous change in the pure solvent and by ternary collisions when the catalyst is concentrated : correction can be easily made for the former, since the velocity constant of the process is known, and the latter is eliminated by extrapolating the catalytic coefficients to zero concentration of the catalyst. When nitromethane is the catalyst the observed activation energy is 23,800 cals., and this leads to a calculated velocity constant at 81° C. of $6{\cdot}9 \times 10^{-6}$, compared with the observed value of $3{\cdot}65 \times 10^{-6}$. The corresponding data for ethylene dichloride as catalyst are 24,400 cals. as the activation energy, and $2{\cdot}6 \times 10^{-6}$ and $0{\cdot}68 \times 10^{-6}$, as calculated and observed velocity constants, respectively. It is of interest that the oxime ether and the product of the Beckmann change are both able to catalyse the change, and assuming the efficiencies to be the same, so that the concentration of catalyst may be regarded as constant, the catalytic coefficient for this process is $15{\cdot}6 \times 10^{-6}$ and the activation energy is 22,620 cals. ; the velocity constant calculated by the gas-collision formula is $6{\cdot}7 \times 10^{-6}$. The agreement between the

experimental coefficients and those computed is determined to some extent by the collision diameters in equation (iv.), but those used in the calculations were all of the correct order, namely, 5 to 9 Å.

An interesting example of catalysis in solution is the reaction between acetone and iodine: although the process is studied in this way, by estimating the iodine used up, the actual change of which the velocity is measured is the catalytic conversion of the ketonic form of acetone into the enol (see Chapter VIII.). The change is accelerated by a variety of ions and molecules, but it is possible nevertheless to determine the catalytic coefficients for each of these, and by making experiments at two or more temperatures to calculate the respective activation energies. The figures quoted in Table LIII. are taken from the work of G. F. Smith (1934); they give the values of E and the observed catalytic coefficients for various catalysts, and also the corresponding P factor, representing the ratio of $k_{obs.}/k_{calc.}$

TABLE LIII

Enolisation of Acetone in Aqueous Solution.

Catalyst.	E (cals.).	$k \times 10^7$.	$P = k_{obs.}/k_{calc.}$
Hydrogen ion . . .	20,680	287	$1{\cdot}5 \times 10^{-1}$
Dichloroacetic acid . .	19,230	123	$5{\cdot}7 \times 10^{-3}$
Chloroacetic acid . .	19,230	13·7	$6{\cdot}4 \times 10^{-4}$
Acetic acid	20,100	0·83	$1{\cdot}4 \times 10^{-4}$
Propionic acid . . .	19,370	0·68	$0{\cdot}4 \times 10^{-4}$

According to these results one collision in six involving an acetone molecule and a hydrogen ion, with the appropriate amount of energy, is effective in bringing about reaction, but with the other catalysts there is a marked difference between the observed and the calculated velocity constants. The P factors were found to run parallel with the dissociation constants of the acid catalysts, including H_3O^+ as an acid, a result suggesting that the effectiveness of a collision between activated molecules of

acetone and catalyst is limited by the probability of the simultaneous ionisation of the molecule of the acid catalyst.

Alternative Calculation of Bimolecular Collision Numbers. An alternative method for calculating the number of collisions between two molecular species in solution, giving a formula similar to one previously deduced by Ölander (1929), which allows for the specific properties of the liquid phase, has been proposed by Bradley (1934). A liquid is supposed to possess a quasi-solid structure, of a nature analogous to that suggested by Bernal and Fowler (1933) for water, in which the molecules are oscillating about more or less mean positions. A molecule of solute will be surrounded by solvent molecules almost entirely, especially in dilute solution, and it must diffuse through this envelope before it can approach another dissolved molecule with which to react. The number of collisions should thus depend on the diffusion coefficient of the solute, and hence indirectly on the viscosity of the solvent. By correlating the diffusion with the oscillations of the molecules, and assuming the diffusion coefficient to be an exponential function of temperature, an equation can be developed for the collision number in terms of measurable quantities. The equation for the rate of a bimolecular reaction, in which *each* molecule contributes energy in two square terms, represented by potential and kinetic energy of oscillation, then becomes

$$k = \frac{\pi}{36}\left(\frac{d_A^2 v_A}{a_A} + \frac{d_B^2 v_B}{a_B}\right)\left(\frac{3\pi}{2}\right)^{1/2} \cdot \frac{Nd}{1000} \cdot \frac{E}{RT} e^{-(E+E_D)/RT} \quad \text{(x.)}^*$$

where $d = r_A + r_B$; $d_A = r_A + r_S$; $d_B = r_B + r_S$; and r_A, r_B and r_S are the "virtual" radii of the respective molecules, s representing the solvent, calculated from the densities (ρ) and the molecular weights (M) of the liquids on the assumption of close packing; thus

$$r = \left(\frac{3}{4} \times \frac{0{\cdot}74M}{N\pi\rho}\right)^{1/3} \quad \text{(xi.)}$$

The v terms are the square-roots of the mean square velocities of the molecules, that is, $v^2 = 3RT/M$, and a is the mean double-

* The collision number may be obtained by extracting $(E/RT)e^{-E/RT}$ from this equation.

amplitude of oscillation of the molecule obtained from the relationships $r = r_0(1 + bT)$, r being as already defined, and b a constant representing its temperature variation, and $a = 2(r - r_0)$ at any particular temperature. The factor b is of the order of 10^{-3}, and so for ordinary temperatures a is approximately $2r_0/3$, that is, of the order of 10^{-8} cm. The energy E is not equal to the value given by the simple Arrhenius equation (E_A), but it is derived from it by the equation

$$E_A = E + E_D - 3RT/2, \quad . \quad . \quad . \quad . \quad . \quad \text{(xii.)}$$

where E_D is the sum of the activation energies for the diffusion of the two reacting molecules. These latter quantities are obtained for each reactant by means of the relationship

$$D = D_0 e^{-E_D/RT}/T^{1/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiii.)}$$

so that

$$\frac{d\ln D}{dT} = \frac{E_D - RT/2}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad \text{(xiv.)}$$

If $\ln D$ is plotted against $1/T$ the slope of the straight line, which should be obtained, gives the value of $E_D - RT/2$; hence E_D may be evaluated. Bradley (1934) has used these equations to calculate a, assuming a_A and a_B to be equal, for a number of reactions with known velocity constants: in most cases, for processes involving a molecule and an ion, which have been found to be normal by the use of the gas-collision formula, the values of a required to give the observed experimental results were found to be of the expected order, viz., from 0·2 to 2·8 $\times$ 10^{-8} cm. It should be noted that since equation (x.) involves E_D, which depends on the temperature coefficient of the diffusion constant, it indirectly involves the variation with temperature of the viscosity of the solvent; it is in this respect that the new formula differs fundamentally from that previously considered. At present there does not seem any means for deciding which of the collision formulæ is the more accurate, but the fact remains that since the gas-collision equation (iv.) is so much easier to apply, and gives results not very greatly different from those obtained by the aid of the alternative equation, the former is likely to remain for the present in possession of the field. It is possible that the

activated-collision hypothesis may eventually prove to give only an approximate picture of the mechanism of chemical reactions (*vide infra*), and so it is hardly worth while discussing the relative merits of different equations for the application of this hypothesis.

UNIMOLECULAR REACTIONS IN SOLUTION

Unimolecular Reactions in Solution. It has been already seen that in certain unimolecular reactions, *e.g.*, the decomposition of nitrogen pentoxide, and the isomerisation of *d*-pinene, the velocity constant is approximately the same in the gaseous phase as in certain solutions; hence in these cases it is possible that the solvent is exerting no effect, either in activating or de-activating. In other instances, however, there is good reason to believe that the molecules of solvent are able to take part in activating collisions, so that a consideration of the reaction requires some knowledge of the number of collisions occurring between molecules of solvent and of solute in a given time. Even in such unimolecular reactions as those previously mentioned, it is not possible to state that solvent–solute collisions have no influence on the reaction, but the striking agreement between the velocity constants in a number of solvents and in the gaseous phase makes it improbable that such collisions play an important part in the activation of the reacting molecules. It must be recorded, however, that views to the contrary have been expressed (Moelwyn-Hughes, 1932).

Kinetics of Unimolecular Reactions. The decomposition of gaseous ozone is a bimolecular reaction, but in carbon tetrachloride solution it is kinetically of the first order, with an activation energy of 26,160 cals., which is markedly lower than for the gas reaction. It was suggested by Bowen, Moelwyn-Hughes and Hinshelwood (1931) that this could be interpreted if collisions between ozone molecules and solvent molecules would result in the decomposition of the former, provided the necessary energy of activation were available. The mechanism of a unimolecular reaction in solution may be assumed to be the same as for a gas, namely, activation by collision followed by an interval before decomposi-

tion occurs, during which de-activation can occur. This results in a definite concentration of activated molecules of the reactant ("Recent Advances in Physical Chemistry," Chapter V.). If c is the concentration of solute, s that of the solvent, and a that of the activated molecules of solute, then if activation can result from solute–solute and from solute–solvent collisions, it follows that

$$\text{rate of activation} = k_1c^2 + k_2cs \quad . \quad . \quad . \quad . \quad \text{(xv.)}$$

Since both solute and solvent molecules can presumably also bring about de-activation, it is seen that

$$\text{rate of de-activation} = k_3ac + k_4as \quad . \quad . \quad . \quad \text{(xvi.)}$$

The rate of the chemical change is proportional to the concentration of activated molecules; that is,

$$\text{rate of reaction} = k_5a \quad . \quad . \quad . \quad . \quad . \quad \text{(xvii.)}$$

When the stationary state is attained the rate of activation is equal to the sum of the rates of de-activation and of removal by reaction; hence

$$k_1c^2 + k_2cs = k_3ac + k_4as + k_5a \quad . \quad . \quad . \quad \text{(xviii.)}$$

Extracting the value of a from this expression and substituting in equation (xvii.), it follows that

$$\text{rate of reaction} = k_5(k_1c^2 + k_2cs)/(k_3c + k_4s + k_5) \quad . \quad \text{(xix.)}$$

If the solvent has no influence on the reaction, either in activation or de-activation, then k_2 and k_4 are zero, and if the time interval between activation and reaction is large compared with the normal time between two collisions, k_3 is much greater than k_5, and so equation (xix.) reduces to

$$\text{rate of reaction} = (k_5k_1/k_3)c \quad . \quad . \quad . \quad . \quad . \quad \text{(xx.)}$$

The rate is then proportional to the concentration of the reacting substance, and so the reaction is of the first order.

When the solvent molecules can, equally with solute molecules, take part in activation and de-activation, then since c is small in comparison with s, it is possible to write equation (xix.) in the form

$$\text{rate of reaction} = k_5k_2cs/(k_4s + k_5) \quad . \quad . \quad . \quad \text{(xxi.)}$$

If, as before, k_5 is small, compared with k_4, indicating an appreciable interval between activation and decomposition, it is seen that

$$\text{rate of reaction} = (k_5k_2/k_4)c, \quad . \quad . \quad . \quad . \quad \text{(xxii.)}$$

making the process again kinetically of the first order, although collisions with solvent molecules are responsible for most of the activation and consequent reaction of the solute.

Solvent-Solute Collision Number. In developing this subject further, it is necessary to be able to calculate the number of collisions between molecules of solute and solvent : unfortunately this cannot be done rigidly, but several formulæ are available which are more or less accurate. Using arguments based on the kinetic theory of diffusion, Jowett (1929) has deduced the number of collisions in which *each solute molecule* will be involved per second, as

$$Z = 1{\cdot}05 \times 8N\eta\sigma_A/M_A \quad . \quad . \quad . \quad \text{(xxiii.)}$$

where M_A is the molecular weight of the solute, σ_A its molecular diameter, η the viscosity of the solvent, and N the Avogadro number. On the other hand, Moelwyn-Hughes (1932), employing Einstein's theory of the Brownian movement as a basis, has deduced the approximate relationship

$$Z = 3\pi N\eta\sigma_A/2M_A \quad . \quad . \quad . \quad . \quad . \quad \text{(xxiv.)}$$

In both cases the calculated value of Z should be multiplied by the factor $(M_A + M_S)/M_S$, where M_S is the molecular weight of the solvent, to allow for the persistence of velocity after collision ; when M_A is small in comparison with M_S the correction is negligible.

The Viscosity Correction. It will be observed that the expressions in both equations (xxiii.) and (xxiv.) include the viscosity of the solvent, and this fact has important consequences. In the first place, since η decreases with increasing temperature, the number of collisions should consequently be greater at lower than at higher temperatures ; this result, surprising at first sight, is explained on the ground that the " free space " in a liquid increases rapidly as the temperature is raised, so that the chances of a collision are reduced. Secondly, it can be shown that the activa-

tion energy obtained from the Arrhenius equation, that is, by plotting log k against $1/T$, is not the true value for the reaction, but should include a viscosity correction. If n is the number of molecules of solute per c.c., then the total number taking part in collisions per sec. per c.c. is $n\mathbf{Z}$, where $\mathbf{Z}$ is given by either equation (xxiii.) or (xxiv.). If every collision involving the activation energy E, reckoned in two square terms only, leads to reaction, then the rate of reaction is given by

$$-\frac{dn}{dt} = n\mathbf{Z}e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxv.)}$$

Since the reaction, as already shown, is kinetically of the first order, the rate is directly proportional to the concentration of solute molecules; that is,

$$-\frac{dn}{dt} = kn, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxvi.)}$$

and consequently, from equations (xxv.) and (xxvi.),

$$k = \mathbf{Z}e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxvii.)}$$

In either of the expressions given for $\mathbf{Z}$, all the terms except η are independent of temperature, and so it is possible to write

$$k = k'\eta e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxviii.)}$$

where k' is a constant for the given reacting system, involving only the molecular weights of solvent and solute, the diameter of the solute molecule and numerical constants. Dividing both sides by η, there is obtained

$$k/\eta = k'e^{-E/RT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxix.)}$$

and consequently in order to obtain the true energy of activation E, it is necessary to plot log k/η, instead of log k, against $1/T$. If the variation of viscosity with temperature is expressed as an exponential function, $\eta = \eta_0 e^{b/T}$, where η_0 and b are constants for the given solvent, then

$$k = \eta_0 k' e^{-(E-b)/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxx.)}$$

On taking logarithms, differentiating with respect to T, and compared with the Arrhenius equation (vii.), it is seen that

$$E = E_A + Rb \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxi.)}$$

The value of the correction factor *Rb* varies with the nature of the solvent; it is only 880 cals. for chloroform over the temperature range of 40° to 70° C., but as high as 5680 cals. for acetophenone between 70° and 140° C. Values of *Rb* of the order of 2000 to 3000 cals. are quite common: they account for the relatively low apparent activation energies given by the direct application of the Arrhenius equation.

Since the correct activation energy can be determined by equation (xxxi.), it should be possible to calculate by means of equation (xxvii.) the velocity constant for a unimolecular reaction, such as the decomposition of ozone in carbon tetrachloride solution, in which the solvent molecules are responsible for activation of the solute. In the particular case mentioned, the application of the viscosity correction to the Arrhenius activation energy (26,160 cals.) gives a value for E of 28,750 cals., which is quite close to that obtained for decomposition in the gas phase. The calculated velocity constant depends on which of the equations, (xxiii.) or (xxiv.), is used to determine the collision number Z, and so the results for both are given in Table LIV., which is taken from the work of Moelwyn-Hughes (1933).

TABLE LIV

Unimolecular Decomposition of Ozone in Carbon Tetrachloride Solution.

Temp. °C.	Velocity Constants.		
	Observed.	Calc. (Equn. xxiii.).	Calc. (Equn. xxiv.)
54·7	$1{\cdot}82 \times 10^{-5}$	$1{\cdot}77 \times 10^{-6}$	$0{\cdot}85 \times 10^{-6}$
71·0	$1{\cdot}24 \times 10^{-4}$	$1{\cdot}34 \times 10^{-5}$	$0{\cdot}58 \times 10^{-5}$

Jowett's equation (xxiii.) for the collision number gives, in this instance, calculated velocity constants which are certainly of the right order, although they are somewhat smaller than the observed values. For the unimolecular decomposition of dibromosuccinic acid into hydrobromic and bromomaleic acids in aqueous solution (van't Hoff), on the other hand, better agreement between the

experimental and calculated velocity constants is obtained by the use of the Moelwyn-Hughes equation (xxiv.), as shown in Table LV.

TABLE LV

Unimolecular Decomposition of Dibromosuccinic Acid in Aqueous Solution.

Temp. °C.	Velocity Constants.		
	Observed.	Calc. (Equn. xxiii)..	Calc. (Equn. xxiv.).
15°	$1{\cdot}61 \times 10^{-7}$	$2{\cdot}91 \times 10^{-5}$	$7{\cdot}75 \times 10^{-7}$
60°	$1{\cdot}09 \times 10^{-5}$	$4{\cdot}31 \times 10^{-3}$	$1{\cdot}15 \times 10^{-4}$
101°	$5{\cdot}30 \times 10^{-4}$	$1{\cdot}61 \times 10^{-1}$	$4{\cdot}28 \times 10^{-3}$

In the Beckmann transformation of benzophenoneoxime picryl ether (p. 286) the " spontaneous " process in carbon tetrachloride solution is of the first order and appears to take place at every collision between a molecule of reactant and one of solvent. The activation energy corrected for the viscosity effect is 30,250 cals., leading to velocity constant of $2{\cdot}24 \times 10^{-6}$, by the use of equation (xxiv.), as compared with the observed result of $0{\cdot}47 \times 10^{-6}$ at 81° (Chapman, 1934).

In other instances of unimolecular processes, however, such as the decomposition of triethylsulphonium bromide and of 2 : 4 : 6-trinitrobenzoic acid, the calculated rate constant is of the order of 10^3 to 10^6 times *less* than the observed value, using either of the methods for obtaining the collision number. It is then necessary, as with unimolecular reactions in the gas phase (see p. 272), to suppose that energy from internal degrees of freedom contributes to the activation energy of the molecules. In Table LVI. are given some of the results, calculated by Moelwyn-Hughes (1932), showing the number of degrees of freedom F, equal to $\frac{1}{2}s - 1$, necessary to give reaction constants close to the observed values.

The number of internal degrees of freedom which it is necessary to postulate is by no means large, but it is somewhat surprising that it should vary with the nature of the solvent. If the general theory upon which the calculations are based is correct, and this is

TABLE LVI

Degrees of Freedom Contributing to Activation Energy in Unimolecular Reactions.

Reaction.	Solvent.	k (obs.).	F	k (calc.).
Decomposition of: Triethylsulphonium bromide . .	Nitrobenzene	$2{\cdot}11 \times 10^{-4}$	4	$2{\cdot}96 \times 10^{-4}$
	Tetrachloroethane	$2{\cdot}19 \times 10^{-4}$	6	$1{\cdot}66 \times 10^{-4}$
	Chloroform	$2{\cdot}07 \times 10^{-4}$	7	$0{\cdot}98 \times 10^{-4}$
	n-Propyl alcohol	$1{\cdot}53 \times 10^{-6}$	7	$2{\cdot}14 \times 10^{-6}$
	Acetic acid	$8{\cdot}51 \times 10^{-7}$	3	$5{\cdot}43 \times 10^{-7}$
2 : 4 : 6-Trinitrobenzoic acid.	Water	$3{\cdot}33 \times 10^{-6}$	4	$3{\cdot}91 \times 10^{-6}$
	Acetophenone	$5{\cdot}79 \times 10^{-7}$	2	$4{\cdot}39 \times 10^{-7}$
	Nitrobenzene	$4{\cdot}07 \times 10^{-9}$	3	$8{\cdot}61 \times 10^{-9}$
	Toluene	$1{\cdot}62 \times 10^{-9}$	1	$4{\cdot}20 \times 10^{-9}$

open to question, then the result implies that the different solvents enter into some kind of association with the reactant to different extents.

Solvent as Reactant—Unimolecular Reactions. When the solute reacts with the solvent, as in the cases already mentioned previously (p. 279) and in others, such as the hydrolysis of monochloroacetic acid in aqueous solution or of substituted benzyl chlorides in 50 per cent. aqueous alcohol, the reaction, although actually involving two molecules, is kinetically of the first order. In processes of this type decomposition occurs immediately two molecules, one of solvent and one of solute, possessing the necessary energy of activation collide, without the lapse of any interval, so that the general velocity equation (xix.) can be simplified: in the first place, reaction can only occur when a molecule of solvent encounters one of solute, and so k_1c^2 can be eliminated; secondly, since reaction is rapid in comparison with activation, k_5 is much larger than k_3 and k_4, so that the result is

$$\text{rate of reaction} = k_2cs \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxii.)}$$

Since s is virtually constant in a relatively dilute solution, the reaction is of the first order with respect to the solute. The velocity constant should in this case be given by equation (xxvii.),

since reaction depends on collision between solvent and solute and, as with other bimolecular processes, only two square terms are concerned in the activation energy. In Table LVII. are recorded the calculations of Moelwyn-Hughes (1932), compared with the experimental observations of Olivier (1923), of the velocity of hydrolysis of a series of substituted benzyl chlorides in an alcohol–water mixture at 30° C. The collision numbers were calculated by means of equation (xxiv.), the molecular diameters varying from 5·3 to 7·0 $\times$ 10^{-8} cm.; the viscosity correction for the solvent to be applied to the Arrhenius activation energy (E_A) was taken as 3425 cals.

TABLE LVII

Hydrolysis of Substituted Benzyl Chlorides in Aqueous Alcohol at 30° C.

Substituent.	E_A (cals.)	k (obs.) $\times$ 10^7.	$P = k_{obs.}/k_{calc.}$
None	19,900	18·5	6·8
o-Methyl	19,790	91·7	1·5
m-Methyl	20,190	24·0	3·1
p-Methyl	20,390	173	0·4
o-Nitro	22,250	0·867	2·5
m-Nitro	21,780	1·05	4·5
p-Nitro	21,990	0·818	4·1
o-Bromo	21,110	3·93	3·2
2 : 6-Dibromo	22,460	1·19	0·9

The values in the last column show that the method of calculation applied gives a reasonably satisfactory velocity constant, and a similar agreement has been obtained for the hydrolysis of carbonyl sulphide (p. 279).

Ternary Collisions Involving Solvent. The expression for the collision number between solvent and solute may be extended to cover the case of a ternary collision between molecules of two reactants, A and B, and of the solvent (S). The number of collisions in which one molecule of the reactant A is involved is given by equation (xxiv.) as $3\pi N\eta\sigma_A/2M_A$ per sec., and when n_A molecules of this substance are present in 1 c.c., the total number

of collisions in unit volume is $3\pi N\eta\sigma_A n_A/2M_A$ per sec. The chance that a molecule of the second reactant, B, will take part in one of these collisions is approximately given by $v_B/(v_A + v_B + v_S)$, where the v terms represent the actual volumes of the respective molecules present per c.c. of solution; in dilute solution this is practically equal to v_B/v_S. If as a further approximation the difference in the diameters of the molecules B and S is neglected, this probability of a ternary collision becomes n_B/n_S, where the n terms are the corresponding number of molecules per c.c. It follows, therefore, that the total number of ternary collisions in unit volume per second is given by

$$z = 3\pi N\eta\sigma_A n_A n_B/2M_A n_S \quad . \quad . \quad . \quad \text{(xxxiii.)}$$

If the energy of activation is still expressible in two square terms, then the reaction velocity is obtained by multiplying z by $e^{-E/RT}$, where E is the true activation energy; thus,

$$\text{rate of reaction} = (3\pi N\eta\sigma_A n_A n_B/2M_A n_S)e^{-E/RT} \quad . \quad . \quad \text{(xxxiv.)}$$

Since the concentration of solvent molecules is constant, a reaction of the type being considered behaves as if it were of the second order, provided there is no delay between activation and reaction, so that it is possible to write

$$\text{rate of reaction} = kn_A n_B \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxv.)}$$

where k is the velocity constant. From equations (xxxiv.) and (xxxv.) it follows that

$$k = (3\pi N\eta\sigma_A/2M_A n_S)e^{-E/RT} \quad . \quad . \quad . \quad \text{(xxxvi.)}$$

and this can, of course, be written in the form $k = Ze^{-E/RT}$, where the value of the collision number Z is given by the term within the brackets. It should be noted that equation (xxxvi.) gives the velocity constant expressed in terms of c.c./molecule/sec. units.

The only factor included in the collision number which varies appreciably with temperature is the viscosity η, and so equation (xxxvi.) may be written in the same form as equation (xxviii.), and it follows, as before, that E is not the same as the Arrhenius energy of activation, but is obtained by plotting $\log k/\eta$ against $1/T$, or by applying the Rb correction as explained previously. Moelwyn-Hughes and Legard (1933) have used this method to calculate the

velocity constant of the reaction between phenylpropiolic acid and iodine :

$$C(Ph){:}C{\cdot}CO_2H + I_2 = C(Ph)I{:}CI{\cdot}COOH,$$

which apparently requires the presence of a molecule of water at the moment of impact ; the calculated value of the velocity constant, $1{\cdot}16 \times 10^{-3}$ at 24·8° C., may be compared with the experimental result of approximately $1{\cdot}1 \times 10^{-3}$. By postulating the necessity for the presence of a solvent molecule the relative slowness of the bimolecular reaction velocity can be explained in this case, but a similar interpretation is not always applicable. Williams and Hinshelwood (1934) showed that the low velocity of reaction between aromatic amines and substituted benzoyl chlorides in benzene solution could not be accounted for by assuming the necessity of a solvent molecule at the instant of collision : even if this were the case the calculated velocity would still be very greatly in excess of the observed value, and so the process must be definitely classed as a " slow reaction."

Catalysed Esterification and Hydrolysis. When a carboxylic acid is dissolved in an alcohol esterification occurs with the molecules of acid acting as catalyst : the rate of reaction will then depend on a collision between two molecules of solute and one of solvent, so that the method of calculation just described can be used, by making A and B identical. If hydrogen chloride is added to a mixture of acid and alcohol the hydrogen ions become the effective catalyst, and then A and B are not identical. In a number of cases studied by Hinshelwood, with Legard, Rolfe and Williamson (1934, 1935), the reactions were found to be of the slow type : when the catalyst was a molecule, the probability factor P, giving the ratio of the observed to the calculated velocity constants, was about 10^{-7}, but with hydrogen ions as catalyst a much larger value, approximately 10^{-2} to 10^{-3}, was found. This latter result is in general harmony with the view already stated (p. 283), that reactions involving a molecule and an ion behave in an almost normal manner from the standpoint of the theory of kinetic activation ; the observed P factor might possibly be explained by steric effects.

The hydrolysis of esters and of other compounds in aqueous

solution, with hydrogen ion as catalyst, belongs to the same category kinetically as the reactions just considered, but the agreement between observed and calculated velocity constants obtained from equation (xxxvi.) is better. Although these reactions are relatively complicated, as will be seen in Chapter VIII., the rate-determining stage is evidently one depending on a ternary collision, or on an equivalent process. The results in Table LVIII. are taken from the book by Moelwyn-Hughes (1933); they show the general order of the agreement between observed and calculated velocity constants, for hydrolysis in aqueous solution catalysed by hydrogen ions. The values of E have been corrected for the viscosity factor, and the velocity constants are for unit concentration of catalyst.

TABLE LVIII

Hydrolysis in Aqueous Solution Catalysed by Hydrogen Ions.

Reactant.	E (cals.).	Temp. °C.	k (obs.).	k (calc.)
Methyl acetate . .	20,790	30	$2{\cdot}16 \times 10^{-4}$	$2{\cdot}55 \times 10^{-4}$
Ethyl acetate . .	20,840	25	$9{\cdot}38 \times 10^{-5}$	$1{\cdot}23 \times 10^{-4}$
Acetamide . . .	22,790	25	$6{\cdot}60 \times 10^{-6}$	$6{\cdot}79 \times 10^{-6}$
Benzoyl glycine . .	25,210	80	$5{\cdot}05 \times 10^{-8}$	$4{\cdot}08 \times 10^{-4}$

In other cases of hydrolysis, *e.g.*, of disaccharides, the observed velocity is much greater than that calculated so that it is necessary to postulate 9 or 10 internal degrees of freedom as contributing to the energy of activation. It is true that the molecules involved are of a complicated type and it is not impossible that this number of degrees of freedom should be concerned, but it is unusual for any internal energy to contribute towards activation for a bimolecular reaction. The result may possibly be due to uncertainty in calculating the number of collisions from the approximate equations.

Alternative Equation for Collision Number. Before leaving the subject of collisions in which molecules of solvent take part, mention may be made of the alternative approach to the subject as developed by Bradley (1934); this author, employing the

treatment already described (p. 288), finds the number of collisions per second between molecules of solvent and *one molecule* of a single solute to be given by

$$Z = \frac{v}{a}\left(\frac{3\pi}{2}\right)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxvii.)}$$

where v and a apply to the solute and have the significance given on p. 288. The reaction constant is obtained by multiplying this collision number by $e^{-E/RT}.E/RT$, since two square terms are assumed to be involved for each colliding molecule ; thus

$$k = \frac{v}{a}\left(\frac{3\pi}{2}\right)^{1/2}\frac{E}{RT}e^{-E/RT} \quad . \quad . \quad . \quad . \quad \text{(xxxviii.)}$$

The energy of activation is related to the Arrhenius quantity E_A by the expression $E = E_A + 3RT/2$, as may be seen by logarithmic differentiation of equation (xxxviii.) with respect to temperature, and comparing with equation (vi.). It will be noted that the formula for k contains no reference to the viscosity and in this respect differs essentially from those of Jowett and of Moelwyn-Hughes already described. Bradley has applied his equation to calculate the term a from the measured velocity constants for a number of unimolecular decompositions occurring in solution, on the assumption that solvent molecules are involved in the process of activation ; the results are all of the expected order, namely, about 10^{-8} cm. It is important to note that in these calculations it was not necessary to postulate contribution to the energy of activation from any degrees of freedom other than those corresponding to the four square terms involved in equation (xxxviii.), whereas the alternative method of treatment has required a number, up to 7, of internal degrees of freedom, equivalent to a total of 16 square terms, to be concerned. The formula given above is certainly of interest ; it does not contribute anything new to the theory of kinetic activation in solution, but gives an alternative method of calculation based on the same fundamental hypothesis.

FACTORS INFLUENCING REACTION VELOCITY

Apparent Constancy of *E* and *P*. In attempting to elucidate the mechanism of chemical reactions in solution, particularly those

which are kinetically of the second order, it is of value to express the velocity constant in the form $PZe^{-E/RT}$, where E is strictly the Arrhenius activation energy determined from the observed velocity constants at two or more temperatures and Z is the collision number. It is then possible to study the variations in P and E for a series of similar reactions in the hope of obtaining some correlation between them and the substituent groups present in the molecule. An examination of Table XLIX., for the reaction between sodium phenoxide and a series of alkyl iodides, shows that E remains practically constant, and P is not very far from unity : the haphazard variation of the actual figures probably has no significance. Similar results, of apparent constancy in both P and E, within the limits of experimental error, are to be found in other reactions between alkyl iodides and alkyloxides or phenoxides, in the alkaline hydrolysis of a series of esters of acetic acid, and in the reactions between potassium iodide and a series of substituted β-chloroethyl sulphides or of benzyl chlorides. In all these cases one of the reactants is an ion and the velocities are normal in so far as they are close to the calculated values. In the last-mentioned instance, however, it is clear that since the reaction velocities for different substituents, *e.g.*, halogens and the nitro-group, in the *ortho-*, *meta-*, and *para*-positions of the benzene ring, are in the definite order to be expected from their inductive and mesomeric effects (Bennett and B. Jones, 1935), there must be some small variation either in the probability factor P or in the energy of activation. Unfortunately, the uncertainties involved in the calculation of the collision number Z, and in the experimental determination of E, make it impossible at present to distinguish between the two possibilities, or to say whether both are operative.

Another problem of a similar type is presented by the " slow " reaction resulting in quaternary ammonium salt formation between a *p*-substituted benzyl bromide and pyridine or α-picoline in acetone solution (Baker and Nathan, 1935) : the values of E appear to be constant within the limits of experimental error, and consequently the variation in the velocity constant for different substituents must be ascribed to changes in the probability factor. The latter, however, does not vary considerably in any

one type of reaction, *e.g.*, from $0{\cdot}607 \times 10^{-6}$ for *p*-nitrobenzyl bromide to $2{\cdot}61 \times 10^{-6}$ for the 2 : 4-dimethyl-compound when reacting with pyridine, and so it is by no means certain that this factor carries the whole of the change in the reaction velocity.

Variation of *E* or *P* in a Series of Reactions. In other cases of quaternary salt formation there is no doubt that both *P*, which is of the order of 10^{-6} to 10^{-8}, and *E* can vary ; for example, in the reactions with pyridine in benzene solution, *E* increases steadily from 14,250 to 16,100 cals., in passing from methyl to *n*-propyl iodide. The change from methyl to ethyl results in little alteration in *P*, but the next stage to *n*-propyl iodide is accompanied by a marked fall in the probability factor. On the other hand, the change from ethyl to *iso*-propyl iodide brings about no change in *P*, although the activation energy increases by over 2000 cals. For a given halide *P* falls, although *E* remains virtually constant, when the amine is altered from trimethylamine to triethylamine, or from pyridine to quinoline ; similarly, the very slow velocity of reaction with pyridine or quinoline, as compared with that for an aliphatic tertiary amine, is accounted for mainly by the larger energy of activation in the former instances (Winkler and Hinshelwood, 1935). Since quaternary ammonium salt formation may be regarded as involving the simultaneous transfer of an electron from the nitrogen to the alkyl group of the halide, and from the alkyl group to the halogen atom, it is possible to explain to some extent, although not completely, the observed variations in *E* in terms of the availability of the electrons ; the presence of groups able to facilitate electron transfers should tend to decrease the energy of activation of the reaction. Other effects are, however, operative and these yet remain to be elucidated.

For the benzoylation of amines in benzene solution, by the interaction of an aniline with a *p*-substituted or unsubstituted benzoyl chloride, the probability factor remains almost constant at 10^{-7}, but the energy of activation increases from 5900 cals. for the reaction between aniline and *p*-nitrobenzoyl chloride, to 11,800 cals. for that involving *p*-nitraniline and benzoyl chloride itself. The results in this instance are complete enough to present a clear picture ; the energy of activation is decreased,

and the reaction velocity consequently increased, by the presence of (*a*) an electron-attracting substituent, *e.g.*, halogen or nitro-group, in the amine, or of (*b*) an electron-repelling substituent, *e.g.*, methyl group, in the benzoyl chloride (Williams and Hinshelwood, 1934).

Analogous results have been reported in the alkaline hydrolysis of a number of *p*-substituted ethyl benzoates in 85 per cent. ethyl alcohol solution. The results of the experiments, which covered a five-thousand-fold range of velocities, are quoted in Table LIX., taken from the work of Ingold and Nathan (1936).

TABLE LIX

Hydrolysis of p-*Substituted Ethyl Benzoates at* 25° *C.*

Substituent.	$k \times 10^5$.	E (cals.).	$PZ \times 10^9$.
NH_2 . .	1·27	20,000	5·42
OMe . .	11·5	18,650	5·38
Me . .	25·1	18,200	5·73
H . .	55·0	17,700	5·32
Cl . .	237	16,800	4·93
I . .	278	16,700	4·93
Br . .	289	16,800	5·82
NO_2 . .	5670	14,500	2·30

Assuming the collision number Z to be practically constant, as it will be for such a series of compounds, it is evident that P remains virtually unchanged throughout the series, whereas the activation energy decreases steadily as the electron-attracting tendency of the substituent group increases.

The nuclear chlorination of substituted anisoles and phentoles takes place more slowly than is to be expected theoretically; although a complete analysis of the results has not yet been made it appears that, in the main, variations in the velocity constant are determined by the change in the activation energy resulting from the introduction of a particular substituent group and not from any large variation in the probability factor. The influence of a given group on E is probably the same for the chlorination of a

number of different ethers, the effect being related in magnitude to the polar properties of the group (Bradfield and B. Jones, 1928, *et seq.*).

There are evidently a number of reactions in which the polarity of the substituent group exerts a primary influence on the activation energy of the process, and it has been suggested that E is related to the dipole moment (μ) of the group by the equation

$$E = E_0 \pm C(\mu + a\mu^2) \quad . \quad . \quad . \quad . \quad \text{(xxxix.)}$$

where E_0, C and a are constants. This relationship is said to apply to the benzoylation process already considered: when the substituent is in the acid chloride the positive sign holds, and the negative sign is used when the substituent is in the aniline (Watson, *et al.*, 1935). The equation is, however, not altogether satisfactory for halogen-substituted compounds. It may be noted that an expression of the same form is supposed to relate the energy of activation in a number of side-chain reactions with the dipole moment of the group substituted in the nucleus.

Simultaneous Variation of E and P. Simultaneous variations in the probability factor and in the activation energy for a series of related reactions have been observed in esterification processes: if an organic acid is dissolved in an alcohol reaction ensues, the molecules of acid acting as catalyst. The following results (Table LX.) were obtained for a number of acids in benzyl alcohol at 100° C. (Hinshelwood and Legard, 1935).

TABLE LX

Esterification in Benzyl Alcohol at 100° *C.*

Acid.	$k \times 10^7$.	E (cals.).	PZ.
Trichloroacetic . . .	2760	13,130	$2{\cdot}5 \times 10^{-17}$
Acetic	72·1	15,350	$1{\cdot}3 \times 10^{-17}$
Diphenylacetic . . .	21·0	16,350	$1{\cdot}5 \times 10^{-17}$
Benzoic	4·19	19,750	$3{\cdot}0 \times 10^{-16}$
2 : 4 : 6-Trimethylbenzoic .	0·00741	27,700	$2{\cdot}5 \times 10^{-14}$

Apart from the result with trichloroacetic acid, which may perhaps be due to experimental error, it is seen that as the velocity

of esterification decreases the value of E increases, as is to be expected, but the probability factor increases at the same time. This means that the slowness of the reaction is to be ascribed exclusively to the increase of the energy of activation necessary for esterification with the different acids. The reason for this is not clear, especially as there seems to be no connection between the value of E and the strength of the acid being esterified, the acid being at the same time catalyst for the reaction.

"Steric Hindrance" in Esterification. One of the most interesting results of the work on esterification is seen from a comparison of the data in Table LX. for benzoic and 2 : 4 : 6-trimethylbenzoic acids; the velocity for the former is about 530 times that for the latter, an effect generally ascribed to "steric hindrance." It is a striking fact, however, that the P factor, which should be small if *steric* factors are really involved, is actually greater for the trimethylbenzoic acid, the low velocity of esterification being entirely accounted for by the exceptionally high activation energy required for the reaction.

Mechanism of Esterification. The esterification process under consideration requires a ternary collision between two molecules of acid, one reactant and one catalyst, and a molecule of the alcohol used as solvent; the theoretical collision number Z is not known with certainty, but if P were unity the value of PZ should be about 10^{-10}. It is evident, therefore, that for the reactions given in Table LX., P varies from 10^{-4} to 10^{-7}, approximately; they belong, therefore, definitely to the category of slow reactions. This fact has been utilised to confirm the generally accepted views on the mechanism of ester formation. There is good reason to believe that in the reaction between a carboxylic acid and an alcohol, the breaking of the linkages occurs at the points indicated in the equation

$$\mathrm{R{\cdot}CO|OH + RO|H \rightarrow R{\cdot}CO{\cdot}OR + H_2O.}$$

When hydrogen chloride reacts with an alcohol the process must involve the alternative mechanism

$$\mathrm{H|Cl + R|OH \rightarrow R{\cdot}Cl + H_2O,}$$

and so the kinetics should be of a type quite different from that observed in the esterification of a carboxylic acid.

The kinetics of the reaction of hydrogen chloride with methyl alcohol has been studied (Hinshelwood, 1935), and the reaction has been shown definitely *not* to be of the " slow " type, the velocity being greater than that calculated by the collision hypothesis. It seems, therefore, that the first stage in the combination is the rapid formation of an oxonium salt, $RH_2O^+Cl^-$, and it is the decomposition of this which determines the rate of the reaction : this process, like that of the decomposition of iodonium salts (Fletcher and Hinshelwood, 1935) and of sulphonium salts (p. 295) is evidently a unimolecular reaction in which several degrees of freedom contribute to the energy of activation.

Hydrolysis of Phenyl Sulphates. The rate of hydrolysis of a number of substituted potassium phenyl sulphates into phenol and potassium bisulphate, catalysed by hydrochloric acid, is apparently another example of a " slow " reaction in which there is a parallelism between the energy of activation and the probability factor ; as in the esterification reactions, already discussed, both quantities either increase or decrease simultaneously with the introduction of a particular substituent into the benzene ring (Burkhardt, 1936).

THE "ACTIVATED COMPLEX" THEORY OF REACTION VELOCITY

The "Activated Complex." A new approach to the subject of reaction velocities, based on the earlier work of Tolman, Pelzer and Wigner, La Mer, and others (1927–1935), has been developed recently by Eyring (1935) and by Evans and Polanyi (1935), and is likely to have important consequences in many aspects of the study of reactions in the gas phase and in solution. It is of particular interest at the moment in so far as it gives a simple interpretation of the small probability factors in the so-called " slow " reactions. It has been accepted for many years that the first stage in a chemical reaction is the formation of a " critical complex " between the reacting molecules, and that this breaks

down at a definite rate to give the resultants. The older view has been that the complex can either disintegrate into its constituents or into reaction products, but the newer theory attributes to the activated complex the property of moving in one direction only. Instead of the speed of a reaction being determined by the relative degrees to which the complex breaks up in the two alternative

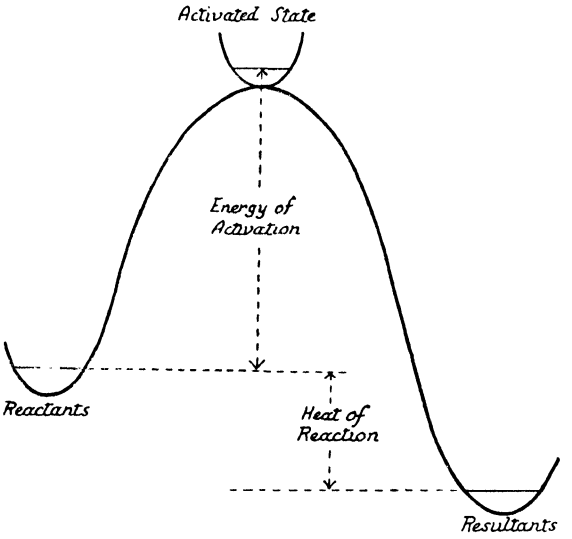


FIG. 21.—Potential energy curve: profile of a potential energy surface.

ways, it is now attributed mainly to the probability of the formation of the complex in the first place.

The potential energy path of a reacting system may be represented diagrammatically by Fig. 21, which is really the profile of a three-dimensional surface ("Recent Advances in Physical Chemistry," Chapter V.); in this the reactants may be imagined as moving from left to right along the line depicting the energy barrier. At the top of the barrier the system is in the form known as the "activated complex" (Eyring) or "transition state" (Polanyi): it then has energy E, the activation energy, in excess of the zero-point energy of the initial state. It is possible, at least in certain cases, to calculate approximate values of E by means of

wave mechanics, but this need not concern us here. The important point to note is that " the activated complex has very nearly the properties of an ordinary molecule except that instead of having the three regular translational degrees of freedom it has a fourth, along which it approaches the barrier, crosses it, and then flies to pieces " (Eyring).

Calculation of Velocity Constants. The rate constant of the reaction is determined by the probability of the formation of the activated complex and by its average velocity " along the normal co-ordinate corresponding to passing over the barrier " ; this velocity has been shown by Eyring to be equal to the term $(kT/2\pi\mu)^{1/2}$ for all reactions, where k is the Boltzmann constant and μ the " reduced mass " (see p. 156) of the complex. The probability of the formation of the complex is equal to the equilibrium constant (K) of the system formed by the reactants and the complex, so that the velocity constant of the reaction (k_v) is given by

$$k_v = K(kT/2\pi\mu)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xl.)}$$

(It should be noted that k_v will be used for the velocity constant to distinguish it from the Boltzmann constant.)

If two reacting molecules, A and B, form the intermediate activated complex AB*, the equilibrium may be represented as

$$A + B \rightleftharpoons AB^*.$$

It has been shown in Chapter II., equation (xxiv.), that the concentration equilibrium constant, for a reaction involving ideal gases, may be expressed in terms of the appropriate complete partition functions (G), thus

$$K = \frac{G_{AB^*}}{G_A G_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xli.)}$$

the function G including the translational, vibrational and rotational contributions and the zero-point factor. In the activated complex one of the normal vibrational degrees of freedom is replaced by one of translation along the co-ordinate of decomposition, and the partition function for this new degree of freedom is $(2\pi\mu kT/h^2)^{1/2}$; this is the normal value for one degree of translational freedom (p. 61), except that the reduced mass μ,

representing the mass along the decomposition co-ordinate, is used instead of the ordinary mass. Extracting this factor from the complete partition function of the complex, the term G_{AB^*} may be replaced by $G^*_{AB^*}\,(2\pi\mu kT/h^2)^{1/2}$, so that

$$K = \frac{G^*_{AB^*}}{G_A\,G_B}\,(2\pi\mu kT/h^2)^{1/2} \quad . \quad . \quad . \quad . \quad \text{(xlii.)}$$

where $G^*_{AB^*}$ includes one less than the normal number of vibrational partition functions. Multiplying by the average velocity of the complex over the barrier, it follows from equation (xl.) that for an ideal system

$$k_v = \frac{G^*_{AB^*}}{G_A G_B}\left(\frac{kT}{h}\right) \quad . \quad . \quad . \quad . \quad . \quad \text{(xliii.)}$$

$$= K^*(kT/h) \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xliii}a\text{.)}$$

where K^* is the equilibrium constant obtained by treating the activated complex as a normal molecule in which one of the vibrations is very stiff, that is to say its frequency is so low that it is virtually zero. This is equivalent to the postulate made above that the complex has one vibrational degree of freedom less than normal, but the new degree of translation is ignored. Comparison of equations (xl.) and (xliii*a*.) shows that if this assumption is made, the velocity of crossing the barrier becomes kT/h, instead of $(kT/2\pi\mu)^{1/2}$. (Strictly speaking the right-hand side of these equations should be multiplied by a "transmission coefficient," representing the fraction of the total number of complexes passing over the barrier which actually fly to pieces; according to Eyring, this is probably so close to unity that it need not be considered further.) If from the complete partition function the zero-point energy factor is extracted, leaving the factor F, that is,

$$G = Fe^{-E_0/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xliv.)}$$

then it follows by substitution in equation (xliii.) that

$$k_v = \frac{F^*_{AB^*}}{F_A F_B}\left(\frac{kT}{h}\right)e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad \text{(xlv.)}$$

where E, equal to ΔE_0, is the difference in the zero-point energies of the activated complex and the reactants, and is consequently

equal to the activation energy of the process.† This equation is identical in form with the usual expression based on the theory of kinetic activation, viz., $k_v = PZe^{-E/RT}$.

Reaction Between Two Atoms. Consider a reaction involving two atoms: that is to say in the general case considered both A and B are atomic, so that they have no internal degrees of freedom, and the F function includes the value for three degrees of translational freedom only; thus

$$F_A = (2\pi m_A kT/h^2)^{3/2}$$

and

$$F_B = (2\pi m_B kT/h^2)^{3/2}$$

The complex AB* is to be regarded as a diatomic molecule and so has three normal translational and two normal rotational degrees of freedom, but one vibration is supposed to be so stiff as to be non-existent. The molecule AB* may then be regarded as being rigid, so that it is possible to write, for translation and rotation,

$$F^*_{AB*} = \{2\pi(m_A + m_B)kT/h^2\}^{3/2} [8\pi^2 IkT/h^2]$$

where the term in the square brackets is the rotational partition function (p. 72). The moment of inertia of a diatomic molecule, which has the general form μr^2, where μ is the reduced mass and r is the distance apart of the centres of the two atoms, can in this case be written

$$I = \sigma^2_{A,B} m_A m_B/(m_A + m_B)$$

where $\sigma_{A,B}$ is the mean diameter of the atoms A and B. Inserting these values in equation (xlv.) it follows that

$$k_v = \sigma^2_{A,B}\{8\pi RT(M_A + M_B)/M_A M_B\}^{1/2} e^{-E/RT} \quad . \quad \text{(iv}a\text{.)}$$

where the M terms are the molecular weights, equal to mN, and R is of course equal to kN, where N is the Avogadro number. This equation for k_v is identical with equation (iv.) derived from the activated collision hypothesis, and so it is seen that this gives a result identical with that derived from the new theory, *provided the reactants are both atoms.*

† It is tacitly assumed here that the activation energy is a constant and independent of temperature: this is not strictly true but the variation is not important for the present purpose. Actually E is the activation energy at the zero-point.

Reactions between Molecules. The extension of the treatment developed to reactions involving molecules can be carried out on similar lines, but as this becomes somewhat complicated the following simplified method will be adopted; it gives results sufficient for present purposes. In the first place it will be assumed that the partition function for each type of energy consists of a number of *equal* terms, one for each degree of freedom. Thus, writing f_T, f_R and f_V as the contributions of each appropriate degree of freedom to the total translational, rotational and vibrational partition function, respectively, then

$$F = f_T^t f_R^r f_V^v,$$

assuming the partition function F to be the product of the separate functions (see p. 71). For the reaction already discussed, in which A and B are atoms, it follows that

$$F_A = f_T^3, \quad F_B = f_T^3 \quad \text{and} \quad F^*_{AB*} = f_T^3 f_R^2,$$

and hence

$$k_v = (f_T^3 f_R^2 / f_T^3 f_T^3) \frac{kT}{h} e^{-E/RT}$$

$$= (f_R^2 / f_T^3) \frac{kT}{h} e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xlvi.)}$$

Comparing this relationship with equations (v.) and (xlv.), it follows that the quantity $(f_R^2/f_T^3)kT/h$ is effectively the theoretical collision number Z (see p. 270). It is now possible to consider the general case in which the reactants A and B are molecules containing n and n' atoms, respectively. The numbers of the various degrees of freedom for A, B and AB* are given below, assuming both n and n' to be greater than three.

Molecule.	A	B	AB*
Number of atoms. .	n	n'	$n + n'$
Degrees of freedom :—			
Translational .	3	3	3
Rotational . .	3	3	3
Vibrational . .	$3n - 6$	$3n' - 6$	$3(n + n') - 7$

In this tabulation it is assumed that there are no free rotations within the molecules, so that each has three degrees of rotational freedom ; the complex AB* has, of course, one vibrational degree of freedom less than for a normal molecule. Applying the data to equation (xlv.) it is seen that

$$k_v = \frac{f_T^3 f_R^3 f_V^{3n+3n'-7}}{(f_T^3 f_R^3 f_V^{3n-6})(f_T^3 f_R^3 f_V^{3n'-6})} \left(\frac{kT}{h}\right) e^{-E/RT}$$

$$= \frac{f_V^5}{f_T^3 f_R^3} \left(\frac{kT}{h}\right) e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xlvii.)}$$

assuming that f_T, f_R and f_V are the same for the three molecular species. Writing this equation in the form $k_v = PZe^{-E/RT}$, and noting, as shown above, that Z is approximately equivalent to $(f_R^2/f_T^3)kT/h$, it follows that

$$P = (f_V/f_R)^5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xlviii.)}$$

At ordinary temperatures f_V is generally of the order of unity, whereas f_R is in the vicinity of 10 to 100, so that, according to equation (xlviii.), in the reaction between two molecules, each containing more than three atoms, the probability factor in the kinetic-activation equation must have a value of the order of 10^{-5} to 10^{-10}. The larger the molecule the greater the value of f_R and so the smaller will be the P factor. The theory of the transition state, described above, thus explains in a direct manner the discrepancy between observed and calculated reaction velocities found for a large number of processes in the gas phase and in solution* : an examination of the examples recorded shows that in every case of a " slow " reaction the reactants are relatively complex molecules. If one of the reacting substances is a simple ion, *e.g.*, OH', Cl', I' or H^+, or an atom, *e.g.*, iodine, then application of the approximate method used above shows that since the activated complex differs little from one of the reactants, the P factor will not include such a large number of f_R terms in the denominator, and consequently its value will approximate to unity. A somewhat similar result is found for reactions between

* Strictly speaking the deduction given applies to ideal gases, but the general arguments may be extended to solutions (*cf.* p. 322).

two diatomic molecules ; as these have only two rotational degrees of freedom the value of P, by the method described, is found to be $(f_V/f_R)^3$. In this case, for relatively small molecules, f_R may be less than 10, so that the probability factor may be of the order of 10^{-1}, and in fact it is not unusual for the calculated velocity constant with a reaction involving two simple molecules to be within a factor of ten of the observed value.

Physical Interpretation of Results. The next point is obviously to attempt to give a physical interpretation to the results obtained from mathematical considerations. In the example of the two polyatomic molecules, the formation of the activated complex requires the disappearance of three translational and of three rotational degrees of freedom and the formation of five new vibrational frequencies, in addition to the new translational degree of freedom along the decomposition co-ordinate ; it is the reluctance connected with the energy transitions thus required which underlies the small value of the probability factor. The simple theory of kinetic activation requires that reaction should take place at every collision between molecules possessing the necessary energy of activation, but it seems that the activated complex, which is an essential intermediate in the reaction, will only form at a suitable collision provided the necessary rearrangement of the activation energy into the new degrees of freedom can occur. For atoms* and simple molecules this transfer occurs readily and almost every collision involving the activation energy results in the formation of the transition state and subsequent reaction ; with more complicated reactants, however, the probability of the formation of the intermediate complex, involving energy transitions in six degrees of freedom, is low and only a small fraction of the activated collisions results in reaction. Such factors as the necessity for suitable orientation and internal phase of the reacting molecules, as well as certain steric considerations and solvent influences, can explain the low values of P, either from the standpoint of the collision hypothesis (Hinshelwood and

* For a reaction involving two atoms, however, the situation is often rendered complicated by the necessity for the presence of a third body, *e.g.*, a molecule or the wall of the vessel, to remove the energy evolved (see "Recent Advances in Physical Chemistry," Chapter V.)

Winkler, 1936) or from the point of view of the necessity for the rearrangement of activation energy in the activated complex.

It has been seen that for a series of similar reactions involving related substances, such as the interaction of an amine with a substituted benzoyl chloride, there are often variations in the energy of activation whereas P remains almost constant: this means that the vibrational frequencies in the reacting molecules and the intermediate complex, which determine E, vary from molecule to molecule, but that the moments of inertia, the main factors in the PZ terms, remain almost constant throughout a series of related reactions. Any influences which tend to bring about marked changes in the dimensions and vibrational frequencies of the activated complex will affect both f_R and f_V, and so result in changes in the probability factor, as well as in the energy of activation. This aspect of the subject is at present somewhat speculative, but further developments may be expected as the transition-state theory is more fully considered.

Steric Restriction. Another factor, apart from molecular complexity, which will tend to decrease the probability of the transition state, and hence make the reaction a " slow " one, is a real steric factor. It can be shown that the more restricted the position of the reacting molecules in the activated complex the smaller will be the expression representing the PZ quantity, and the slower will be the reaction for a given activation energy. As an example may be quoted the association of triphenylmethyl radicals to form hexaphenylethane, for as the two carbon atoms come together the position of the phenyl groups must become more restricted than in the free radicals. The rate of combination is consequently much smaller than would be normally expected for two particles each possessing an odd electron (Evans and Polanyi, 1935). Another illustration is to be found in a comparison of the velocities of the processes:

$$(a)\ CH_3\cdot + CH_3\cdot = C_2H_6$$

and

$$(b)\ CH_3{\cdot}CO\cdot + CH_3\cdot = CH_3{\cdot}CO{\cdot}CH_3.$$

In the former case there is steric restriction when the activated complex is formed, but in the latter the presence of the bridge

between the two methyl groups is said to prevent such restriction in movement; the reaction (*a*) is thus slower than reaction (*b*) (Bawn, 1935).

Reference may now be made to unimolecular reactions: it is well known that these are rarely of the "slow" type, and this is quite explicable with the aid of the theory of the transition state. If a molecule ABC undergoes apparent unimolecular decomposition it will, as a result of a collision, pass through the activated-complex state ABC*, which is not fundamentally different from the molecule of reactant. The only energy transition involved is the change from one vibrational to the new translational degree of freedom along the decomposition co-ordinate, and should be able to take place quite readily. The probability of the formation of the transition state is therefore high, and an approximate calculation shows that the rate of reaction may well be considerably in excess of that determined by the simple collision hypothesis. It is this almost complete retention of the degrees of freedom of the original reactant in the activated complex which is interpreted in the classical theory as the contribution of several degrees of freedom to the energy of activation. When a unimolecular reaction occurs in solution there is a possibility that the solvent molecule may be involved in the activated complex: if this is the case then the process becomes virtually equivalent to a bimolecular reaction, and so there will be a reduced probability of the formation of the transition state. This factor must be borne in mind when considering unimolecular processes in solution.

Entropy Change and the Probability Factor. A further development of equation (xliii*a*.) giving the relation between reaction velocity and the equilibrium constant of the system consisting of reactants and activated complex, provides a new point of view in connection with slow reactions. By utilising the two familiar thermodynamic equations:—

$$-\Delta F^\circ = RT \ln K$$

and

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ,$$

it follows that

$$K = e^{\Delta S^\circ/R} \cdot e^{-\Delta H^\circ/RT} \quad \text{. . . . . (xlix.)}$$

If this is substituted in equation (xliii*a*.), $k_v = K(kT/h)$, it is evident that

$$k_v = e^{\Delta S^*/R} \cdot e^{-\Delta H^*/R} \cdot kT/h \quad . \quad . \quad . \quad . \quad . \quad . \quad (l.)$$

where ΔS^* and ΔH^* represent the increase of entropy and of heat content, respectively, in forming the activated state from the reactants. The values of ΔS^* and ΔH^* refer, of course, to the substances in the standard state; this must be chosen appropriately so that equation (l.) gives k_v in the correct units. The quantity ΔH^* is virtually the same as the activation energy, and comparing equation (l.) with the expression $k_v = PZe^{-E/RT}$, it follows that

$$PZ = e^{\Delta S^*/R} \cdot kT/h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (li.)$$

Since Z, the theoretical collision number, and kT/h are both virtually constant, the probability factor P will clearly be related to the entropy of activation, ΔS^*; if this is large and positive, then P is large, and the reaction will be normal or fast, as with unimolecular processes generally, but if ΔS^* is negative or small, actually it should be less than -7 units, then the reaction will be "slow." This result is, of course, an inevitable consequence of the relationship between entropy and probability: the greater the entropy increase the larger the probability of the transition state. There is not sufficient known of the properties of the activated complex for its entropy to be calculated, and so the relationship between P and ΔS^* is not yet of direct value, but since the activated state lies between the initial and final states, some information may perhaps be obtained from ΔS, the entropy change for the *complete* reaction. It is to be anticipated, therefore, that if ΔS is large and positive the reaction will be rapid, but if negative it will probably be slow. A somewhat similar conclusion has been reached by Soper (1935), who based his arguments on the older view that the activated complex could dissociate either into reactants or resultants, the probability of the two processes being determined by the entropy changes in the two directions. Whichever method is used for deducing the connection between the P factor and the entropy change involved in the process, the fact remains that it is of some importance, as the results in Table LXI., taken from the calculations of Soper (1935), show.

TABLE LXI

Comparison of Probability and Entropy Factors in Chemical Reactions.

Reaction.	*P*.	$e^{\Delta S/R}$.
Dimethylaniline + methyl iodide	$0{\cdot}5 \times 10^{-7}$	$0{\cdot}9 \times 10^{-8}$
Saponification of ethyl acetate	$2{\cdot}0 \times 10^{-5}$	5×10^{-4}
Chlorination of phenolic ethers	$1{\cdot}5 \times 10^{-5}$	$2{\cdot}2 \times 10^{-5}$
Sodium arsenite + tellurate	10^{-5}	10^{-11}
Isomerisation of am. cyanate to urea	*circa* 1	0·1
Dissociation of nitrous oxide (gas)	,, 1	*circa* 1
Dissociation of hydrogen iodide (gas)	0·47	0·15
Ethylene + hydrogen	0·05	10^{-6}

Strictly speaking, of course, the relationship between the probability factor and entropy should apply to ΔS^*, the entropy change involved in the formation of the activated complex, and so it is not improbable that cases may be found, such as the last quoted in Table LXI., in which the correspondence apparently breaks down; the discrepancy must then be attributed to the difference between ΔS^* and ΔS, which might be considerable.

It is perhaps desirable to emphasise at this point the fact that the new transition-state theory of reaction velocity does not displace the kinetic-activation, or collision, hypothesis: they may be regarded as complementary methods of examining the problem (Hinshelwood and Winkler, 1936). The newer theory is undoubtedly more fundamental and may eventually prove of great importance when more is known of the transition state, but in the meantime it is still necessary to consider reactions from the standpoint of the equation $k_v = PZe^{-E/RT}$ and to try to elucidate the factors which bring about variations in P and E; in due course it may be possible to connect these with the properties of the activated complex.

INFLUENCE OF SOLVENT ON REACTION VELOCITY

Formation of Quaternary Ammonium Salts. The problem of the influence of the solvent on reaction velocity has interested

chemists since the effect was discovered by Berthelot and St. Gilles in 1862, but in spite of a great deal of investigation the position was, at least until recently, very complex. The first systematic study of the subject was the well-known work of Menschutkin (1890) on the rate of reaction between triethylamine and ethyl iodide in a large number of solvents: this author concluded that there was some relationship between the dielectric constant of the medium and its influence on the reaction velocity. The smallest rates were observed in hexane and benzene, which have low dielectric constants, whereas the high velocities were found in acetone and benzyl alcohol, but the parallelism was by no means exact. Grimm, Ruf and Wolff (1931) in making a further examination of the Menschutkin reaction noted striking changes in passing through the series of solvents: diphenyl ether, diphenylamine and diphenylmethane, in which there are the groups $>O$, $>NH$ and $>CH_2$, respectively, each with two phenyl radicals attached. The velocity constants at 100° C. are quoted in Table LXII., together with other properties of the solvents.

TABLE LXII

Reaction between Triethylamine and Ethyl Iodide and Properties of Solvents.

Solvent.	k	Melting Pt.	Boiling Pt.	Dipole Moment.
Diphenyl ether . .	0·07	28°	257°	1·0 *D*
Diphenylamine . .	1·1	54°	302°	1·3
Diphenylmethane .	0·06	26°	260°	$<$ 0·4

The high reaction rate in diphenylamine has been attributed to the high melting and boiling points of this solvent, but the difference seems hardly sufficient to account for the sixteen-fold increase in the velocity constant. The value in diphenylmethane is also much larger than is to be expected for a hydrocarbon, although there is other evidence that the rates are often higher in an asymmetrical solvent, than in a similar one having a symmetrical molecule. In general, for other cases of quaternary salt formation the influence

of solvents is very much in the same order as that found by Menschutkin, the non-polar molecules, having small dielectric constants and zero dipole moments, giving the lowest velocities (Cox, 1921); the parallelism is, however, by no means exact.

Other Reactions. The rate of removal of hydrogen bromide from αβ-diphenyl-ααβ-tribromoethane by means of sodium methylate in benzene solution, to which various amounts of other solvents were added, has been examined by Lütgert (1934). The polar substances chloroform, and chloro- and bromo-benzene decrease the rate of reaction, whereas other polar molecules, such as nitro-benzene, ether and acetone, increase the velocity. There seems, in this case, to be no clear relationship evident between the properties of the solvent and its influence: there is reason to believe, however, that mixed solvents may present exceptional problems. Ziegler (1933) and his co-workers have investigated the decomposition of hexaphenylethane in a number of solvents, and found that the rate is almost independent of the nature of the solvent: in any case no connection could be discovered between the velocity constant and the dipole moment of the solvent. Attention may also be called to the unimolecular decomposition of nitrogen pentoxide (p. 276) and the isomerisation of pinene (p. 277) in solution, the rates of which are often independent of the nature of the solvent.

Although it has become widely accepted that, when there is a definite solvent effect, polar solvents as a rule increase reaction velocities, there are a few definite examples wherein the exact reverse is true. A most striking case is one of those originally studied by Menschutkin (1897) and recently extended by Soper and Williams (1931), namely, the acetylation of ethyl alcohol by means of acetic anhydride at 50° C. The results are shown in Table LXIII., the velocity constants for the triethylamine–ethyl iodide reaction being included for comparison.

Cohesion and Polarity of Solvent. Richardson and Soper (1929) have given two empirical rules, for which it will be seen later that there may be some theoretical justification, which appear to cover a number of cases of solvent influence. (1) If the reaction is one

TABLE LXIII

Influence of Solvent on Reaction Velocity.

Solvent.	Acetic Anhydride and Ethyl Alcohol.	Triethylamine and Ethyl Iodide.
Hexane	0·0119	0·0018
Carbon tetrachloride	0·0113	—
Chlorobenzene	0·00533	0·023
Benzene	0·00462	0·0058
Chloroform	0·00404	—
Anisole	0·00293	0·040
Nitrobenzene	0·00245	70·1

in which the products are substances of higher cohesion, that is, of higher internal pressure (Chapter VI.), than the reagents then it is accelerated by solvents of high cohesion, and (2) if the products are of lower cohesion, however, it will be retarded by solvents of high cohesion. In general, a solvent will favour either reactants or products, and consequently give either a low or high velocity, respectively, according as to which of them resembles it more closely in cohesion. Since cohesion and polarity often run parallel, a polar solvent will favour the formation of a polar product and will retard the formation of one which is non-polar; a non-polar solvent would be expected to have the reverse effect (Soper and Williams, 1931). A somewhat analogous conclusion has been deduced for a wide range of reaction types, involving the production or removal of an ion, by Hughes and Ingold (1935), who used arguments of a different kind.

The formation of a quaternary ammonium salt from an amine and an alkyl iodide, or of a sulphonium salt from diethyl sulphide and an iodide, are cases in which the product is much more polar than the reactants, and consequently these processes, as they are in fact, should be favoured by polar solvents. On the other hand, in the reverse reactions, such as the decomposition of sulphonium salts, or in the acetylation of alcohol the products are less polar than the reactants, and so the reaction should occur more rapidly, as has been observed, the less polar the solvent. Another example

is the decomposition of the trichloroacetate ion, according to the equation

$$CCl_3 \cdot COO' \rightarrow CCl_3 + CO_2,$$

the CCl_3' ion immediately reacting with the solvent to yield chloroform ; the reaction velocity increases in the three solvents studied in the order : water, ethyl alcohol and aniline (Verhoek, 1934). If chloroform is regarded as the product then it is clearly less polar than the trichloroacetate ion, and so the less polar the solvent the more rapid should be the reaction, as found experimentally. It is perhaps surprising that although trichloroacetic acid decomposes in aqueous solution it undergoes almost no decomposition in a number of other solvents.

Before leaving the subject of polarity of the solvent it is necessary to point out an apparent exception to the rule considered. The decomposition of 2 : 4 : 6-trinitrobenzoic acid into trinitrobenzene and carbon dioxide has been investigated in water, acetophenone, nitrobenzene and toluene (Moelwyn-Hughes and Hinshelwood, 1931), and the rate found to decrease in the order of solvents as given here. Since the acid might be expected to be more polar than the products, the velocity should be greater in the non-polar solvent toluene than in water, although actually the reverse was found to be the case. Molecular association in the non-polar solvent may, however, have an important influence.

THE ACTIVATED-COMPLEX THEORY AND REACTIONS IN SOLUTION

Non-Ideal Systems. The application of the theory of the activated complex, or the transition state, to reactions in solution (Wynne-Jones and Eyring, 1935) is likely to give results of some importance, as the following treatment will show. If c^* represents the concentration of the activated complex, treated as a normal molecule, except that one of the modes of vibration is supposed to be very stiff, then the rate of passage over the barrier, which represents the occurrence of the reaction, is equal to kT/h (p. 310). The product of the concentration and the rate of decomposition

of the complex evidently gives the rate of the reaction, so that it is possible to write :

$$\text{rate of reaction} = c^*kT/h \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lii.)}$$

If a reaction in the gas phase involves the reactant molecules A and B, the rate of reaction is proportional to the concentration of each, so that

$$\text{rate of reaction} = k_v c_A c_B \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(liii.)}$$

Combining equations (lii.) and (liii.) it follows that

$$k_v = \frac{c^*}{c_A c_B}\left(\frac{kT}{h}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(liv.)}$$

The equilibrium constant K^* (see p. 310) between A, B and the activated complex, may be written

$$K^* = \frac{a^*}{a_A a_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lv.)}$$

where the a terms are the activities of the respective species. Replacing the activity by the product of the concentration (c) and the activity coefficient of the gas (α), equation (lv.) becomes

$$K^* = \frac{c^*}{c_A c_B}\left(\frac{\alpha^*}{\alpha_A \alpha_B}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lvi.)}$$

By combination of equations (liv.) and (lvi.), it follows directly that

$$k_v = K^*\frac{kT}{h}\left(\frac{\alpha_A \alpha_B}{\alpha^*}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lvii.)}$$

For an ideal gaseous system the activity coefficients are unity, and so equation (lvii.) becomes identical with (xliii*a*.), for which ideal gases were postulated.

Comparison of Reaction Rates in Gas and Solution. When considering a reaction in solution it is convenient to compare it with the process occurring in the gaseous system ; equation (lvii.) is then applicable, but the activity coefficient (α) becomes equivalent to the distribution coefficient of the particular species between the gas phase and the solution, thus

$$\alpha = \frac{\text{Concentration in gas phase}}{\text{Concentration in solution}} \quad . \quad . \quad . \quad \text{(lviii.)}$$

The rate of a reaction in solution, as compared with that in the ideal, or approximately ideal, gaseous state will clearly depend on the value of the fraction $\alpha_A\alpha_B/\alpha^*$, and it is only when this, probably by chance, is equal to unity that the two rates are equal. A modification of an equation proposed by Langmuir (1932) gives the value of α, for a solution, in the form

$$\alpha = \beta T^{1/2} e^{-\Delta H/RT} \quad \text{(lix.)}$$

where β is a constant, about 5·0, provided the solute is non-associated and does not combine with the solvent, and ΔH is the latent heat of vaporisation of the dissolved substance.

It is evident that for a bimolecular reaction α^* is rarely likely to be equal to $\alpha_A\alpha_B$, but for a unimolecular reaction, where there is only one reacting molecule, it is quite possible for α_A/α^* to be approximately unity : the velocity constant will then be the same in solution as in the gas phase, provided the solvent molecules play no *direct* part in the reaction. This is apparently the case for the decomposition of nitrogen pentoxide and the isomerisation of pinene, in a number of solvents. The difference between α_A and α^* can be due either to a difference in the numerical factor β, or to a difference in the latent heats of vaporisation ; the former will result in a change in the P factor of the equation $k = PZe^{-E/RT}$, whereas the latter will mean a quantity $\Delta H - \Delta H^*$ will be included in the apparent energy of activation. For a bimolecular process the fraction $\beta_A\beta_B/\beta^*$ will be involved in the probability factor P, and $(\Delta H_A + \Delta H_B) - \Delta H^*$ in the E value ; if the dissolved substances are normal and do not unite with the solvent the β term will be equal to about 5·0, whereas that involving the ΔH quantities will be no more than a few thousand calories. The change in the reaction velocity constant in solution, from that in the gas phase, will consequently be relatively small, but exact agreement is certain to be uncommon. It is possible, however, for much larger discrepancies to arise as a result of variations in β and of large differences in the heats of vaporisation.

Solvent Effects. Some information concerning the effects of different solvents on the velocity of a given reaction may be obtained by comparing the $\alpha_A\alpha_B/\alpha^*$ factors for various media.

The activity coefficients of a solute in a series of solvents are related by the reciprocal of the solubility of the substance in the different solvents; hence the $\alpha_A\alpha_B/\alpha^*$ factor may be replaced by the quantity s^*/s_As_B where the s terms represent the saturation solubilities of the various species in the given solvent. It has been seen in Chapter VI. that when a solute and solvent have internal pressures which are approximately the same their solubilities will be normal, but if the internal pressures differ appreciably the solubility will be low. Applying this principle, it is evident that when the solvent has an internal pressure, or cohesion, which is the same as that of the reactants but different from that of the activated complex, then s^*/s_As_B will be small, and so also will the fraction $\alpha_A\alpha_B/\alpha^*$, and the reaction will be relatively slow. On the other hand, a solvent having an internal pressure similar to that of the complex but different from that of the reacting substances, will give a high rate of reaction (Glasstone, 1936). Since the activated complex will, in general, approach the products in its nature (*cf.* p. 317), it is seen that the arguments presented here provide a theoretical basis for the empirical rules of Richardson and Soper (p. 320) concerning the influence of solvents on reaction velocity.

If the difference in solubilities of reactants and activated complex, or resultants, depends on a difference of internal pressure, it means that the β terms in equation (lix.) are almost constant, but the heats of vaporisation differ (*cf.* p. 247); consequently, it is to be expected that the different reaction velocities in different media will be manifest in different values of the apparent energy of activation, whereas the P factor will remain almost the same for all the solvents. Other factors, such as compound formation, association and differences in polarity, in addition to differences of internal pressure, result in solubility differences, and these may, in general, be expected to influence the probability factor as well as the apparent activation energy. Differences of polarity between the solvent and solute will mean a decrease of ΔH, whereas compound formation increases the ΔH value. The actual effect on the velocity constant will depend on the resultant of the changes for reactants and the activated complex. It is probable

that any form of association between the solute and solvent, which need not go to the extent of compound formation, will increase ΔH and effect the reaction velocity accordingly (Moelwyn-Hughes and Sherman, 1936). If compound formation or dipole association occurs between reactants and solvent, but not between the latter and the activated complex, the apparent, that is the observed, activation energy will be increased and the reaction velocity will be low. The application of the new theory to reactions in solution is only in its infancy and important developments may be forecast, especially in connection with the problem of solvent influence.

REFERENCES

ARNOLD and KISTIAKOWSKY. *J. Chem. Physics*, 1933, **1**, 166.
BAKER and NATHAN. *J. Chem. Soc.*, 1935, 519, 1840.
BAWN. *Trans. Faraday Soc.*, 1935, **31**, 1536.
BENNETT and JONES. *J. Chem. Soc.*, 1935, 1815.
BOWEN, MOELWYN-HUGHES and HINSHELWOOD. *Proc. Roy. Soc.*, 1931, [*A*], **134**, 211.
BRADLEY. *J. Chem. Soc.*, 1934, 1910.
CHAPMAN. *Ibid.*, 1934, 1550.
CHRISTIANSEN. *Z. physikal. Chem.*, 1924, **113**, 35.
EVANS and POLANYI. *Trans. Faraday Soc.*, 1935, **31**, 875.
EYRING. *J. Chem. Physics*, 1935, **3**, 107 ; *Chem. Reviews*, 1935, **17**, 65.*
EYRING and DANIELS. *J. Amer. Chem. Soc.*, 1930, **52**, 472.
GLASSTONE. *J. Chem. Soc.*, 1936, 723
GRIMM, RUF and WOLFF. *Z. physikal. Chem.*, 1931, [*B*], **13**, 301.
HARDWICK. *J. Chem. Soc.*, 1935, 141.
HUGHES and INGOLD. *Ibid.*, p., 244.
INGOLD and NATHAN. *Ibid.*, 1936, 222
JOWETT. *Phil. Mag.*, 1929, **8**, 1059.
HINSHELWOOD *et al.*, *J. Chem. Soc.*, 1933, 258, 424, 1351, 1357 ; 1934, 1079 ; 1935, 587, 596, 1147, 1588 ; 1936, 371* ; *Trans. Faraday Soc.*, 1934, **30**, 935, 1144 ; 1936, **32**, 970.
KILPATRICK and KILPATRICK. *J. Amer. Chem. Soc.*, 1931, **53**, 3698.
LANGMUIR. *Ibid.*, 1932, **54**, 2798
LÜTGERT. *Z. Elektrochem.*, 1934, **40**, 499.
MOELWYN-HUGHES and HINSHELWOOD. *Proc. Roy. Soc.*, 1931, [*A*], **131**, 177, 186 ; *J. Chem. Soc.*, 1932, 230.
MOELWYN-HUGHES *et al.* *Ibid.*, 1932, 95, 241 ; 1933, 1576 ; 1936, 101 ; *Phil. Mag.*, 1932, **14**, 112 ; *Nature*, 1932, **129**, 316 ; *Chem. Reviews*, 1932, **10**, 241* ; *Ann. Reports Chem. Soc.*, 1935, **32**, 89* ; "Kinetics of Reactions in Solution," 1933*.
NORRISH and SMITH, F. F. P. *J. Chem. Soc.*, 1928, 129.
ÖLANDER. *Z. physikal. Chem.*, 1929, **144**, 118.
POLISSAR. *J. Amer. Chem. Soc.*, 1932, **54**, 3105.
SMITH, D. F. *Ibid.* 1927, **49**, 43.
SMITH, G. F. *J. Chem. Soc.*, 1934, 1744.

SOPER *et al.* *Ibid.*, 1929, 1873 ; 1931, 2297 ; 1935, 1393 ; *Proc. Roy. Soc.*, 1933, [*A*], **140**, 59, 71.
THOMPSON *et al.* *J. Chem. Soc.*, 1933, 1237 ; 1935, 1033.
TRAILL. *Phil. Mag.*, 1932, **13**, 225.
VERHOEK. *J. Amer. Chem. Soc.*, 1934, **56**, 571.
WATSON *et al.* *J. Chem. Soc.*, 1935, 1174.
WYNNE-JONES and EYRING. *J. Chem. Physics*, 1935, **3**, 492.
ZIEGLER. *Annalen*, 1933, **504**, 131.

* Review papers and books, wherein further references can be found, are marked with an asterisk.

CHAPTER VIII

ACID-BASE AND SALT CATALYSIS

EVEN before Arrhenius proposed the theory of electrolytic dissociation, Ostwald (1884) had studied the influence of various acids on the rate of hydrolysis of methyl acetate, and of the inversion of cane sugar, and found that the order of the velocities was the same as that of the strengths of the acids obtained from independent measurements. Subsequently it was found that this same order held for the conductances or the dissociation constants of the acids, and the contemporaneous development of the Arrhenius theory indicated that these quantities measured the tendency for an acid to split off hydrogen ions. Ostwald, therefore, reached the conclusion that the active catalyst, in hydrolytic and other similar reactions, was the hydrogen ion, or the hydroxyl ion where a base was the catalytic substance. This view appeared to receive support from the observations made by Arrhenius (1893) that the catalytic effect of a mixture of a weak acid and its salt, *e.g.*, sodium acetate and acetic acid, on the inversion of cane sugar was less than that of the acid alone. The hydrogen ion concentration resulting from the addition of a salt to an acid may be readily calculated from the mass action equation, and the velocity constant of the inversion process may be estimated by assuming it to be proportional to this concentration; in Table LXIV. are given the actual velocity constants together with the values calculated in the manner described.

The agreement is good enough to have established the theory on which it was based, but a few years later (1899) Arrhenius found that the addition of neutral salts, *e.g.*, potassium chloride, to acetic acid produced a marked increase in the rate of the inversion of cane sugar; thus the addition of $N/8$-potassium chloride to $N/4$-acetic acid increased the velocity by 12·6 per cent.

This difficulty was overcome, for the time, by the suggestion that the neutral salts caused an increase in the dissociation of the weak acid; there was no independent evidence for this view, but it was accepted for some years.

TABLE LXIV

Observed and Calculated Velocity Constants for Cane Sugar Inversion at 54° C.

Catalyst.	Velocity Constant × 10^3.	
	Observed.	Calculated.
0·25 *N*-Acetic acid . .	0·75	—
+ 0·0125 *N*-Sodium acetate	0·122	0·129
+ 0·025 ,, ,,	0·070	0·070
+ 0·05 ,, ,,	0·040	0·038
+ 0·125 ,, ,,	0·019	0·017
+ 0·25 ,, ,,	0·0105	0·0100

The Dual Theory of Catalysis. About 1907 much evidence began to accumulate which indicated that in acid and base catalysis the activity could not be restricted merely to the hydrogen or hydroxyl ions, and the view that the undissociated molecules of the acid, or base, are also effective in this respect gained prominence. This concept, called by Dawson the "dual theory" of catalysis, received support from Senter, Lapworth and Dawson, amongst others in England, from Acree in America, and from Goldschmidt in Germany. In recent years, mainly as a result of the studies of Brønsted, Dawson and Lowry, and of many others, it has been made clear that in addition to hydrogen or hydroxyl ions and the molecules of undissociated acid or base, the anions of weak acids and the cations of weak bases can also act as catalysts.

Acids and Bases. Although these catalysts do not at first sight appear to have any distinctive property in common, a further examination in the light of suggestions made independently by Lowry and by Brønsted (1923), shows an important connection

between them. These authors proposed that the old definitions of acid and base as sources of hydrogen and hydroxyl ions, respectively, be abandoned, and that an acid be defined as a source, or donor, of protons, the proton being the bare, unhydrated hydrogen ion, H^+; a base, on the other hand, is defined as a substance which can unite with protons, that is, a proton acceptor. According to these definitions the relationship between an acid and a base may be expressed in the form of the equation

$$\underset{\text{Acid.}}{A} \rightleftharpoons H^+ + \underset{\text{Base.}}{B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

where A is an acid, and B is the "conjugate" base. From this point of view substances such as acetic acid, and other common acids, are still to be regarded as acids, and they dissociate thus:

$$\underset{\text{Acid.}}{HAc} \rightleftharpoons H^+ + \underset{\text{Base.}}{Ac^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

but in addition it is seen from the equation that the acetate ion, according to the newer concepts, is to be regarded as a base, or proton acceptor. The anions of strong acids are *not* bases, since these acids are assumed to be almost completely ionised in solution, and consequently their anions have no appreciable tendency to unite with protons to form undissociated molecules of acid; with weak acids, however, the situation is quite different, and the tendency to form undissociated molecules of acid makes the anions proton acceptors, or bases. Further, the cations of a weak base must be regarded as *acids* according to the new definitions of acid and base; the ammonium ion, for example, is in equilibrium with ammonia and a proton, thus

$$\underset{\text{Acid.}}{NH_4^+} \rightleftharpoons H^+ + \underset{\text{Base.}}{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

and so is an acid, whereas ammonia is a base.

The position of water from the Brønsted-Lowry viewpoint is of interest. It is generally accepted at the present time that the free unsolvated hydrogen ion, or proton (H^+), probably does not exist in solution to any appreciable extent, for Fajans (1919) has calculated that over 250,000 cals. would be involved in the formation of 1 gm. ion. It is believed, therefore, that the entity generally described as a "hydrogen ion," in aqueous solution is

mainly $H(H_2O)^+$ or H_3O^+, sometimes called the " oxonium " ion. The following equilibria may then be regarded as existing in water or in aqueous solutions

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(iv.)}$$

$$H^+ + H_2O \rightleftharpoons H_3O^+ \quad \text{(v.)}$$

and hence

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad \text{(vi.)}$$

From equilibrium equation (iv.) it follows that H_2O is an acid and OH^- a base, whereas from equation (v.) H_3O^+ is an acid and H_2O a base. Water itself may therefore be considered to be amphoteric, and capable of acting as either an acid or a base ; in addition it can produce on ionisation an acid H_3O^+ and a base OH^-, but in pure water these are only formed to a small extent.

Returning now to the substances which have been found to be catalytically active in a number of reactions, it is seen that they may be divided into two groups : (*a*) hydrogen ions, *i.e.*, H_3O^+ ions, undissociated molecules of weak acid, and cations of weak bases : these are all acids according to the new definition ; and (*b*) hydroxyl ions, undissociated molecules of bases, and anions of weak acids, which are all bases. In addition it will be seen later that undissociated water molecules also have catalytic activity. It may be concluded, therefore, that the capacity to act as a catalyst, in hydrolytic and other reactions, is not an exclusive property of hydrogen and hydroxyl ions, but is possessed by all substances coming within the new categories of acid and base : that is, proton donors and acceptors, respectively. The title of " acid and base catalysis," therefore, has taken on in recent years a much wider significance than it had previously ; moreover, there is reason to believe that in many processes catalysed by acids the presence of a base is essential, and *vice versâ*. It should be pointed out, however, that there are reactions which are catalysed by acids only or by bases only.

THE MUTAROTATION OF GLUCOSE

One of the most interesting discoveries in connection with the subject of acid and base catalysis was made by Lowry (1925–6)

when investigating the mutarotation of glucose, and of its tetramethyl derivative. It is well known that the optical activity of a freshly prepared solution of glucose falls rapidly: the change, which can occur even in pure water, is known as "mutarotation," and is attributed to the isomeric change of the original α-glucose into an equilibrium mixture of the α- and β-forms of the compound. The difference between these two isomers is in the spatial arrangement of the — H and — OH groups about the terminal carbon atom of the glucose molecule. The mutarotation change can be accelerated by acids and bases, and Hudson (1907) represented the influence of hydrogen and hydroxyl ions in the form of an equation

$$k = 0{\cdot}0096 + 0{\cdot}258\,[H_3O^+] + 9750\,[OH^-]$$

where k is the velocity constant of the mutarotation; in view of recent developments, allowance must be made for the effect of other acidic and basic catalysts.

It has been a matter of controversy as to whether water is essential to the occurrence of mutarotation at all, and many conflicting conclusions appear in the literature of the subject; the work of Lowry has, however, clarified the situation very considerably. This author studied the mutarotation of tetramethylglucose, as it is soluble in non-aqueous media as well as in water, and can be readily purified and crystallised from such solvents. He found that in the complete absence of water neither pyridine nor *m*-cresol could be regarded as catalysts for the mutarotation, but a mixture of these two substances, in the ratio of one part of pyridine to two parts of *m*-cresol, was *twenty* times as effective as water in promoting the mutarotation of tetramethylglucose. Similarly it was found that a mixture of pyridine and water was a much better catalyst than water alone, and mixtures of methyl alcohol with either pyridine or with *m*-cresol were more effective than the pure alcohol. Further, in one experiment Lowry found that the mutarotation of tetramethylglucose was arrested for a period of nine days by the use of chloroform as solvent; this was attributed to the fact that traces of carbonyl chloride in the chloroform reacted with, and so removed, any catalysts which might otherwise have been present.

It seems definitely established, therefore, that mutarotation involves the presence of catalysts, and these must be taken into consideration in discussing the mechanism of the process. Lowry has explained his observations by assuming that mutarotation occurs in two stages : the first involves the addition of a proton, and the second the removal of a proton. The process cannot take place, therefore, unless a source of protons, *i.e.*, an acid, is present, *e.g.*, water, acids, or *m*-cresol, and also a proton acceptor, *i.e.*, a base, for example, water, methyl alcohol or pyridine. According to this theory, water, which is capable of acting as an acid and a base, and also to some extent methyl and ethyl alcohols, are complete catalysts for the mutarotation of tetramethylglucose, and presumably also of glucose itself. In the same way an aqueous solution of any acid or base is a complete catalyst, for the water molecules will act as proton donors or acceptors, as required. Pyridine can only act as a base, and so by itself it is not a catalyst ; *m*-cresol is only an acid, and so is also ineffective, but a mixture of these two substances should be, as it is, a powerful catalyst. The effectiveness of other mixtures can be accounted for in a similar manner. According to the theory developed catalysis in aqueous solutions of acids and bases should not be restricted to the hydrogen and hydroxyl ions, but should be a property of all acids and bases in the widest sense of the terms. In harmony with this view, Lowry (1927) has shown that undissociated acetic acid and hydrogen chloride molecules are effective catalysts ; the coefficients for these species, which must be included in the Hudson equation (p. 332), are as follows :

HCl	about 0·5	NH_4^+	0·0012
$CH_3.COOH$	0·0065	$CH_3{\cdot}COO^-$	0·069.

Brønsted and Guggenheim (1927) have also found that a number of weak acids and their anions, as well as various cobaltammine and chromiumammine cations, are effective catalysts for the mutarotation of glucose in aqueous solution. Although sodium chloride has no appreciable effect in accelerating the reaction (Lowry), presumably because the chlorine ions are unable to act as proton acceptors, Brønsted has found that sulphate ions are

able to catalyse the mutarotation. In the second stage of its ionisation,

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{--},$$

sulphuric acid is a comparatively weak acid and so the SO_4^{--} ion can act as a base to some extent.

It is of interest that in the mutarotation of glucose the catalytic activity of H_2O molecules and of H_3O^+ ions is definitely greater in ordinary water than in heavy water : this result is in harmony with the view that the mutarotation process takes place as the result of a transfer of a proton, or a deuteron. It can be predicted from the zero-point energies of hydrogen and deuterium compounds (see Chapter IV.) that the velocity of transfer of a proton, which occurs in light water, will be greater than that for a deuteron, taking place in heavy water. In general, it may be anticipated that all processes involving acid–base catalysis will be more rapid in ordinary aqueous solution than in deuterium oxide (Wynne-Jones, 1935).

It should be mentioned here that the mutarotation of beryllium and aluminium benzoyl camphor (Lowry and Traill, 1931) involves quite a different type of mechanism ; the reactions are not specifically catalysed by proton acceptors and donors.

THE IODINATION OF ACETONE

Another reaction catalysed by acids and bases is the " iodination " of acetone, which has been studied extensively in recent years by Dawson and his co-workers. This reaction really involves the enolisation of the ketone as the first stage, thus

$$\underset{\underset{\underset{\text{Keto form.}}{\|}}{\underset{\underset{\text{O}}{|}}{\text{CH}_3\cdot\text{C}\cdot\text{CH}_3}}}{}} \rightleftharpoons \underset{\underset{\underset{\text{Enol form.}}{|}}{\underset{\underset{\text{OH}}{|}}{\text{CH}_3\cdot\text{C}=\text{CH}_2}}}{}}$$

and probably occurs as a result of the addition and subsequent removal of a proton.

The iodine is able to react almost instantaneously with the enolic compound to form iodoacetone, so that the stages involving the proton donation and removal determine the speed of the total reaction between iodine and acetone. It is clear from what has

already been said that in aqueous solution both acids and bases can act as catalysts ; in the presence of a strong acid presumably the hydroxyl ions in the water, as well as the water molecules themselves, act as bases, whereas with a weak acid the anions are also able to exercise basic functions as proton acceptors. Dawson (1926 *et seq.*) and his collaborators have found the following catalytic velocity coefficients for aqueous solutions of acetic acid and acetate mixtures in the acetone–iodine reaction ; the values are relative since they depend on the concentration of the acetone.

Hydroxyl ions	7
Hydrogen ions (H_3O^+) . .	$4{\cdot}68 \times 10^{-4}$
Acetate ions	4×10^{-6}
Acetic acid molecules .	$1{\cdot}5 \times 10^{-6}$
Water molecules . . .	$1{\cdot}3 \times 10^{-10}$

The methods used to determine these constants will be described later.

HYDROLYTIC REACTIONS

Hydrolysis of Esters. Apart from the reactions involving tautomeric changes there are hydrolytic reactions, *e.g.*, the conversion of an ester into acid and alcohol, which are catalysed by acids and bases ; in these cases the presence of water is, of course, essential, as it is one of the reacting substances, *e.g.*,

$$CH_3{\cdot}COOC_2H_5 + H_2O = CH_3{\cdot}COOH + C_2H_5OH,$$

but otherwise the mechanism is similar in some ways to that involved in the processes already discussed.

According to this view all proton donors and acceptors, in aqueous solution, should act as catalysts in the hydrolysis of esters ; in agreement with this expectation, Dawson has obtained the velocity coefficients for the hydrolysis of ethyl acetate by means of acetic acid–sodium acetate mixtures, as follows :

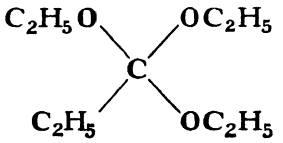
Hydroxyl ions	6·5
Hydrogen ions	$6{\cdot}1 \times 10^{-3}$
Acetate ions	$2{\cdot}0 \times 10^{-7}$
Acetic acid molecules . .	$1{\cdot}45 \times 10^{-6}$
Water molecules . . .	Negligible.

It is possible that there is a fundamental difference between the mechanism of the hydrolysis of esters and that of other processes, such as the mutarotation of glucose; for, whereas the catalytic effect of H_3O^+ ions, for example, is greater in ordinary water for the latter reaction, the effect for the former is definitely greater in heavy water (Wynne-Jones, 1935).

Ortho-Esters. The hydrolysis of a number of ortho-esters, *e.g.*, ethyl orthocarbonate, has been studied by Brønsted and Wynne-Jones (1929); the catalytic coefficients for the particular ester mentioned in acetic acid solutions were found to be:

Hydrogen ions	$2{\cdot}35 \times 10^3$
Acetic acid molecules . .	$0{\cdot}22$
Water molecules . . .	$1{\cdot}8 \times 10^{-6}$.

In this reaction water, hydroxyl ions and the anions of weak acids were found to have no measurable catalytic influence, in contrast to the behaviour observed with other esters. The ortho-esters, as Skrabal (1927) has pointed out, are quite different from ordinary esters; the formula of ethyl orthocarbonate, for example,



shows that the molecule contains no $-C{=}O$ group, as do esters in general, but that it is somewhat similar to an ether, having all its oxygen atoms linked to two atoms of carbon. The hydrolytic mechanism may, therefore, be different from that operative with esters.

Decomposition of Nitramide. The decomposition of nitramide ($NH_2{\cdot}NO_2$) into nitrous oxide and water

$$NH_2{\cdot}NO_2 = N_2O + H_2O$$

is a reaction which, according to Brønsted and his co-workers (1924 *et seq.*), is catalysed by hydroxyl ions, by the anions of weak acids, and by certain complex hydroxo-cations, that is, by bases in the widest sense of the term, but not at all by acids, including hydrogen (oxonium) ions. According to more recent investigations

(Marlies and La Mer, 1935) there is a small but definite acid catalysis, the mechanism being of a different type to that brought about by bases.

CATALYTIC ACTIVITY OF IONS AND MOLECULES

Apart from any theories of mechanism there seems to be little doubt at present that various ions as well as undissociated molecules are capable of exercising catalytic activity; in this connection the work of Dawson and of Brønsted has supplied the most important results in recent years. In 1913 Dawson had noted that if increasing amounts of sodium acetate were added to a solution of acetic acid of fixed concentration used as catalyst in the iodination of acetone, the reaction velocity passed through a fairly sharp minimum and then began to increase in a linear manner as the salt concentration was increased. If catalysis is due to the hydrogen ions, or even to the undissociated molecules of acetic acid as well, as the "dual theory" required, then addition of sodium acetate should cause the reaction velocity to decrease steadily and approach asymptotically a limiting minimum value. Hence this theory is not sufficient to explain the observations, and it appeared that the salt, or more probably the acetate ion, was exerting a catalytic effect; this view has been abundantly confirmed as a result of a detailed analysis of the reaction velocities of several catalysed reactions.

Analysis of Experimental Results. The method devised by Dawson of analysing the results is as follows. In general, for a reaction involving acid–base catalysis by a solution of an acid and its salt, the reaction velocity (v) for a given concentration of reactant may be written

$$v = k_H[\mathrm{H_3O^+}] + k_A[\mathrm{A^-}] + k_M[\mathrm{HA}] + k_{OH}[\mathrm{OH^-}] + k_W[\mathrm{H_2O}] \quad \text{(vii.)}$$

where k_H, k_A, k_M, k_{OH} and k_W represent the catalytic coefficients of the hydrogen (oxonium) ions, anions, molecules of undissociated acid, hydroxyl ions and water respectively, and the concentrations* of the various species are given in square brackets.

* The question of whether concentrations or activities should be used in reaction velocity equations will be discussed later, p. 355.

If the solution is fairly acid the hydroxyl ion effect is probably negligible, and in any case that of the water will be small, so as a first approximation it is possible to write

$$v = k_H[H_3O^+] + k_A[A^-] + k_M[HA] \quad . \quad . \quad . \quad \text{(viii.)}$$

Suppose, as in Dawson's experiments to which reference has already been made, a series of catalytic mixtures is used consisting of c equivs. of a weak acid HA, and x equivs. of salt NaA, where c is a constant and x variable, then

$$v = k_H[H_3O^+] + k_A x + k_M c \quad . \quad . \quad . \quad . \quad . \quad \text{(ix.)}$$

assuming that the salt is completely dissociated, and the acid almost entirely undissociated. Since the acid HA is weak the law of mass action may be regarded as applicable in its simplest form, although this is not exactly true; hence if

$$H_2O + HA \rightleftharpoons H_3O^+ + A^-$$

then

$$K = \frac{[H_3O^+][A^-]}{[HA]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(x.)}$$

if the activity of the water is constant; this K is the ordinary dissociation constant of the acid as determined from conductance or other measurements. Substituting x for $[A^-]$ and c for $[HA]$, then

$$[H_3O^+] = K\frac{c}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xi.)}$$

As x, that is, the amount of salt NaA, is increased the value of $[H_3O^+]$, and so of $k_H[H_3O^+]$, becomes negligibly small, so that the velocity equation at high salt concentrations has the form

$$v = k_A x + k_M c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xii.)}$$

The term $k_M c$ is constant, since c is kept unchanged, and so it follows that the plot of the reaction velocity v, against the salt concentration x should be a straight line at high concentrations; the slope of this line gives the value of k_A, whereas its intercept when extrapolated to cut the v-axis ($x = 0$) is equal to $k_M c$. Alternatively k_M may be calculated by inserting the values of c, x

and k_A into the equation (xii.) for known values of v, the reaction velocity.

The rate of iodination of acetone depends only on the acetone concentration for a given catalyst, and is independent of the iodine concentration; and, as already indicated, the reaction velocity is determined by the tautomeric change of the ketonic form of acetone into the enolic form. During the course of the

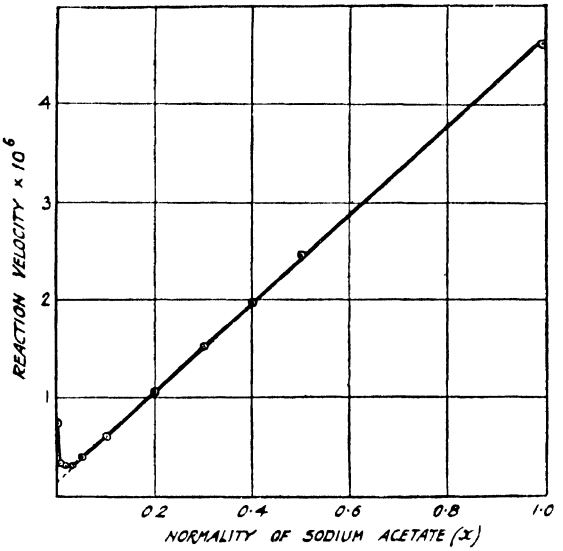


FIG. 22.—Velocity of the acetone–iodine reaction at 25° in the presence of 0·1 *N*-acetic acid + x *N*-sodium acetate. Concentration of acetone 0·272 *M*. (Plotted from the results of Dawson and Carter.)

reaction hydriodic acid is produced, and this affects the catalytic activity of the medium; hence if it is intended to study the efficiency of the original catalyst the velocity at the commencement of the reaction is required: this is incidentally the value corresponding to the original concentration of acetone, which is used up in the course of the experiment. Dawson and Powis (1913) found that satisfactory results could be obtained by plotting the average velocities, as determined by titration of the iodine, for various intervals of time after the commencement, and extra-

polating to zero time ; in this way the initial reaction velocity was determined, and it is this velocity which is used in applying the equations deduced in the previous section.

The results obtained by Dawson and Carter (1926) for the velocity (v) of the reaction between iodine and acetone (0·272 M) in the presence of various mixtures of sodium acetate and 0·1 N-acetic acid, at 25° C., are given in Table LXV.

These results are plotted in Fig. 22 ; the plot, as is to be anticipated, is a straight line for high values of x. The slope of the curve (k_A) is $4{\cdot}5 \times 10^{-6}$, and k_M is $1{\cdot}5 \times 10^{-6}$ gm.-mol. per litre per minute.

TABLE LXV

Catalysis of Acetone–Iodine Reaction by Acetic Acid–Acetate Mixtures.

Catalyst : 0·1 N-acetic acid + x N-sodium acetate.						
$v \times 10^6$.	0·75	0·335	0·285	0·29	0·30	0·395
x .	—	0·005	0·01	0·02	0·025	0·05
$v \times 10^6$.	0·61	1·055	1·505	1·95	2·40	4·65
x .	0·1	0·2	0·3	0·4	0·5	1·0

In order to determine the value of k_H, that is, the catalytic coefficient for the hydrogen ion, experiments can be made with a dilute solution of hydrochloric acid. The whole of the catalytic activity may be ascribed to the hydrogen ion concentration, which is known, since the effects due to hydroxyl ions and the water molecules are so small as to be negligible. The chlorine ions have, of course, no catalytic influence. The initial reaction velocity is now given by

$$v = k_H[H_3O^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xiii.)}$$

k_H is thus found to be about 465×10^{-6} gm.-mol. per litre per minute. With the known values of k_H, k_M and k_A it is now possible to see how far the sum of the three catalytic effects, determined in the manner described, represents the total catalytic power of a mixture of acetic acid and sodium acetate in the iodination of acetone. The values given in Table LXVI. are taken from the

work of Dawson and Carter; the hydrogen ion concentrations of the solutions were determined either by means of the hydrogen electrode or by calculation from the mass law equation. Strictly speaking, the results cannot be expected to be the same, but in dilute solutions the agreement is close enough for either value to be considered as representing the hydrogen (oxonium) ion concentration and used in Dawson's velocity equations. The columns headed v_H, v_M and v_A give $k_H[H_3O^+]$, $k_M[HA]$ and $k_A[A^-]$, respectively, and represent the velocity components due to catalysis by each of the species mentioned. Since the concentration of the acetic acid in the mixtures was always 0·1 *N*, the value of [HA]was equal to $0{\cdot}1 - [H_3O^+]$, and that of $[A^-]$was $x + [H_3O^+]$. The term v (cal.) is equal to the sum of v_H, v_M and v_A, and v (obs.) is the corresponding value determined experimentally.

TABLE LXVI

Observed and Calculated Velocities in the Acetone–Iodine Reaction.

Catalyst: 0·1 *N*-acetic acid + x *N*-sodium acetate.

x.	$[H_3O^+]\times10^4$.	$v_H \times 10^4$.	$v_M \times 10^4$.	$v_A \times 10^4$.	v (cal.)$\times10^4$.	v(obs.)$\times10^4$.
0	13·5	0·596	0·148	0·006	0·75	0·75
0·010	2·00	0·088	0·150	0·046	0·285	0·31
0·025	0·86	0·038	0·150	0·113	0·30	0·32
0·050	0·45	0·020	0·150	0·225	0·395	0·405
0·10	0·24	0·010	0·150	0·450	0·61	0·60
0·20	0·13	0·006	0·150	0·900	1·055	1·04
0·40	0·07	0·003	0·150	1·800	1·95	1·95
1·0	0·03	0·001	0·150	4·500	4·65	4·6

A study of these results shows quite clearly that any theory which does not take into account the catalytic effect of undissociated molecules and particularly that of the acetate ion does not seem sufficient to explain the experimental observations.

Concentration and Catalytic Activity of a Weak Acid. Since the degree of dissociation of a weak acid varies with the concentration, it follows that the catalytic activity of the acid, which includes that of its molecules as well as of the ions into which it dissociates, cannot be directly proportional to the concentration.

The actual relationship may be developed as follows ; incidentally a new method for the determination of k_M becomes available. For catalysis by means of a solution containing acid only, then $[H_3O^+]$ and $[A^-]$ may be taken as equal, and the concentration of undissociated acid [HA] is approximately equal to $c - [H_3O^+]$, where c is the total acid concentration. Neglecting the catalytic effects of the hydroxyl ions and of the water molecules, which are small in comparison with those of the other catalysts, the general equation (vii.) for reaction velocity becomes

$$v = (k_H + k_A - k_M)[H_3O^+] + k_M c \quad . \quad . \quad . \quad \text{(xiv.)}$$

Since the acid is weak the law of mass action is applicable in the simple form

$$K = \frac{[H_3O^+]\,[A^-]}{[HA]} = \frac{[H_3O^+]^2}{c - [H_3O^+]}, \quad . \quad . \quad . \quad \text{(xv.)}$$

K being the dissociation constant of the acid. As a general rule $[H_3O^+]$ may be neglected in comparison with c, since the degree of dissociation is small, and so

$$[H_3O^+] = \sqrt{Kc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xvi.)}$$

Substituting this value in equation (xiv.), it follows that

$$v/\sqrt{c} = (k_H + k_A - k_M)\sqrt{K} + k_M\sqrt{c} \quad . \quad . \quad . \quad \text{(xvii.)}$$

This equation, according to which $v/\sqrt{c}$ is a linear function of $\sqrt{c}$, represents the variation of the reaction velocity with the concentration of a weak acid. The slope of the straight line, plotting $v/\sqrt{c}$ against $\sqrt{c}$, gives the value of k_M, whereas the intercept on the $\sqrt{c}$-axis is equal to $(k_H + k_A - k_M)\sqrt{K}$. This method has the advantage of giving k_M independently of k_A, which is required in the method already given (p. 338). Dawson, Hall and Key (1928) studied the catalytic influence of a number of acids at various concentrations on the reaction between iodine and acetone, and found that the plot of $v/\sqrt{c}$ against $\sqrt{c}$ was invariably a straight line ; the values of k_M obtained from the slope of the line were in excellent agreement with those obtained by the method already described involving acid–salt mixtures. For example, with acetic

acid as catalyst the results in Table LXVII. were obtained; the acetone concentration, as before, was 0·272 *M*.

TABLE LXVII.—*Catalytic Influence of Acetic Acid at Various Concentrations on the Acetone–Iodine Reaction.*

c . . .	0·01	0·02	0·05	0·1	0·2	0·4	0·8
$v \times 10^6$ . .	0·216	0·317	0·512	0·770	1·17	1·79	2·85
$v/\sqrt{c} \times 10^6$ (obs.).	2·16	2·24	2·29	2·43	2·62	2·83	3·18
$v/\sqrt{c} \times 10^6$ (cal.) .	2·14	2·20	2·31	2·44	2·64	2·86	3·22

The calculated values given by the equation

$$v/\sqrt{c} = (2{\cdot}01 + 1{\cdot}35\sqrt{c}) \times 10^{-6} \quad . \quad . \quad . \quad \text{(xviii.)}$$

are in excellent agreement with the observed values, and it follows that

$$k_M = 1{\cdot}35 \times 10^{-6}$$

and

$$(k_H + k_A - k_M)\sqrt{K} = 2{\cdot}01 \times 10^{-6} \quad . \quad . \quad . \quad \text{(xix.)}$$

The value for k_M is in good agreement with that previously given ($1{\cdot}5 \times 10^{-6}$). Since k_H is known to be 465×10^{-6} and k_A is $4{\cdot}5 \times 10^{-6}$, the value of K, the dissociation constant of acetic acid, may be calculated from equation (xix.) as $1{\cdot}85 \times 10^{-5}$. This is almost identical with the generally accepted value determined from conductance or *E.M.F.* data.

Constant Ratio Acid-Salt Mixtures. An alternative method for evaluating k_A and k_M depends on the determination of the initial reaction velocity in the presence of a series of acid–salt mixtures having a constant *ratio* of c equivs. of acid to x equivs. of salt. The hydrogen and hydroxyl ion concentrations of such solutions may be regarded as almost constant, $[H_3O^+] = Kc/x$, and so the general equation (vii.) for v, the reaction velocity, may be written

$$v = v_o + k_A x + k_M c, \quad . \quad . \quad . \quad . \quad . \quad \text{(xx.)}$$

where v_o, which is equal to $k_H[H_3O^+] + k_{OH}[OH^-] + k_W[H_2O]$, represents the velocity in the absence of undissociated acid and salt at the same hydrogen ion concentration as in the acid–salt mixtures. Since c/x is a constant, it may be put equal to q, and the equation (xx.) becomes

$$v = v_o + x(k_A + qk_M) \quad . \quad . \quad . \quad \text{(xxi.)}$$

According to this equation (xxi.) v is a linear function of x; the slope of the line, which may be represented by l, is then equal to $k_A + qk_M$. For another series of solutions in which the c/x ratio is equal to q', the slope l' of the v against x line is equal to $k_A + q'k_M$; that is

$$l = k_A + qk_M \quad \text{and} \quad l' = k_A + q'k_M \quad . \quad . \quad . \quad \text{(xxii.)}$$

Hence

$$k_A = \frac{l'q - lq'}{q - q'} \quad \text{and} \quad k_M = \frac{l - l'}{q - q'} \quad . \quad . \quad . \quad . \quad \text{(xxiii.)}$$

This method was used by Dawson and Key (1928) to determine the values of k_A and k_M for acetic acid–acetate mixtures in the catalytic iodination of mesityl oxide (0·035 M); the values found were 7×10^{-6} and $3{\cdot}5 \times 10^{-6}$ respectively, at 25°. By means of experiments with hydrochloric acid the catalytic coefficient of the hydrogen ions, k_H, was determined as 0·0147 for the same reaction.

Iso-Catalytic Mixtures. If the observed reaction velocities for a given value of q, that is, for a given hydrogen ion concentration, are plotted against the corresponding values of x, and the straight line extrapolated to $x = 0$, the intercept on the v-axis gives the term v_o. By working with a series of mixtures of a weak acid and its salt, it is possible to evaluate v_o for various hydrogen ion concentrations; the plot of v_o against log $[H_3O^+]$, for a given reaction, is found to be a catenary curve with a definite minimum value for v_o. A curve of this type would, of course, be anticipated from general principles, since

$$v_o = k_H[H_3O^+] + k_{OH}[OH^-] + k_W[H_2O] \quad . \quad \text{(xxiv.)}$$

and $[OH^-]$ increases whilst $[H_3O^+]$ is decreasing; $[H_2O]$ remains practically constant the whole time. The product of hydrogen and hydroxyl ion concentrations may be regarded as constant in dilute solution, and equal to K_w the ionic product of water (note that this is quite different from k_W); that is

$$[H_3O^+][OH^-] = K_w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xxv.)}$$

$$\therefore \quad [OH^-] = K_w/[H_3O^+] \quad . \quad . \quad . \quad . \quad \text{(xxvi.)}$$

The equation for v_o may therefore be written

$$v_o = k_H[H_3O^+] + k_{OH}K_w/[H_3O^+] + k_W[H_2O] \quad . \quad \text{(xxvii.)}$$

Differentiating this expression with respect to $[H_3O^+]$, it follows that

$$\frac{dv_o}{d[H_3O^+]} = k_H - k_{OH}K_w/[H_3O^+]^2 \quad . \quad . \quad . \quad . \quad \text{(xxviii.)}$$

This gives the slope of the curve of v_o against $[H_3O^+]$, and at the minimum value of v_o the term $dv_o/d[H_3O^+]$ must be equal to zero ; hence

$$k_H - k_{OH}K_w/[H_3O^+]_i^2 = 0 \quad . \quad . \quad . \quad . \quad \text{(xxix.)}$$

where $[H_3O^+]_i$ is the value of the hydrogen ion concentration for which v_o is a minimum, and so

$$[H_3O^+]_i = \sqrt{k_{OH}K_w/k_H} \quad . \quad . \quad . \quad . \quad . \quad \text{(xxx.)}$$

Substituting in equation (xxvii.) it is found that

$$(v_o)_i = 2k_H[H_3O^+]_i + k_W[H_2O] \quad . \quad . \quad . \quad . \quad \text{(xxxi.)}$$

where $(v_o)_i$ is the minimum value of v_o. By means of this equation it is possible to evaluate k_W, provided k_H is known, and $(v_o)_i$ and $[H_3O^+]_i$ are found by a series of measurements with solutions of different hydrogen ion concentration ; the concentration of water molecules $[H_2O]$ is taken as $1000/18 = 55$ gm.-mols. per litre. If k_H and k_W are known, then k_{OH} may be determined by substituting in the general equation (xxvii.) for v_o at any definite hydrogen ion concentration. Comparing equations (xxiv.) and (xxxi.) it will be noted that at the point of minimum velocity $(v_o)_i$,

$$k_H[H_3O^+]_i + k_{OH}[OH^-]_i = 2k_H[H_3O^+]_i \quad . \quad . \quad \text{(xxxii.)}$$

that is

$$k_H[H_3O^+]_i = k_{OH}[OH^-]_i \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxiii.)}$$

In other words, at this point the catalytic effects due to the hydrogen and the hydroxyl ions are equal ; the minimum velocity condition, for this reason, is sometimes called the " iso-catalytic " point. It should be noted that for some reactions, *e.g.*, the hydrolysis of an ester, it is possible to determine k_{OH} from experiments in alkaline solutions ; in these circumstances the catalytic effect is due almost exclusively to the hydroxyl ions, that of the other ions being quite negligible in comparison. Incidentally if k_H and k_{OH} are known, the ionic product of water (K_w) may be calculated from the hydrogen ion concentration at the iso-catalytic point by means of equation (xxx.).

The Catalytic Catenary. The curve which has just been discussed, gives the values of v_0 for different hydrogen ion concentrations in the *absence of acid and salt,* that is, in pure water; it is therefore called the "water catenary." That similar catenary curves should, however, be obtainable for acid–salt mixtures can be deduced in the following manner, on the basis of the theory that catalytic activity may be attributed to all acidic and basic molecules and ions. For an acid–salt mixture the hydrogen ion concentration may be attributed entirely to the dissociation of the acid; hence [HA], the undissociated portion, can be put equal to $c - [H_3O^+]$, where c is the total acid concentration. If the law of mass action involving concentrations is applicable to the mixture then

$$K = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+][A^-]}{c - [H_3O^+]} \quad . \quad . \quad . \quad . \quad \text{(xxxiv.)}$$

$$\therefore \quad [A^-] = K(c - [H_3O^+])/[H_3O^+] \quad . \quad . \quad . \quad . \text{(xxxv.)}$$

where K is the dissociation constant of the acid. Substituting for [HA] and $[A^-]$ in the simplified equation (viii.)

$$v = k_H[H_3O^+] + k_A[A^-] + k_M[HA] \quad . \quad . \quad . \quad . \quad \text{(viii.)}$$

it follows that

$$v = (k_H - k_M)[H_3O^+] + ck_AK/[H_3O^+] + k_Mc - k_AK \quad \text{(xxxvi.)}$$

For a series of acid–salt mixtures in which the concentration (c) of the acid remains constant, whereas that of the salt (x) varies, this equation indicates that v, for the given reaction and acid, depends only on the hydrogen ion concentration of the solution. Further, since the relationship is of the type

$$v = q[H_3O^+] + p/[H_3O^+] + r \quad . \quad . \quad . \quad \text{(xxxvii.)}$$

where p, q and r are constants, the plot of v against $[H_3O^+]$ must be a curve of the catenary type having a minimum value of v for a definite hydrogen ion concentration. The slope of this curve is obtained by differentiating equation (xxxvi.), thus

$$\frac{dv}{d[H_3O^+]} = k_H - k_M - ck_AK/[H_3O^+]^2 \quad . \quad \text{(xxxviii.)}$$

and the minimum occurs when $dv/d[H_3O^+]$ is zero, that is when

$$k_H - k_M = ck_AK/[H_3O^+]_i^2 \quad . \quad . \quad . \quad . \quad . \quad \text{(xxxix.)}$$

or

$$[H_3O^+]_i = \sqrt{ck_AK/(k_H - k_M)} \quad . \quad . \quad . \quad . \quad . \quad \text{(xl.)}$$

where $[H_3O^+]_i$ is the hydrogen ion concentration at which the particular reaction velocity is a minimum in the given series of acid–salt mixtures (c, constant; x, variable). Substituting this value for $[H_3O^+]$ in equation (xxxvi.), and neglecting k_AK as likely to be very small, the minimum velocity v_i is found to be

$$v_i = 2\sqrt{(k_H - k_M)ck_AK} + k_Mc \quad . \quad . \quad . \quad . \quad . \quad \text{(xli.)}$$

In performing this substitution it will have been noted that the first two terms of equation (xxxvi.), which represent the catalytic effects of the hydrogen ions and of the anions (A^-), respectively, are each equal to $\sqrt{(k_H - k_M)ck_AK}$ for the solution of minimum reaction velocity. This condition, therefore, represents an iso-catalytic point for the particular series of acid–salt mixtures being used.

If each side of equation (xxxviii.) is multiplied by $[H_3O^+]$, it is seen that

$$[H_3O^+] \cdot \frac{dv}{d[H_3O^+]} = \frac{dv}{d \ln [H_3O^+]}$$

$$= (k_H - k_M)[H_3O^+] - ck_AK/[H_3O^+] \quad . \quad . \quad \text{(xlii.)}$$

Since c is a constant, this equation indicates that the curve obtained by plotting the velocity (v) of the reaction against log $[H_3O^+]$, or against pH, *i.e.*, $-\log [H_3O^+]$, should be a catenary symmetrical about the minimum at which

$$[H_3O^+]_i = \sqrt{ck_AK/(k_H - k_M)}; \quad . \quad . \quad . \quad \text{(xliii.)}$$

this minimum is, of course, identical with the iso-catalytic point (see equation xl.). The symmetry of the catalytic catenary, of v against pH, for acid–salt mixtures may be shown by considering any two reaction velocities v_1 and v_2 corresponding to the hydrogen ion concentrations $[H_3O^+]_1$ and $[H_3O^+]_2$, respectively; then

$$v_1 = (k_H - k_M)[H_3O^+]_1 + ck_AK/[H_3O^+]_1 + k_Mc \quad . \quad \text{(xliv } a.\text{)}$$

and

$$v_2 = (k_H - k_M)[H_3O^+]_2 + ck_AK/[H_3O^+]_2 + k_Mc \quad . \quad \text{(xliv } b.\text{)}$$

If v_1 and v_2 are equal,

$$(k_H - k_M)[H_3O^+]_1 + ck_AK/[H_3O^+]_1 = (k_H - k_M)[H_3O^+]_2 + ck_AK/[H_3O^+]_2 \quad . \quad . \quad \text{(xlv.)}$$

or

$$[H_3O^+]_1 \cdot [H_3O^+]_2 = ck_AK/(k_H - k_M) \quad . \quad . \quad . \quad \text{(xlvi.)}$$

The right side of this expression, as will be seen by comparison with the results already given, is equal to $[H_3O^+]_i^2$, and so

$$[H_3O^+]_1 \cdot [H_3O^+]_2 = [H_3O^+]_i^2 \quad . \quad . \quad . \quad . \quad \text{(xlvii.)}$$

or

$$p\mathrm{H}_1 + p\mathrm{H}_2 = 2p\mathrm{H}_i \quad . \quad . \quad . \quad . \quad . \quad \text{(xlviii.)}$$

It follows, therefore, that the *p*H value of the iso-catalytic mixture, *i.e.*, the minimum of the catalytic catenary for a given acid–salt series, is the arithmetic mean of the *p*H values of any pair of solutions for which the reaction velocities are equal; the curve of v against *p*H must then be symmetrical.

The accuracy of equation (xlviii.), as well as the existence of catalytic catenaries, has been verified by Dawson and his co-workers for the acetone–iodine reaction, and for the hydrolysis of ethyl acetate. The observed results are in excellent agreement with those to be anticipated from the theoretical deductions, and provide a powerful argument for the hypothesis upon which they are based. In Table LXVIII. are given some of the results obtained in a study of the iodine–acetone reaction in the presence of the acid–salt series consisting of 0·05 *N*-acetic acid and x *N*-sodium acetate, where x varied from mixture to mixture; the first column gives a reaction velocity (v) and the second and third columns give the two different *p*H values for which this velocity was observed. The mean of these two values, which should be equal to the iso-catalytic value of the particular acid–salt series, is given in the last column of the Table LXVIII.

The constancy of the results in the last column is very striking, and indicates that the value of $p\mathrm{H}_i$ is 4·03. From the known values of k_A, k_H, k_M and K determined by the methods already described, $p\mathrm{H}_i$ may be calculated from equation (xl.) as about 4·1.

The equation for the catalytic catenary, as well as the *p*H of its minimum point, depends on c, the constant acid concentration of

TABLE LXVIII

Hydrogen Ion Concentrations for Equal Reaction Velocities.

$v \times 10^5$.	$p\mathrm{H}_1$.	$p\mathrm{H}_2$.	$\frac{1}{2}(p\mathrm{H}_1 + p\mathrm{H}_2)$.
50	3·63	4·43	4·03
60	3·46	4·59	4·025
70	3·36	4·70	4·03
80	3·28	4·78	4·03
90	3·22	4·84	4·03
100	3·16	4·90	4·03
110	3·10	4·96	4·03
120	3·04	5·01	4·025

the acid–salt mixtures. For each value of c there is a catenary curve, and so in order to represent the catalytic activity of any mixture of an acid and its salt, it is necessary to have a series of such curves. In the limit these curves merge into a catenary surface in three dimensions, which are defined by co-ordinates representing reaction velocity (v), hydrogen ion concentration (pH), and concentration of acid (c). This catenary surface has been obtained for the acetone–iodine reaction using mixtures of acetic acid, varying in concentration from 0·01 to 1·0 gm.-mol. per litre, with sodium acetate. Except at the highest acid concentrations the results obtained (Dawson, 1927) were in agreement with the theoretical deductions.

GENERALISED CATALYTIC CATENARY

One of the most remarkable consequences of the theory of acid–base catalysis developed by Dawson is in connection with the general catalytic catenary. In the type of acid–salt mixtures just considered, where c is a constant and x variable, the portion of the reaction velocity which is due to the catalytic action of ions (u) is equal to $v - k_M c$, since the portion $k_M c$ is due to undissociated molecules of acid. That is

$$u = v - k_M c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xlix.)}$$

and if $k_A K$ can be neglected as being very small, then

$$u = (k_H - k_M)[H_3O^+] + ck_A K/[H_3O^+] \quad . \quad . \quad . \quad (l.)$$

from equation (xxxvi.). If the hydrogen ion concentration $[H_3O^+]$ for any solution of the constant acid series is expressed in terms of the hydrogen ion concentration $[H_3O^+]_i$ of the corresponding iso-catalytic mixture, that is

$$[H_3O^+]/[H_3O^+]_i = n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (li.)$$

then equation (l.) takes the form

$$u = (k_H - k_M)n[H_3O^+]_i + ck_A K/n[H_3O^+]_i \quad . \quad . \quad . \quad (lii.)$$

Since from equation (xl.)

$$[H_3O^+]_i = \sqrt{ck_A K/(k_H - k_M)} \quad . \quad . \quad . \quad . \quad (liii.)$$

then

$$u = \sqrt{(k_H - k_M)ck_A K} \cdot (n + 1/n) \quad . \quad . \quad . \quad (liv.)$$

Further, if the ionic reaction velocity (u) is expressed in terms of the corresponding velocity (u_i) for the iso-catalytic solution, that is

$$u/u_i = r, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (lv.)$$

then since

$$u_i = v_i - k_M c = 2\sqrt{(k_H - k_M)ck_A K} \quad . \quad . \quad (lvi.)$$

it follows that

$$r = \tfrac{1}{2}(n + 1/n) \quad . \quad . \quad . \quad . \quad . \quad (lvii.)$$

$$= cosh \ln n \quad . \quad . \quad . \quad . \quad . \quad . \quad (lviii.)$$

This equation expresses in its most general form the connection between the *reduced* ionic reaction velocity (r), and the *reduced* hydrogen ion concentration (n). It is very striking that the equation, which is, of course, that for a catenary, contains no reference to the concentration and nature of the catalysing acid, nor to the nature of the reaction being catalysed; the equation is also independent of the temperature. Dawson (1927) has tested the accuracy of the " reduced catenary " by means of his own observations made on the influence of acetic acid and chloroacetic acid, and mixtures of these acids and their respective salts, on the reaction between iodine and acetone at 25°, and of the

results obtained by Karlsson (1921) for the rates of hydrolysis of methyl and ethyl acetates in the presence of aqueous acetic acid–acetate solutions at 85·5°. In spite of the variation in the reaction, the temperature and the nature of the catalysts the values of r, the reduced ionic velocities, when plotted against log n, the reduced

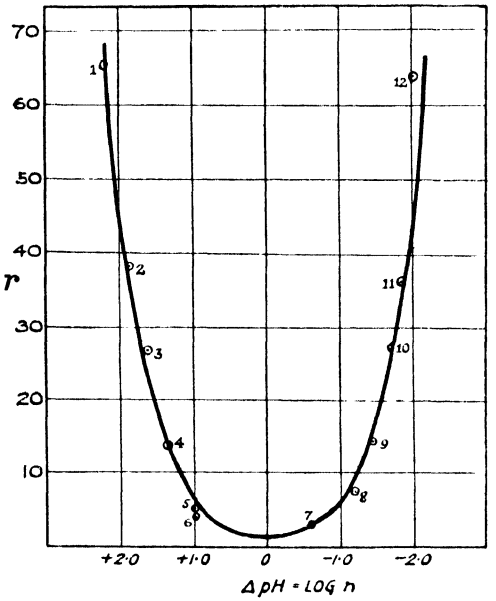


FIG. 23.—The reduced catalytic catenary. (After Dawson.) Points 5, 7, 8, 9, 10, 11 and 12 refer to the acetone–iodine reaction at 25° with acetic acid and sodium acetate catalysts; points 3 and 4 are for the same reaction in the presence of chloroacetic acid and its sodium salt. Points 1, and 2 and 6 refer to the hydrolysis of ethyl and methyl acetates, respectively, at 85·5°.

hydrogen ion concentrations, all fall on one single curve, which is definitely a catenary of the type required by the equation deduced by Dawson (Fig. 23).

DISSOCIATION CONSTANT AND CATALYTIC COEFFICIENT

If the catalytic activity (k_M) of the undissociated molecules of an acid is due to their proton donating capacity, it would appear

that this activity should be related in a simple manner to the strength of the acid, or, in other words, to its dissociation constant. The latter, like all equilibrium constants, may be regarded as the quotient of the velocity constants of the direct and reverse reactions ; hence

$$K = \frac{\text{velocity constant of dissociation}}{\text{velocity constant of association}} = \frac{k_1}{k_2} \quad . \quad . \quad \text{(lix.)}$$

Although in aqueous solution the acid actually dissociates into oxonium ions and anions, the former are probably in definite equilibrium with protons, thus

$$H_3O^+ \rightleftharpoons H^+ + H_2O,$$

and so k_1 is proportional to the rate of formation of protons from a given acid. For a particular reaction, therefore, the catalytic effect due to the acid molecules should be approximately proportional to k_1 ; in actual practice it is not possible to separate K into k_1 and k_2, but Brønsted (1924) suggested the relationship

$$k_M = GK_a^x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lx.)}$$

where G and x are constants for a specific reaction, and k_M is the catalytic coefficient for the undissociated acid having a dissociation constant K_a. When a basic molecule is acting as catalyst, Brønsted considers that the same type of equation applies :

$$k_M = GK_b^x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxi.)}$$

K_b now represents the dissociation constant of the base, and the values of G and x are not the same as for the acid catalysed reaction. If B and A are conjugate base and acid respectively, thus

$$B + H^+ \rightleftharpoons A,$$

then

$$K_b = \frac{[A]}{[B][H^+]},$$

and so K_b may be regarded as representing the proton accepting tendency of the base. This value of K_b is not the ordinary dissociation constant of the base, but the latter is proportional to K_b, and so may also be regarded as a measure of the proton accepting power. Incidentally, it may be shown that K_b is

inversely proportional to K_a for the *conjugate acid*, and so $1/K_a$ may be used for K_b in equation (lxi.); this does not affect the main argument, but merely alters the value of the constant G. The values of K_b for H_2O and $CH_3{\cdot}COO^-$ may be obtained in this manner.

The relationship proposed by Brønsted has been tested by him and his collaborators in connection with the catalytic decomposition of nitramide (1924), the mutarotation of glucose (1927), the hydrolysis of a number of ortho-esters (1929) and the decomposition of diazoacetic ester (1931), and also by Dawson (1929) for the acetone–iodine reaction, and by Bell (1934) for the rearrangement of N-bromoacetanilide, as catalysed by a number of acids in chlorobenzene solution. The observations are generally in good agreement with the equation, which requires the plot of $\log K_a$ (or K_b) against the appropriate $\log k_M$ value to be a straight line. An apparent exception has been found by Kilpatrick (1928, 1930) in the catalytic hydration of acid anhydrides; it is very probable, however, that the reactions occurring are not simple, and mixed anhydrides are formed with the catalysing acids. The equation $k_M = GK^x$ is of wide enough applicability to include even H_3O^+ and H_2O as acids, and OH^- and H_2O as bases. The acid dissociation constant of H_3O^+, for example, to be comparable with the ordinary values for other acids (cf. equation (x.), p. 338), is given by Brønsted as

$$K_a = \frac{[H_3O^+][H_2O]}{[H_3O^+]} = [H_2O]$$
$$= 55,$$

since the concentration of water in a dilute solution may be regarded as 55 gm.-mols. per litre. The conjugate base is H_2O, since

$$H_2O + H^+ \rightleftharpoons H_3O^+,$$

and so its dissociation constant is 1/55. Similarly for H_2O as an acid the dissociation constant is given by

$$K_a = \frac{[H_3O^+][OH^-]}{[H_2O]} = \frac{K_w}{[H_2O]}$$
$$= 0{\cdot}8 \times 10^{-14}/55$$
$$= 1{\cdot}5 \times 10^{-16}$$

at a temperature of 18°, when K_w is $0{\cdot}8 \times 10^{-14}$; the conjugate base is OH^-, and so its K_b is $66{\cdot}6 \times 10^{14}$.

By means of the Brønsted relationship it is possible to obtain an approximate value of k_M for any acid, provided it is known for two other acids acting as catalysts in the same reaction. Two cases which are particularly convenient for experimental study are (1) catalysis by a strong acid, when H_3O^+ may be regarded as the only catalyst, and so the value of k_M for H_3O^+ is obtained, and (2) catalysis by pure water, which gives the value for H_2O, since the H_3O^+ and OH^- concentrations are negligible. In this latter determination it is, of course, necessary to allow for the possible formation of H_3O^+ ions during the progress of the reaction, *e.g.*, the hydrolysis of ethyl acetate. This correction is not necessary in the decomposition of nitramide, the mutarotation of glucose and the hydrolysis of acetals studied by Brønsted, and so these reactions may be used for the calculations to be described. If the equation $k_M = GK^x$ is applied to three acids, for which the suffixes 1, 2 and 3 are used and the suffix M omitted, then G and x may be eliminated and the following equation obtained

$$\log \frac{k_1}{k_2} = \log \frac{k_3}{k_2} \cdot \frac{\log \dfrac{K_1}{K_2}}{\log \dfrac{K_3}{K_2}} \quad . \quad . \quad . \quad . \quad . \quad \text{(lxii.)}$$

If the suffix 1 refers to any acid HA, then k_1 may be put equal to k_M which is to be calculated; if the suffixes 2 and 3 refer to H_3O^+ and H_2O, respectively, as acids, then

$$k_2 = (k_M)_{H_3O^+} \quad \text{or} \quad k_{H_3O^+} (= k_H) \quad . \quad . \quad . \quad \text{(lxiii.)}$$

and

$$k_3 = (k_M)_{H_2O} \quad \text{or} \quad k_{H_2O} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxiv.)}$$

both of which are known from experiments with strong acid and pure water respectively. Further, as already shown, K_2 and K_3 are equal to 55 and $1{\cdot}5 \times 10^{-16}$ respectively. The equation (lxii.) then becomes

$$\log \frac{k_M}{k_{H_3O^+}} = 0{\cdot}06 \log \frac{K_a}{55} \cdot \log \frac{k_{H_2O}}{k_{H_3O^+}} \quad . \quad . \quad . \quad \text{(lxv.)}$$

where K_a is the dissociation constant of the acid HA, and so k_M for this acid may be calculated. An exactly similar equation applies, of course, to catalysis by bases. For the mutarotation of glucose, k_M for the ion H_3O^+ and for H_2O were found by Brønsted and Guggenheim (1927) to be 0·14 and $9{\cdot}5 \times 10^{-5}$ respectively; hence for mandelic acid, for which K_a is $4{\cdot}3 \times 10^{-4}$, the value of k_M may be calculated as 19×10^{-3}, whereas the observed value is 6×10^{-3}. The agreement is good enough to give an indication of the catalytic activity of the undissociated molecules of mandelic acid, and hence the coefficients for other acids may be calculated approximately by means of equation (lxv.).

CONCENTRATIONS OR ACTIVITIES IN VELOCITY EQUATIONS

In the discussion hitherto it has been tacitly assumed that the catalytic effect of any species is proportional to its concentration, and *not* to its thermodynamic activity. This may not matter very seriously when working in dilute solutions, but in the presence of neutral salts the concentration and activity may differ appreciably from one another, and it is important to know which of these functions is to be used in reaction velocity equations. At first sight it would appear that activities should be used: for consider any reaction, *e.g.*,

$$A + B \rightleftharpoons C + D,$$

then the equilibrium constant K, which is the quotient of the velocity constants of the direct (k_1) and reverse (k_2) reactions, is given by

$$K = \frac{k_1}{k_2} = \frac{a_C \times a_D}{a_A \times a_B} \quad . \quad . \quad . \quad . \quad . \quad \text{(lxvi.)}$$

where the a terms represent the activities of the respective species. From this it might be concluded that v_1, the velocity of the direct reaction, is given by

$$v_1 = k_1 a_A a_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxvii.)}$$

This is, however, not necessarily the case, for it is possible to write

$$v_1 = k_1 c_A c_B \cdot F \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxviii.)}$$

where the c terms represent concentrations and F is a "kinetic factor," which varies with the nature of the medium, and may be different for the forward and reverse reactions; a velocity equation of this type may still satisfy the requirements of the equilibrium constant, but makes the reaction rate dependent primarily on concentrations. In catalytic reactions it may be assumed that the same arguments apply. There is no *a priori* reason, therefore, for regarding concentrations or activities as fundamental, and so it is necessary to turn to actual experiments for a decision between these two possibilities. Unfortunately, however, the results are so conflicting as to render an impartial decision impossible.

At one time Harned, W. C. McC. Lewis, Scatchard and others considered that for catalysis by hydrogen, hydroxyl and iodine ions, in the inversion of cane sugar, hydrolysis of esters and decomposition of hydrogen peroxide, respectively, in the presence of neutral salts, the reaction velocity was proportional to the activities of these ions. Later Harned (1928) realised that the *E.M.F.* method which had been used to determine ionic activities was not satisfactory, as it gave the mean activity of the ions, of an acid for example, rather than the individual activity of the hydrogen ion; hence the apparent dependence of reaction velocities on ionic activities was not conclusive. This objection does not, however, apply to the reaction involving the conversion of N-chloroacetanilide into the isomeric *p*-chloroacetanilide, which is catalysed by hydrogen and chlorine ions simultaneously. According to Orton and Jones (1910) this reaction occurs in two stages

$$C_6H_5{\cdot}NClAc + H^{\cdot} + Cl' \rightarrow C_6H_5{\cdot}NHAc + Cl_2$$

and

$$C_6H_5{\cdot}NHAc + Cl_2 \rightarrow C_6H_4Cl{\cdot}NHAc + H^{\cdot} + Cl'.$$

The first stage is comparatively slow and determines the reaction velocity. According to the activity theory of reaction velocity, therefore, the rate should be given by the equation

$$v = ka_{H^{\cdot}}\, a_{Cl'}\, a_N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxix.)}$$

where $a_{H^{\cdot}}$, $a_{Cl'}$ and a_N represent the activities of the hydrogen (oxonium) and chlorine ions and of the N-chloroacetanilide,

respectively. Since the velocity equation involves $a_{H^\cdot} \times a_{Cl'}$ the value for the mean activity of hydrochloric acid, at various concentrations and in the presence of neutral salts as determined by *E.M.F.* measurements, may justifiably be used to test its applicability.

According to Harned and Seltz (1922), who used solutions of hydrochloric acid up to 1·0 *N*, the observed reaction velocities comply with the expression

$$v = k\, a_{H^\cdot}\, a_{Cl'}\, c_N \quad \ldots\ldots \quad \text{(lxx.)}$$

The result is in agreement with the activity theory if the activity coefficient of the non-electrolyte, N-chloroacetanilide, is assumed to be constant. This is actually not the case, and Soper and Pryde (1927) found that much better agreement was obtained if allowance were made for the variation in activity of this compound, as determined by solubility measurements; these conclusions appeared to support the activity theory in a satisfactory manner. In 1930, however, Belton studied the velocity of the reaction in the presence of hydrochloric acid to which had been added sodium chloride in concentrations varying from zero to 4·2 molar. The results were not at all in harmony with the activity theory, but agreed reasonably well with the equation involving concentrations only, viz.,

$$v = k\, c_{H^\cdot}\, c_{Cl'}\, c_N \quad \ldots\ldots \quad \text{(lxxi.)}$$

assuming the hydrochloric acid and sodium chloride to be completely dissociated.

The confusion in connection with this reaction appears to have been resolved by Dawson and Millet (1932) by assuming that the effective catalyst is molecular hydrogen chloride and not the ions into which it dissociates, and that the reaction velocity is proportional to its *concentration* and to that of the N-chloroacetanilide; thus

$$v = k c_{HCl} c_N \quad \ldots\ldots \quad \text{(lxxii.)}$$

For constant concentration of the chloroacetanilide this becomes

$$v = k\,[\mathrm{HCl}] \quad \ldots\ldots \quad \text{(lxxiii.)}$$

The classical dissociation " constant," K_c, for hydrochloric acid may be written

$$K_c = \frac{[H^{\cdot}]\,[Cl']}{[HCl]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxiv.)}$$

$$\therefore \quad v = k[H^{\cdot}]\,[Cl']/K_c \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxv.)}$$

If K_a is the activity dissociation constant of the acid, then by introducing this into equation (lxxv.) it becomes on re-arrangement

$$\frac{v}{[H^{\cdot}]\,[Cl']} \cdot \frac{K_c}{K_a} = \frac{k}{K_a} = \text{a constant} \quad . \quad . \quad . \quad \text{(lxxvi.)}$$

since k and K_a are both constants independent of the ionic strength of the solution or concentration of reactants. The assumptions made by Dawson and Millet require, therefore, that the left-hand side of equation (lxxvi.) should be a constant in a solution of definite concentration of N-chloroacetanilide. The reaction velocity v can be measured and the concentration terms $[H^{\cdot}]$ and $[Cl']$ are obtained by assuming practically complete dissociation of the hydrochloric acid, and so in order to test the accuracy of the relationship deduced it is necessary to know the ratio K_c/K_a. By the application of the Debye-Hückel equation (" Recent Advances in Physical Chemistry," Chapter IX.) to the equation for the dissociation constant of an acid, it is possible to derive a connection between K_c, K_a and the ionic strength of the solution (*vide infra*, equation cvii.); for the purpose of the work under discussion this may be written in the form

$$\log K_c/K_a = a\sqrt{x + c} - bx - b'c \quad . \quad . \quad \text{(lxxvii.)}$$

where c represents the concentration of hydrochloric acid and x that of a neutral salt in the experimental medium, a is a constant for all aqueous solutions (taken as 0·56) and b and b' are empirical constants for the acid and added salt respectively. By choosing appropriate values for the latter, Dawson and Millet found that in three sets of experiments with (i) 0·2 N-hydrochloric acid and x N-sodium nitrate, x being varied from 0 to 3·5, (ii) 0·2 N-hydrochloric acid and x N-sodium chloride, x being varied from 0 to 3·5, and (iii) 0·1 to 1·02 N-hydrochloric acid, the mean results for the

left-hand side of equation (lxxvi.) were *0·0626*, *0·0628* and *0·0620* respectively. The agreement is striking and lends support to the view that the velocity of reaction is dependent on the concentration factor and not on the activity. The effect of neutral salts is attributed to their influence on the ionisation of the acid and consequent change in the concentration of undissociated molecules; this is allowed for in equation (lxxvii.).

Another instance of the controversy over activities and concentrations is found in connection with the hydrolysis of ethyl acetate. Harned and Pfanstiel (1922) considered that in the presence of hydrochloric acid the reaction rate is dependent on the activity of the acid, but the accurate work of Dawson and Lowson (1928) indicated that the velocity was directly proportional to the concentration of the acid over the range 0·0002 to 0·2 molar, in which the activity coefficient falls by about 14 per cent.

In the decomposition of diacetone alcohol to acetone, which is catalysed by hydroxyl ions, Åkerlöf (1926) found that in dilute solutions of alkali the reaction velocity was proportional to the concentration of hydroxide, but in more concentrated solutions, the relation

$$v = k c_A c_{OH'} \gamma_{MOH} \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxviii.)}$$

applied, where c_A and $c_{OH'}$ represent the concentrations of the alcohol and of the hydroxyl ions, respectively, and γ_{MOH} is the mean activity coefficient of the hydroxide. This signifies that the velocity is roughly proportional to the *activity* of the hydroxyl ions, but to the *concentration* of the alcohol. This might be in agreement with the activity theory if the activity coefficient of the alcohol remained constant over the range of the experiments; solubility measurements in the presence of neutral salts show, however, that this is probably not the case. Enough results have been given to show that the situation concerning the use of activities in catalytic reaction velocity equations appears to be somewhat confusing, although in many instances there has been considerable clarification resulting from the application of the Brønsted-Bjerrum equation which will be discussed shortly.

The van't Hoff-Dimroth Equation. It has been shown theoretically (van't Hoff, 1898) that if the saturation solubility (s)

of any substance involved in a given reaction is taken as the unit for expressing its concentration, then the equilibrium constants for the reaction in different solvents should be independent of the nature of the medium. Since the equilibrium constant is the quotient of the velocity constants of direct and reverse processes, Dimroth (1910) suggested that if concentrations are expressed in the same manner, then the reaction velocity constants in different solvents should be independent of the nature of the medium; that is

$$v = k_0 c/s \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxix.)}$$

where k_0 is a constant for all media. This is equivalent to saying that the reaction velocity will be always proportional to the activity, since in a saturated solution the activity of the reactant may be regarded as a constant irrespective of the nature of the solvent, and so c/s is a measure of the activity of the reactant.

The equation (lxxix.), for which there is no real theoretical basis (see, however, p. 325), was tested by Dimroth in connection with a study of the velocity of an intra-molecular transformation (triazole $\rightarrow$ diazo-amide) in different solvents; it was found that whereas the velocity constants varied a hundredfold when ordinary volume concentration terms were used, the values of k_0, using c/s as the "concentration," showed only a threefold difference. A re-calculation by Moelwyn-Hughes (1933), using molar fractions, instead of gm.-mols. per litre, since this is more correct theoretically, gave a sevenfold variation. It would appear, therefore, that reaction velocity is determined to a great extent by the activity of the reactant. There are, however, many cases in which the van't Hoff-Dimroth relationship fails completely, as for example the decomposition of nitrogen pentoxide in the gaseous state, and when dissolved in liquid nitromethane, carbon tetrachloride or nitrogen tetroxide studied by Eyring and Daniels (1930). In each experiment the reacting phase was in equilibrium with solid pentoxide, and so the activity of the reactant was the same in every case. The results at 15° C. are given in Table LXIX.; s is the saturation solubility, and hence, concentration of the reactant, and v is the rate of decomposition.

TABLE LXIX

Decomposition of Nitrogen Pentoxide Solutions in Equilibrium with Solid at 15°.

N_2O_5 crystals saturating.	*s.*	*v.*	*k.*
Vacuum (gas phase) . .	0·0102	$0·0080 \times 10^{-5}$	$0·79 \times 10^{-5}$
Liquid nitromethane . .	4·38	$5·92 \times 10^{-5}$	$1·35 \times 10^{-5}$
Liquid carbon tetrachloride .	4·78	$8·75 \times 10^{-5}$	$1·83 \times 10^{-5}$
Liquid nitrogen tetroxide .	—	—	$1·59 \times 10^{-5}$

If the reaction velocity were proportional to the activity the v terms should have been constant, since the activity is the same in each (saturated) solution ; the results are, however, not constant if the gas phase is included. On the other hand, v/s should be constant if ordinary concentrations determine the reaction velocity, and it appears that the experimental results are more in harmony with this point of view.

THE BRØNSTED-BJERRUM THEORY

An interesting aspect of the whole problem has been opened up by the theory of Brønsted (1922), and its modification by Bjerrum (1924), which helps to clarify many apparently conflicting results obtained in acid–base, and in ionic, catalysis in general, especially in the presence of neutral salts. It is supposed that catalytic reactions, and probably all reactions, involve the primary formation of a "critical complex," which decomposes into the products of the reaction ; thus

$$A + B \rightarrow X \rightarrow C + D,$$

where A and B are the reactants, X the critical complex, and C and D the resultants. Brønsted supposes that the first stage, namely, the formation of X, is slow and so determines the reaction velocity, which is considered to depend on the *activities* of A and B ; using certain arguments concerning the probability of the formation of X, the equation for the reaction velocity

$$v = k a_A a_B \cdot \frac{1}{f_X} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxx.)}$$

is deduced, where a_A and a_B represent the activities of A and B, and f_X is the activity coefficient of the critical complex. The same equation has been deduced by Bjerrum (1924) in a more straightforward manner, which assumes, however, that *concentrations* determine the reaction velocity. In the first place A and B are supposed to be in *equilibrium* with the critical complex, thus

$$A + B \rightleftharpoons X.$$

The latter then is considered to disintegrate spontaneously, and its rate of decomposition, which gives the reaction velocity, is proportional to its concentration ; that is

$$v = k_X c_X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxi.)}$$

where c_X is the concentration of the critical complex. Applying the law of mass action to the equilibrium between A, B and X, it follows that

$$K = \frac{a_X}{a_A a_B} = \frac{c_X}{c_A c_B} \cdot \frac{f_X}{f_A f_B} \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxii.)}$$

where the a, c and f terms represent the activities, concentrations and activity coefficients, respectively, of the species indicated by the suffix. (Note that $a = fc$.) Hence

$$c_X = K c_A c_B \cdot \frac{f_A f_B}{f_X} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxiii.)}$$

$$\therefore \quad v = k_X c_X = k c_A c_B \cdot \frac{f_A f_B}{f_X} ; \quad . \quad . \quad . \quad \text{(lxxxiv.)}$$

this is identical with Brønsted's equation (lxxx.). The term involving the three activity coefficients, that is, $f_A f_B / f_X$, is frequently referred to as the " kinetic activity factor."

The Brønsted-Bjerrum equation also follows simply from the " activated complex " theory of reaction velocity, described in the previous chapter ; this theory is, of course, not fundamentally different from that just considered. Equation (lvii.), p. 323, may be written in the form $k_v = k' \alpha_A \alpha_B / \alpha^*$, where the α terms are the activity coefficients in solution with respect to the ideal gas as the standard state, and k' is a constant for the given reaction. Transferring the activity coefficients to the values for the infinitely

dilute solution as the standard state, as is usual for processes in solution, the relationship becomes

$$k_v = k'' \frac{f_A f_B}{f_X} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxv.)}$$

where k'' is a constant, and the f terms are the new activity coefficients. It will be noted that f_X is used for the activated complex to bring the symbol into line with that used above for the critical complex, with which it is virtually identical. Since in Chapter VII., p. 323, it has been assumed in deducing the various relationships that the reaction velocity (v) is given by $k_v c_A c_B$ (equation liii.), the Brønsted-Bjerrum equation follows directly from (lxxxv.).

PRIMARY KINETIC SALT EFFECT

Salt Effects. In order to obtain further information from this equation, it is necessary to introduce values for the activity coefficients ; these can be obtained, for ions at least, by means of the Debye-Hückel equation ("Recent Advances in Physical Chemistry," Chapter IX.), which for aqueous solutions at 25° C. Brønsted writes in the form

$$-\log f = 0{\cdot}5\, z^2 \sqrt{\mu} - b\mu \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxvi.)}$$

where z is the charge on the ion, μ is the ionic strength * and b is a constant for each ion. The charge on the activated complex X will be the sum of the charge on A and B, and for ordinary acid–base catalysis of a neutral substance by hydrogen or other univalent ions, the complex will have a unit charge. If the activity coefficient of the neutral molecule A may be expressed by the equation

$$\log f = b\mu,$$

or

$$\ln f = \beta\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxvii.)}$$

then it follows that

$$v = k c_A c_B e^{\mu(\beta_A + \beta_H - \beta_X)}$$

$$= k c_A c_B e^{\mu\beta_S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxviii.)}$$

* The ionic strength is defined as half the sum of the cz^2 terms for all the ions present in solution, where c is the concentration and z the valency of each ion.

where $\beta_S = \beta_A + \beta_{H\cdot} - \beta_X$, and e is the base of natural logarithms. If β_S is small, as it generally is, it is possible to write

$$e^{\mu\beta_S} = 1 + \mu\beta_S,$$

and so

$$v = kc_Ac_B(1 + \mu\beta_S) \quad \text{(lxxxix.)}$$

According to this equation the influence of neutral salts on the velocity of a reaction involving a neutral substance, *e.g.*, the hydrolysis of an ester, or the inversion of cane sugar, catalysed by hydrogen, or other univalent, ions is such that if c_A and c_B are kept constant the reaction velocity plotted against μ, the ionic strength, should be a straight line. The *apparent* velocity constant should also vary with the ionic strength in the same manner. Brønsted and his students have found the experimental results, in the hydrolysis of esters and acetals, in the hydration of ethylene oxide, and in the decomposition of diazoacetic ester and of nitrosotriacetoneamine, to be in harmony with this anticipation; this influence of neutral salts on reaction velocity is called by Brønsted the "primary kinetic salt effect." Strictly speaking, the value of b in the Debye-Hückel equation (lxxxvi.), and hence of the β term in equation (lxxxvii.), depends not only on the ion or molecule under consideration, but on the nature of all the ions present in a concentrated solution. The value of β_S in equation (lxxxviii.) may, therefore, change as the neutral salt is altered; the slope of the v — μ curve has actually been found to depend on the nature of the added salt (Brønsted and Grove, 1930).

The value of β for any ion varies, approximately, inversely as its diameter, and so for the hydrogen ion β is larger than for the other ions, and probably much larger than for the complex X; hence $\beta_S(= \beta_A + \beta_{H\cdot} - \beta_X)$ will be definitely positive. For hydrogen ion catalysis, therefore, the reaction velocity will increase with increasing salt concentration, that is, as μ increases. If the catalyst is an anion then the corresponding β will take the place of $\beta_{H\cdot}$, and as it is much smaller, β_S will be negligibly small, since β_X is probably also small but slightly greater than β_A, for the neutral substance. When the undissociated molecules of acid act as catalyst A, B and X will all be neutral, and so the β terms will

all be small, and β_S will again be negligible. In both latter instances, therefore, the " primary salt effect " will be very small, and the catalytic effect of anions and of undissociated molecules will not be appreciably influenced by the addition of neutral salts.

In the earlier parts of the present chapter, when discussing the work of Dawson, it was tacitly assumed that the contribution of any catalytic species C to the reaction velocity, for a given concentration of reactant, was given by

$$v_C = k_C c_C \quad . \quad . \quad .

TABLE LXX

Catalytic Coefficient of Hydrogen Ion in the Presence of Neutral Salts.

Sodium chloride added.		Sodium nitrate added.	
Conc.	$k_H \times 10^4$.	Conc.	$k_H \times 10^4$.
—	4·65	—	4·65
0·1 *N*	4·78	0·1 *N*	4·74
0·5	5·30	0·5	5·11
1·0	5·95	1·0	5·57
2·0	7·26	2·0	6·48
4·0	11·10	4·0	8·30

chloride. The values are given in Table LXXI. and show only a very slight variation with increasing ionic strength of the medium ; similar results have been obtained with chloroacetic acid.

TABLE LXXI.—*Catalytic Coefficient of Anions and Molecules of Acetic Acid in the Presence of Sodium Chloride.*

Conc. of NaCl.	$k_A \times 10^6$.	$k_M \times 10^6$.
—	4·0	1·4
0·1 *N*	4·0	1·4
0·5	3·7	1·4
2·0	3·4	1·4
4·0	3·4	1·3

Since the catalytic coefficients decrease somewhat with increasing ionic strength, it must be assumed that the β_S terms for acetic acid and acetate ions, although not zero, are quite small.

The ionic strength term μ should include all the ions present in the solution whether acting as catalysts or inert, and so the criticism has been raised against Dawson's work (p. 337), that "salt effects," due to the presence of the sodium salt of the catalysing acid, were not taken into consideration. This author

has pointed out, however, that in the majority of solutions used by him, the hydrogen ion concentration was small, and so the value of $k_H[H_3O^+]$, which is chiefly affected by salts, is comparatively small. Any changes observed in the reaction velocity as a result of varying the acid–salt ratio, or concentration, may be attributed almost exclusively to the effects of the undissociated molecules and of the anions, and not merely to salt effects, on the catalytic coefficient of the hydrogen ion. The k_M and k_A coefficients, as already seen, are not markedly influenced by changes in the ionic strength, and so the values determined on the assumption that inert salt effects can be neglected may be regarded as quite reliable.

Further Tests of the Brønsted Equation. The Brønsted equation is capable of being tested in a number of different ways, and some of these will be considered. In the first place for a dilute solution of acid, in the absence of neutral salts of any kind, μ is small, and so the term $\mu\beta_S$, in the equation (lxxxix.) for the catalysis of a neutral reactant by means of a univalent ion, may be neglected, and the equation takes the form

$$v = k c_A c_B.$$

The reaction velocity is thus dependent only on the *concentrations* of the reactant and of the catalyst. This is in agreement with Dawson's observation on the hydrolysis of ethyl acetate in solutions of hydrochloric acid up to 0·2 molar, with the measurements of Arrhenius on the inversion of cane sugar in the presence of alkalis, and with the studies of Holmberg on the hydrolysis of γ-lactones by alkalis. The same type of equation was found by Belton (see p. 357) to apply to the rate of isomeric change of N- to *p*-chloroacetanilide in the presence of neutral salts, but in view of the large ionic strengths of some of the solutions used, the agreement is unexpected.

In dilute solutions the equation (lxxxvi.) for the activity coefficient may be reduced to the form

$$-\log f = 0{\cdot}5\, z^2\sqrt{\mu} \quad . \quad . \quad . \quad \text{(lxxxvi}a\text{.)}$$

and if the reactant A is a neutral substance, then the catalyst B

and the critical complex X will carry the same charge z; hence f_A and f_X will be equal, and the expression for the reaction velocity

$$v = k c_A c_B \cdot \frac{f_A f_B}{f_X} \quad . \quad . \quad . \quad . \quad . \quad \text{(lxxxiv.)}$$

becomes

$$v = k c_A c_B \cdot f_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xci.)}$$

$$= k a_A c_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xcii.)}$$

That is, the reaction velocity should be proportional to the *activity* of the neutral substance and to the *concentration* of the ionic catalyst. The relative activity of a neutral molecule in any salt solution can be determined by the ratio of its concentration to the saturation value in the given solution, since, as already mentioned, saturated solutions are assumed to have the same activity. Hence

$$a_A = c_A/s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xciii.)}$$

where c_A is the concentration of the neutral substance and s its saturation solubility in the given medium. The reaction velocity equation (xcii.) then becomes

$$v = k c_A c_B/s \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xciv.)}$$

For a given concentration of neutral substance (A) and strong acid (B) the reaction velocity in various salt solutions should be proportional to the reciprocal of the solubility of the neutral substance in those solutions. Harned (1928) has found that there is a definite parallelism between the reaction velocity and the reciprocal of the ester solubility in the hydrolysis of ethyl acetate by 0·1 *N*-hydrochloric acid in the presence of either sodium or potassium chlorides or sodium bromide. There is, however, no such parallelism to be observed for the rate of conversion of diacetone alcohol into acetone by means of 0·1 *N*-alkali hydroxide as catalyst in solutions containing various amounts of alkali halides.

Hitherto it has been assumed that the reactant is a neutral molecule, as it generally is in cases of acid–base catalysis. It is possible to make a more extended test of the Brønsted equation if other cases of catalysis are considered in which the reactant may be an ion, or in which two ions are simultaneously involved

as catalysts. Consider, for example, the reaction between the brom-pentammine cobaltic ion and mercuric ions, studied by Brønsted and Livingston (1927); kinetically this reaction is bimolecular, the first stage involving

$$[CoBr(NH_3)_5]^{++} + Hg^{++} \rightarrow X^{++++},$$

and although it is not a catalysed reaction in the ordinary sense, the velocity is markedly increased by the addition of neutral salts. According to the Brønsted equation the reaction velocity is given by the expression

$$v = k c_A c_B . \frac{f_2 f_2}{f_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xcv.)}$$

where f_2 represents the activity coefficient of a bivalent ion, *i.e.*, $[CoBr(NH_3)_5]^{++}$ and Hg^{++}, and f_4 that of a quadrivalent ion, viz., the critical complex. Using the simple form of the Debye-Hückel equation (lxxxvi*a*.) applicable in dilute solutions, it follows that

$$v = k c_A c_B 10^{4\sqrt{\mu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xcvi.)}$$

and so it is obvious that the reaction velocity will increase with increasing concentration of neutral salt, that is, as μ increases. For a given concentration of the two reactants it should follow, on taking logarithms, that

$$\log v = \text{constant} + 4\sqrt{\mu} \quad . \quad . \quad . \quad . \quad . \quad \text{(xcvii.)}$$

If log v is plotted against the square root of the ionic strength, a straight line with a slope of 4 should be obtained; this has been found to be the case in actual experiments. When the brom-pentammine cobaltic ions react with hydroxyl ions, neutral salts have the effect of *decreasing* the reaction velocity; the primary reaction in this case is

$$[CoBr(NH_3)_5]^{++} + OH^- \rightarrow X^+,$$

and so

$$v = k c_A c_B . \frac{f_2 f_1}{f_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xcviii.)}$$

$$= k c_A c_B 10^{-2\sqrt{\mu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(xcix.)}$$

The velocity of the reaction, according to the Brønsted equation, should decrease with increasing ionic strength of the medium, and the plot of log v against $\sqrt{\mu}$ should be, as it is actually, a straight

line with a slope of − 2. In these and many other reactions there is no doubt that the equation deduced by Brønsted and by Bjerrum has been able to account both qualitatively and quantitatively for the catalytic influence of neutral salts.

The decomposition of hydrogen peroxide by bromine ions in acid solution is a reaction closely allied to those concerned in acid–base catalysis; the effective catalysts are the hydrogen and bromine ions, and the reaction may be regarded as involving

$$H_2O_2 + H_3O^+ + Br^- \rightarrow X.$$

The critical complex is, of course, uncharged, and for dilute solutions the velocity of the process should be given by

$$v = k\, c_{H_2O_2}\, c_{H^+}\, c_{Br^-} 10^{-\sqrt{\mu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c.)$$

For a definite concentration of hydrogen peroxide the rate of reaction should be directly proportional to the hydrobromic acid concentration provided the ionic strength of the medium is kept constant, but should decrease with increasing ionic strength. These predictions have been confirmed by Livingston (1926).

An interesting application of the Brønsted equation is in connection with the formation of urea from ammonium cyanate; although Walker and his co-workers had long ago come to the conclusion that ammonium and cyanate ions were concerned in the process, other non-ionic mechanisms had been suggested. If the isomeric change involved molecules only then neutral salts should have relatively little effect on the reaction velocity, and in any case it should be a linear function of the ionic strength (p. 364); on the other hand, if ions are involved and the reaction is to be represented as

$$NH_4^+ + CNO^- \rightarrow X \rightarrow CO(NH_2)_2,$$

then in dilute solution, when the Debye-Hückel limiting law should be applicable, the Brønsted relationship leads to the equation

$$v = k c_{NH_4^+} . c_{CNO^-} 10^{-\sqrt{\mu}} \quad . \quad . \quad . \quad . \quad . \quad (ci.)*$$

* Attention must be called to the fact that this and previous similar velocity equations are for 25° C. when the constant 0·5 appears in the Debye-Hückel equations (lxxxvi.) and (lxxxvi*a*.); in the work of Warner and Stitt (1933) the temperature was 70° C., and the constant 0·565, so that $\sqrt{\mu}$ is replaced by $1{\cdot}13\sqrt{\mu}$.

This expression requires the reaction to be bimolecular, as it is in fact, and the logarithm of the apparent velocity constant at different salt concentrations to be a linear function of the square root of the ionic strength, at least in dilute solution. The experimental results are in harmony with the expectation for an ionic reaction, and the slope of the curve is in excellent agreement with the value to be expected from the Debye-Hückel equation; as indicated by equation (ci.) the reaction velocity decreases with increasing salt concentration (Warner and Stitt, 1933; Warner and Warrick, 1935; Miller, 1934, 1935).

Certain reactions, such as the hydrolysis of sucrose, are catalysed by acids only, and do not fall into line with the processes of general acid–base catalysis. In a number of such instances Hammett and Paul (1934) have found the reaction velocity to be dependent not on the concentration of acid, but on the "acidity function." The latter is defined as $-\log a_{H^\cdot} f_B / f_{BH^\cdot}$ where B represents a base and BH the conjugate acid, and the reaction velocity is found to be proportional to the quantity $a_{H^\cdot} f_B / f_{BH^\cdot}$. For example, the rate of hydrolysis of sucrose is 228 times as great in 4*N*- as in 0·1 *N*-hydrochloric acid; the acid concentration ratio is 40, that of the mean ionic activities is 102, but the ratio of the terms involved in the acidity functions of the two solutions is 204. This result can be readily correlated with the Brønsted equation in the following manner: the reaction may be assumed to involve, as the rate-determining step, the process

$$S + H^+ \rightarrow SH^+,$$

where SH^+ can be regarded as the activated complex. The Brønsted equation then gives

$$v = k c_S c_{H^\cdot} \frac{f_S f_{H^\cdot}}{f_{SH^\cdot}} \quad \ldots\ldots\ldots \text{(cii.)}$$

$$= k c_S a_{H^\cdot} f_S / f_{SH^\cdot} \quad \ldots\ldots\ldots \text{(ciii.)}$$

If S and $SH^\cdot$ may be considered as the conjugate base and acid, then $a_{H^\cdot} f_S / f_{SH^\cdot}$ becomes equivalent to $a_{H^\cdot} f_B / f_{BH^\cdot}$ which is the factor involved in the acidity function; hence the reaction velocity should be directly proportional to this factor, as actually found.

A number of other reactions, *e.g.*, bromoacetate-propionate (La Mer and Fessenden, 1932 ; Kappana and Patwardhan, 1932), persulphate–iodide (King and Jacobs, 1931) and ferric–iodide (von Kiss, 1931), have been studied and it has been found that in dilute solutions, at least, the observed velocities in the presence of neutral salts comply in an excellent manner with the requirements of the Brønsted equation, as modified by the Debye-Hückel equation. In more concentrated solutions or in the presence of high valency ions deviations are observed, but it is in just such circumstances that the simple Debye-Hückel relationship fails to hold. It may be concluded, therefore, that the Brønsted equation is probably correct even if the Debye-Hückel equation is not applicable to the particular solution studied.

An apparent exception to the Brønsted equation was found by La Mer and Kamner (1931) in the reaction between thiosulphate and β-bromopropionate ions ; instead of the velocity increasing with increasing ionic strength of the medium the values actually decreased. This anomalous observation is explained by the suggestion that owing to the configuration of the β-bromopropionate ions a particular orientation is necessary before reaction can occur on collision (see, however, Sturtevant, 1935). Similar results, attributed to an analogous cause, have been obtained in the reactions between thiosulphate ions and the ions of brominated succinic and malonic acids (Bedford, Mason and Morrell, 1934). It has been stated that the Brønsted-Debye-Hückel relationship breaks down for the alkaline hydrolysis of acetylated hydroxy-acids (La Mer and Greenspan, 1934), but according to Kilpatrick (1934) the solutions employed in this work were too concentrated for the Debye-Hückel limiting laws to be applicable, and that consequently no definite conclusions can be drawn from the results.

In reviewing the data presented here it seems that until more decisive evidence is forthcoming it would be advisable to use ordinary concentration terms in reaction velocity equations. As far as the influence of neutral salts is concerned there is little doubt that the Brønsted equation gives a very valuable indication of the trend of the reaction velocity with increasing ionic strength. In

concentrated solutions there is evidence to show that the added ions exert a specific influence, although in dilute solution the effect is not dependent on the nature of the ions but only on their valency and sign.

SECONDARY SALT EFFECT

Apart from the influence of neutral salts, and ions in general, on the catalytic coefficient there is another effect which they produce called by Brønsted the " secondary kinetic salt effect." In a solution of a weak acid, or a mixture of the acid and its salt, the true dissociation constant K_a may be written

$$K_a = \frac{a_{H\cdot} \times a_{A'}}{a_{HA}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \text{(civ.)}$$

$$= \frac{[H_3O^+][A^-]}{[HA]} \cdot \frac{f_{H\cdot} f_{A'}}{f_{HA}} \quad . \quad . \quad . \quad . \quad \text{(cv.)}$$

where a and f represent activities and activity coefficients respectively. Since the activity coefficients of the ions vary with the ionic strength of the medium, the *concentration* of the hydrogen and acetate ions and of the undissociated molecules will also change. The catalytic effect of the acid, or acid–salt mixture, will thus vary with changes in ionic strength of the solution, apart from the primary influence on the catalytic coefficients. The existence of this factor has been proved by Dawson and by Brønsted. Each of these authors has determined the hydrogen ion concentrations of solutions containing neutral salts from catalytic reaction velocity measurements, and so calculated the classical dissociation " constant," K_c, where

$$K_c = \frac{[H_3O^+][A^-]}{[HA]} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(cvi.)}$$

ignoring activity coefficients. Assuming the Debye-Hückel equation (lxxxvi.) applies to the hydrogen ion and to the acid anion, whereas the activity coefficient of the undissociated acid remains unity, it can be readily shown that

$$\log K_c = \log K_a + \sqrt{\mu} - b\mu \quad . \quad . \quad . \quad . \quad \text{(cvii.)}$$

for an aqueous solution ; b is a constant which depends on the nature of all the ions present in the solution. The value of K_c calculated from reaction velocity measurements in solutions of different ionic strengths should thus be related to the constant K_a, determined electrometrically, or taken as the limiting value of K_c in very dilute solution, by this equation.

Dawson and Lowson (1929) studied the hydrolysis of ethyl acetate by means of acetic, glycollic and dichloroacetic acids in the presence of sodium chloride up to 4·0 molar ; in every case it was found that the reaction velocity at first increased and then decreased somewhat with increasing concentration of salt. From the measured velocity and the known value of k_H in the presence of salt solutions, determined by a series of experiments with hydrochloric acid–sodium chloride mixtures (p. 365), and the values of k_A and k_M, which were often small enough to be neglected, the hydrogen ion concentration could be calculated from the equation

$$v = k_H[H_3O^+] + k_A[A^-] + k_M[HA] \quad . \quad . \quad . \quad . \quad \text{(viii.)}$$

It should be noted that in the acid solutions used $[H_3O^+]$ is equal to $[A^-]$, and $[HA]$ is equal to $c - [H_3O^+]$, where c is the acid concentration ; hence K_c (equation cvi.) may be evaluated if $[H_3O^+]$ is known. The results for glycollic acid (0·1 *N*) in sodium chloride solutions are given in Table LXXII.

TABLE LXXII.—*Hydrogen Ion Concentrations in 0·1 N-Glycollic Acid and Sodium Chloride Mixtures.*

NaCl.	$v \times 10^4$.	$[H_3O^+] \times 10^3$.	$K_c \times 10^4$.
—	0·255	3·92	1·60
0·02 *N*	0·271	4·15	1·80
0·04	0·285	4·34	1·93
0·10	0·307	4·61	2·23
0·30	0·350	5·01	2·64
1·0	0·410	5·04	2·67
2·0	0·450	4·55	2·17
3·0	0·492	4·17	1·81
4·0	0·480	3·40	1·20

It will be observed that both the hydrogen ion concentration and the dissociation "constant" increase at first and then decrease as the salt concentration is increased; similar results were obtained for the other acids studied. In general the variation of K_c with salt concentration could be expressed, for all the acids studied, by the equation

$$\log K_c = \log K_a + 0{\cdot}54\sqrt{\mu} - 0{\cdot}32\mu \quad . \quad . \quad . \quad \text{(cviii.)}$$

This is of the form required by the Debye-Hückel theory (equation cvii.), but the factor 0·54 appears instead of unity in front of $\sqrt{\mu}$. Similar divergences have been observed in other applications of the Debye-Hückel equation, and so the agreement is almost as good as could be expected. These results provide evidence, therefore, that neutral salts influence the hydrogen ion concentration of the catalysing acid, and consequently introduce a "secondary salt effect" in catalysis. The corresponding influence of neutral salts on the concentration of undissociated molecules of hydrogen chloride and the consequent variation in the catalysis of the isomeric change of N-chloroacetanilide has already been mentioned (p. 357); if the interpretation of Dawson is correct this must also be regarded as a kind of secondary salt effect.

REFERENCES

ASHDOWN. *J. Amer. Chem. Soc.*, 1930, **52**, 268.

BEDFORD *et al.* *Ibid.*, 1934, **56**, 280.

BELL. *Proc. Roy. Soc.*, 1934, [*A*], **143**, 377; *Ann. Reports Chem. Soc.*, 1934, **31**, 67*.

BJERRUM. *Z. physikal. Chem.*, 1924, **108**, 82; 1925, **118**, 251.

BOWE. *J. Physical Chem.*, 1927, **31**, 291.

BRØNSTED. *Rec. trav. Chim.*, 1923, **42**, 718; *Z. physikal. Chem.*, 1922, **102**, 169; 1924, **108**, 185; 1925, **115**, 337; **117**, 299; 1931, **155**, 211; *J. Physical Chem.*, 1924, **28**, 579; 1926, **30**, 777; *Trans. Faraday Soc.*, 1928. **24**, 630*; 1929, **25**, 59; *J. Amer. Chem. Soc.*, 1925, **47**, 2523; 1927, **49**, 2554; 1930, **52**, 1394; 1931, **53**, 2478; *Chem. Reviews*, 1928, **5**, 231*.

COATES and BUTLER. *Ann. Reports Chem. Soc.*, 1926, **23**, 30*.

DAWSON *et al.* *Trans. Faraday Soc.*, 1928, **24**, 640*; *J. Chem. Soc.*, 1926, 2282, 2872, 3166; 1927, 213, 458, 756, 1146, 1290, 2107, 2444; 1928, 543, 1239, 1248, 2146, 2154, 2844; 1927, 393, 1217, 1884, 2530; 1930, 79, 2180; 1931, 2658; 1932, 1920, 2612.

EYRING and DANIELS. *J. Amer. Chem. Soc.*, 1930, **52**, 1472.

FRENCH. *Ibid.*, 1929, **51**, 3215.

HAMMETT and PAUL. *Ibid.*, 1934, **56**, 830.

HARNED *et al.* *Ibid.*, 1922, **44**, 1476, 2194 ; *Trans. Faraday Soc.*, 1928, **24**, 666.
HINSHELWOOD. *Ann. Reports Chem. Soc.*, 1927, **24**, 330*.
HUNTER. *Ibid.*, 1927, **24**, 33*.
INGOLD *et al.* *J. Chem. Soc.*, 1930, 1032 ; 1932, 756.
KAPANNA and PATWARDHAN. *Rec. trav. Chim.*, 1932, **51**, 379.
KILPATRICK *et al.* *J. Amer. Chem. Soc.*, 1928, **50**, 2891 ; 1930, **52**, 1410, 1418 ; 1931, **53**, 3217, 3698 ; 1934, **56**, 2326 ; *Chem. Reviews*, 1931, **10**, 213*.
LA MER *et al.* *J. Amer. Chem. Soc.*, 1931, **53**, 2832 ; 1932, **54**, 2350 ; 1934, **56**, 1492 ; 1935, **57**, 2662, 2669 ; *Chem. Reviews*, 1931, **10**, 179*.
LIVINGSTON. *J. Amer. Chem. Soc.*, 1926, **48**, 53.
LOWRY *et al.* *Chem. and Ind.*, 1923, **42**, 43 ; *J. Chem. Soc.*, 1925, **127**, 1371, 1385, 2883 ; 1926, 1938 ; 1927, 2539, 2555.
MILLER. *Proc. Roy. Soc.*, 1934, [*A*], **145**, 288 ; 1935, [*A*], **151**, 188.
MUSIL. *Monatsh.*, 1932, **61**, 229.
PEDERSEN. *J. Physical Chem.*, 1934, **38**, 581.
STURTEVANT. *J. Chem. Physics*, 1935, **3**, 295.
VON KISS *et al.* *Z. anorg. Chem.*, 1931, **198**, 102 ; 1932, **206**, 196 ; 1934, **217**, 305.
WARNER *et al.* *J. Amer. Chem. Soc.*, 1933, **55**, 4807 ; 1935, **57**, 1491, 1883.
WYNNE-JONES. *J. Chem. Physics*, 1934, **2**, 381 ; *Chem. Reviews*, 1935, **17**, 115*.

* Review papers and books, wherein further references can be found, are marked with an asterisk.

CHAPTER IX

SIMPLE ORGANIC FREE RADICALS

Introduction. Attempts to isolate radicals, such as the methyl group, in the free state date back to the middle of the past century, when Bunsen, Frankland and Kolbe, in particular, claimed success in this direction. With the gradual recognition of the applicability of the Avogadro hypothesis, and other developments in chemistry, it was realised that the so-called " free radicals " were actually stable molecules. As a consequence it became generally accepted that if radicals had any separate existence, their life period was extremely short, and attempts to isolate them were not likely to be successful. When Gomberg in 1900 succeeded in obtaining triphenylmethyl, having the formula $(C_6H_5)_3C$, this constituting a free radical in the sense that the valency of the carbon was not completely satisfied, new possibilities were opened up; the relative stability of this compound, and related substances, however, placed them in a category different from that occupied by the radicals of short life which have been frequently postulated as playing some part in thermal and photochemical processes. As long ago as 1908, Bone and Coward had suggested the formation of free radicals, for example during the thermal decomposition of hydrocarbons, in order to explain the nature of the products obtained, and Taylor (1925) postulated the production of ethyl radicals as intermediates in the photochemical reaction between ethylene and atomic hydrogen; it was generally accepted, however, that the radicals had only a transient existence, and could not be observed in a direct manner. In the early experiments on positive rays, Sir J. J. Thomson observed parabolas due to the fragments CH_3, CH_2, CH and C, when the discharge tube contained methane, but in view of the high velocity with which the particles move their life period need only be very short for them to be detected in this manner; in any case it must be borne in mind

that each of the radicals observed carried a positive charge, and consequently were ions rather than free radicals, a factor which may have contributed to their stability. The whole subject has received an enormous stimulus in recent years by Paneth's discovery in 1929 that methyl radicals were obtainable under suitable conditions, and that some of their properties could be examined in such a definite manner as to remove all doubts concerning the possibility of their existence. This discovery has been of great importance in connection with developments in

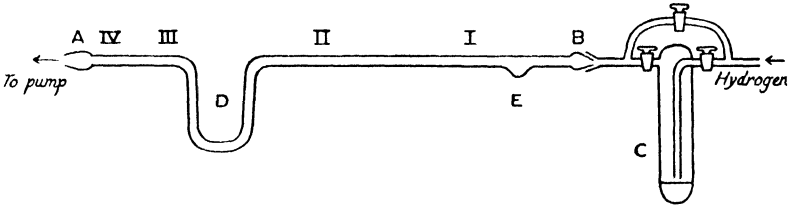


FIG. 24.—Diagrammatic representation of apparatus used by Paneth and Hofeditz for the preparation of free radicals.

physical and organic chemistry, and the subject is of sufficient importance to merit detailed consideration.

PREPARATION AND PROPERTIES OF FREE RADICALS

Preparation of Free Methyl Radicals. The first successful experiments on the production of free methyl radicals were made by Paneth and Hofeditz in 1929, by heating the vapour of tetramethyl lead in a rapid stream of hydrogen at low pressure. The apparatus used is shown diagrammatically in Fig. 24. The quartz tube *AB*, about 60 cm. in length, was attached to a vessel *C* containing the tetramethyl lead kept at a temperature of $-70°$ to $-75°$ C. By means of the three taps associated with *C*, hydrogen alone could first be streamed through the tube so as to free it from air, and then subsequently mixed with a suitable amount of the vapour of the organic lead compound. The end *A* of the quartz tube was connected by means of a tap to a high-speed pump, capable of maintaining a pressure of 1·5 to 2 mm. of

mercury at *A*, and yet able to permit of a high velocity of flow of gas : this factor, namely, high-speed evacuation, was found to be essential for satisfactory results to be obtained. If the tube, at the position indicated by II, was heated by means of a Bunsen burner, the temperature attained being approximately 700° C., a grey metallic mirror, apparently of lead, was observed to form just beyond the hot portion. After allowing the tube to cool in a current of hydrogen the tetramethyl lead vapour was again introduced, and the tube now heated at I : a metallic mirror was observed to form at I, but at the same time the mirror previously deposited at II disappeared, the rate of disappearance being dependent on the rate of decomposition of the organic compound at I, and on the distance between I and II. The greater the distance between the two points the longer was the time required to remove a mirror of definite size at II, under given conditions of flow of gas through the tube and of heating at I, but even when 30 cm. separated the two positions the removal of the mirror at II by the substance produced at I could still be observed. The attack on the lead mirror was shown not to be due to the action of heated hydrogen alone, and cooling the tube between the points I and II, by means of a stream of water, was found to have no influence on the rate of removal of the mirror.

The obvious interpretation of these results is that under the experimental conditions the tetramethyl lead is decomposed on heating to give a deposit of lead on the tube and free methyl radicals which are carried along in the hydrogen stream : in this way the mirror is formed at II. On heating at I the same process occurs, and the methyl radicals have a sufficiently long life to survive passage along as much as 30 cm. of tube : on reaching the mirror II they attack the lead and should, presumably, regenerate tetramethyl lead. That this is the case was verified by placing liquid air around the U-bend *D*, whilst the mirror at II was being removed : on heating the tube at III no mirror was formed, but when the liquid air was taken away, and the substance condensed in *D* allowed to warm up and evaporate, a mirror was formed at this point, and a further mirror at IV could be removed at the same time. It appears highly probable, therefore, that it is

tetramethyl lead which condenses in *D* when the latter is cooled. Attention may be called to the fact that when the tube *AB* is free from metallic deposits and is heated at one point only, say at I, whilst the U-bend is cooled in liquid air, the condensate in *D* on warming shows no activity towards lead mirrors; it presumably consists of inactive hydrocarbons resulting from union of the methyl radicals.

Similar evidence for the formation of free methyl radicals was obtained by using trimethyl bismuth in place of the lead compound, although the results were, on the whole, not quite so satisfactory; with antimony and zinc methyls, however, no indication of the production of radicals was obtained under the experimental conditions used. Nitrogen was employed as carrier gas, instead of hydrogen, with equal success in the formation of the free radicals. Rice, Johnston and Evering (1932) subsequently showed that water vapour, carbon dioxide, or the vapour of an organic compound, such as acetone or heptane, could be used to carry the tetramethyl lead vapour; in this work, as well as in the later work of Paneth, the methyl radicals were generated by heating the tube electrically to a temperature of 500° to 600° C.

Identification of Methyl Radicals. Further evidence that methyl radicals were liberated as a result of heating tetramethyl lead resulted from a study of the action of the decomposition products on other metals. By placing small pieces of zinc or of antimony in the indentation *E* of the tube *AB* (Fig. 24) and heating them, the corresponding mirrors could be formed on the walls and moved, by heating in a current of hydrogen, to any suitable point. The action of the methyl radicals on zinc gave dimethyl zinc, which was condensed and its identity proved; with antimony two coloured organic compounds were isolated, and these were identified (Paneth and Loleit, 1935) as methyl derivatives of antimony, to which reference will be made later.

With tellurium the methyl radicals yield a deep-red liquid, dimethyl ditelluride, freezing at $-19{\cdot}5°$ C., and boiling at 196° C., with decomposition: this substance is sufficiently characteristic to prove a definite test for the presence of free methyl radicals. Another method for their identification has been

used by F. O. Rice and his co-workers (1934) : the radicals attack mercury to form what is believed to be $Hg(CH_3)_2$, and this can react with mercuric bromide to form the well-defined alkyl mercuric bromide, which can be identified by its melting point if pure, or if necessary by its X-ray spectrum. The method can also be used to detect methyl radicals, either alone or in a mixture of methyl and ethyl. The fragments produced by heating tetramethyl lead react with sodium to form sodium methyl, and with carbon tetraiodide to yield methyl iodide; the latter was characterised by its combination with quinoline, yielding a substance identical in properties with quinoline methiodide (Simons and Dull, 1933). Neither sodium nor carbon tetraiodide reacts with tetramethyl lead itself. Methyl and ethyl radicals attack arsenic mirrors to form the corresponding arsines : the latter can combine with mercuric chloride to yield the respective alkylarsine mercurichlorides, which have definite melting points. These facts have been used by Purcell and Pearson (1935) to identify methyl and ethyl radicals formed in photochemical decompositions.

It had been suggested that the removal of lead mirrors was due to atomic hydrogen ; this was shown, however, to be an inadequate explanation, since the presence of iron, which is a good catalyst for the combination of hydrogen atoms, had no effect on the experimental results. . It has also been shown (Pearson, Robinson and Stoddart, 1933) that atomic hydrogen actually does not attack lead mirrors, although it was at one time believed to do so. The hydrocarbons methane, ethylene, ethane, or acetylene, which might have resulted from the decomposition of tetramethyl lead, were also found to have no action on lead deposits, and so the conclusion appears inevitable that free methyl radicals are actually produced by heating certain organo-metallic compounds.

Half-Life Periods. In order to determine the rate of removal of methyl radicals by combination between themselves, after leaving the heated portion of the tube in which they are formed, the time (t_m) required for the radicals to remove a standard antimony mirror, situated at a known distance (d) from their point of origin is measured. From this distance, and the known streaming velocity of the carrier gas, the time (t) elapsing between

the formation of the radicals and their encounter with the antimony could be calculated, and the concentration of radicals remaining in the free state after the interval may be regarded as being determined by the reciprocal of the time required for removal of the standard mirror. The observations made in the original work of Paneth and Hofeditz (1929) are recorded in Table LXXIII.; the quantity A, the logarithm of which is given in the fourth column, is equal to $1000/t_m$, and is thus an approximate measure of the concentration of the radicals still free after time t secs. In the particular experiment, for which the results are given, a tube of 0·5 cm. diameter was used, the streaming velocity of the carrier gas was about 14 metres per sec., and the pressure 2 mm. of mercury.

TABLE LXXIII

Rate of Decay of Activity of Methyl Radicals.

d (cm.).	$t \times 10^3$ (sec.).	t_m (sec.).	log A.
4	2·9	4	2·40
8	5·7	11	1·96
13	9·3	20	1·70
18	12·9	25	1·60
22	15·7	45	1·35
28	20·0	70	1·16
33	23·6	100	1·00
37	26·4	150	0·82

When log A was plotted against t an almost straight line was obtained, indicating a unimolecular rate of disappearance of the radicals, the velocity constant (k) of the process being 118. The average life of the free methyl radicals is thus $1/k$, that is, $8{\cdot}4 \times 10^{-3}$ sec., and the half-life period, or the time required for half the radicals present at any instant to decompose, is 0·69 times the average life, and it is thus found to be $5{\cdot}8 \times 10^{-3}$ sec. This result implies that in about 0·04 sec. after their liberation, the concentration of methyl radicals is reduced to less than 1 per cent. of the original value, under the experimental conditions used, and so the failure of the earlier workers, as for example Frankland, to

detect them can be understood. Later investigation, by Rice, Johnston and Evering (1932) and by Paneth, Hofeditz and Wunsch (1935), has shown that the decay of the activity of methyl radicals is not strictly unimolecular, but a first order reaction is assumed as an approximation, since this permits of a simple expression of the stability of the radicals in the form of the half-life period.

Destruction of Methyl Radicals. It appears that the removal of free methyl radicals is in the main due to two causes: firstly, there is the possibility of reaction with the hydrogen gas used as the carrier for the tetramethyl lead vapour; thus

$$CH_3\cdot + H_2 = CH_4 + H;$$

and secondly, combination of the radicals may occur,

$$2CH_3\cdot = C_2H_6,$$

yielding ethane, or other hydrocarbons together with carbon, the formation of which is frequently observed, and perhaps hydrogen. The former of these processes occurs more readily at elevated temperatures, since the resulting gas contains larger amounts of methane under these conditions (see p. 404), but it also takes place to some extent at ordinary temperatures, for when hydrogen is the carrier gas the decomposition products contain much more methane (40 to 50 per cent.) than if a helium–neon mixture is employed (about 5 per cent.) or if a stream of tetramethyl lead vapour is heated alone. It may be noted that the reaction under consideration would make the removal of free radicals kinetically of the first order, because the hydrogen molecules are in great excess, and their concentration is virtually constant.

The union of two methyl radicals results in the liberation of a large amount of heat, probably about 80,000 cals. per gm.-mol. of ethane formed, and so can only occur either as the result of a ternary collision with another molecule capable of removing some of the excess energy, or else at the walls of the tube ("Recent Advances in Physical Chemistry," Chapter V.). Since the absolute concentration of methyl radicals in the gas is low, and the probability of a ternary collision is in any case very small, it is evident that the combination of the radicals in pairs must be

mainly a wall reaction. This conclusion is partly confirmed by the fact that the half-life period is appreciably increased by the use of a wider tube, for then the number of impacts with the tube walls in a given time is diminished.

The Accommodation Coefficient. It is perhaps surprising that the nature of the material of the tube appears to have little effect on the life of the radicals : this may be due to the accommodation coefficient (α) of most surfaces, providing the radicals do not react with them, being very small. The calculations of Paneth and Herzfeld (1931) show that α is approximately equal to $2kr/v$, where k is the velocity constant for the disappearance of the radicals, r is the radius of the tube, and v is the mean molecular speed of the radicals calculated by the usual kinetic theory expression. Under normal conditions the value of α is thus 10^{-3}, which means that of every thousand radicals striking the walls of the tube only one is captured, the others being reflected : it is this small accommodation coefficient which accounts for the retention of activity by methyl radicals even after passing along 30 cm. of tube. It may be recorded here that for a lead mirror α is unity ; that is to say, every methyl radical hitting the mirror is retained and eventually combines chemically, and a deposit 1 cm. long is able to prevent their further passage. Increase of temperature generally brings about a diminution in the accommodation coefficient, so that the extent of the reaction between two methyl groups to yield ethane, etc., should be diminished. The optimum life period of methyl radicals in a current of hydrogen gas is observed at about 350° C. ; above this temperature the increased reaction with the hydrogen outweighs the decreased combination of radicals at the walls. With helium as carrier gas, at 1 to 2 mm. pressure, however, the stability of the radicals increases up to 500° C. in a tube of 1 cm. diameter : the accommodation coefficient is then 10^{-4}, and the half-life period is increased to 0·1 sec., which is of the same order as for atomic hydrogen. Above 500° C. other reactions, in the gas phase, become important and the life period decreases. There is little doubt that by the use of appropriate experimental conditions the stability of the methyl radicals could be increased still further. Although it is, at first sight, somewhat

surprising that the life of an evanescent particle should be greater at a high than at a low temperature, the observations are readily accounted for when the nature of the reaction by which it is destroyed is understood. By cooling in liquid air the accommodation coefficient is increased almost to unity, and no methyl radicals are able to pass; on the walls combination takes place, perhaps to give ethane and other hydrocarbons.

Ethyl Radicals. Ethyl radicals may be obtained in the free state by the use of a method exactly analogous to that adopted for the production of methyl radicals. Paneth and Lautsch (1931) streamed hydrogen at high velocity over tetraethyl lead, maintained at a temperature of — 25° C., through a tube in which the gas was kept at a pressure of 1 to 3 mm. of mercury. On heating the tube, a lower temperature than that employed for the tetramethyl compound being sufficient, a deposit of lead was produced and ethyl radicals, with properties closely similar to those of the lower homologue, were liberated. These radicals were able to remove mirrors of lead, arsenic, zinc and cadmium placed as far as 40 cm. from their point of origin; they were shown to be ethyl, and not methyl, by definite identification of diethyl zinc, and its subsequent oxidation to $C_2H_5{\cdot}O{\cdot}O{\cdot}ZnC_2H_5$, which on hydrolysis with dilute acid gave ethyl alcohol. The action of the radicals on antimony yielded triethyl antimony, quite different in properties from the compound produced by the action of free methyl groups. The replacement of hydrogen by nitrogen, or by a mixture of helium and neon, as carrier gas did not affect the results. The half-life period of the ethyl radicals was measured in hydrogen, by the method already described, and found to be closely similar, viz., 4 to 5 $\times$ 10^{-3} sec., to that found for methyl radicals.

It is unnecessary to describe the properties of free ethyl in detail, as they are virtually identical with those of methyl, but it is nevertheless necessary on occasion to be able to distinguish between them. This can be done in a number of ways: there is, as already mentioned, a difference in the type of product obtainable by the action on antimony, but if a mixture of the radicals were suspected, it would not be easy to be certain that both were present. By X-ray examination of the alkyl mercuric bromides

(see p. 381), the presence of each radical can be detected, or alternatively application may be made of the fact that whereas tetramethylammonium iodide is insoluble in absolute alcohol, the trimethylethylammonium iodide is able to dissolve in this liquid. The experimental method (Rice and Evering, 1934) is to obtain the alkyl mercuric bromide, and to act on it with a solution of iodine in potassium iodide. The alkyl iodide formed in this manner is distilled off and excess of alcoholic trimethylamine added to the distillate : the reactions which then occur are

$$(CH_3)_3N + CH_3I = (CH_3)_4N{\cdot}I \text{ (insoluble)}$$

and

$$(CH_3)_3N + C_2H_5I = (CH_3)_3(C_2H_5)N{\cdot}I \text{ (soluble)}$$

This method of identification is regarded as being more certain than that depending on the use of the alkyl mercuric bromides alone, since the latter are liable to give erroneous results because of side reactions. According to Paneth and Loleit (1935), ethyl radicals begin to decompose at 600° C., yielding their lower homologue ; the decomposition is appreciable at 800° C., and complete at 950° C., and consequently the presence of methyl, together with ethyl, radicals may sometimes be a result of this disintegration.

Action of Free Radicals on Arsenic, Antimony and Bismuth. In the course of the investigation of the action of free methyl and ethyl on metallic mirrors, Paneth and Loilet (1935) isolated the antimony analogue of cacodyl, that is, bisdimethyl antimony, $[Sb(CH_3)_2]_2$, which chemists had frequently attempted to prepare, but unsuccessfully, by the use of more conventional methods. A striking property of this compound is the colour change it undergoes at the melting point, 17·5° C. : the bright red solid melts to a faintly yellow oil. If the solid is cooled in liquid air the colour is somewhat lighter than at room temperature : on warming the colour deepens gradually, becoming most intense just before melting, and then suddenly turns to the pale colour of the liquid. Evidence was also obtained that the corresponding bismuth cacodyl results when methyl radicals attack a heated mirror of this element. With free ethyl, bisdiethyl antimony, hitherto unknown, was also prepared, and in addition to already known methyl and

ethyl derivatives of arsenic, antimony and bismuth, a compound believed to be cyclic pentamethyl pentarsine, that is, $[As(CH_3)]_5$, was isolated.

Other Free Radicals. A number of attempts have been made to obtain propyl and butyl in the free state by heating the appropriate metallic alkyl derivatives, but without success. If the vapour of tetrapropyl lead is heated at 400° C., the minimum temperature at which decomposition to give a metallic mirror occurs, chemically active fragments are produced capable of attacking antimony and tin ; the products are, however, identical with those obtained from methyl radicals. It is evident that if propyl is formed it decomposes further immediately in the hot portion of the tube, probably according to the equation

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot} = CH_3{\cdot} + CH_2{:}CH_2.$$

If the propyl radical is to be isolated, a lower temperature must evidently be used and it appears, as will be seen later, that a photochemical method has been successful (p. 391). An interesting possibility is opened up by the discovery that certain organic gold compounds, namely, diethylmonocyanogold, $(C_2H_5)_2AuCN$, diethyldicyanodigold, $(C_2H_5)_2Au_2(CN)_2$, and monoethylenediaminotetraethyldicyanodigold, $(C_2H_5)_2Au(CN){\cdot}en{\cdot}(CN)Au(C_2H_5)_2$, on heating at temperatures from 80° to 120° C., gave the hydrocarbon butane, C_4H_{10} ; it appears probable that ethyl radicals are formed and these combine in pairs to give the butane (Burawoy, Gibson and Holt, 1935). The *n*-propyl derivatives corresponding to the two last mentioned organic gold compounds on heating at 120° C. gave hexane, C_6H_{12}, in an analogous manner, and it is not impossible that free propyl is an intermediate stage. By taking advantage of the low temperature of decomposition of the compounds under consideration, it may be found possible to obtain propyl radicals in the free state.

When tetra-*iso*-butyl lead vapour is passed through a tube heated to 300° C., methyl can be detected, but no butyl radicals ; the latter, like the propyl radicals, are evidently unstable and decompose. By heating di-*n*-butyl mercury at 350° to 450° C., at a pressure of 3 mm. of mercury, the resulting gas was found on

analysis to consist of approximately 60 per cent. of ethylene, 20 per cent. of *n*-butane, 10 per cent. of hexane, and 6 per cent. of ethane. This result suggests that if the *n*-butyl radicals are set free they decompose thus

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot} = CH_2 : CH_2 + CH_3{\cdot}CH_2{\cdot}$$

and the resulting ethyl radicals either combine in pairs to form butane, or unite with free butyl, thus

$$CH_3{\cdot}CH_2{\cdot} + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot} = C_6H_{14},$$

to give hexane (Frey and Hepp, 1933). Only a small proportion of methyl radicals can be present under these conditions, since the amount of ethane formed is so small, although Paneth and Lautsch (1935) report these as the main products from tetra-*iso*-butyl lead. Di-*sec.*-butyl mercury at 350° to 450° C. gives a gas containing 30 per cent. of octane, 20 per cent. each of *n*-butane and of 2 : 3-butylene, and 10 per cent. each of propylene and *iso*-pentane. The *sec.*-butyl radicals are probably more stable than *n*-butyl, since their life period is sufficient to permit a considerable proportion of the former to combine in pairs ; thus

$$2CH_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_3 = C_8H_{18}.$$

An important alternative process is evidently

$$2CH_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_3 = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot}CH{:}CH{\cdot}CH_3,$$

which would account for the almost equivalent amounts of butane and 2 : 3-butylene. Decomposition of the *sec.*-butyl radical to yield methyl radicals and propylene must also occur ; the former then unites with *sec.*-butyl to give *iso*-pentane :

$$CH_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_3 = CH_3{\cdot} + CH_3{\cdot}CH{:}CH_2$$

and $$CH_3{\cdot} + CH_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_3 = CH_3{\cdot}CH_2{\cdot}CH(CH_3)_2.$$

It will be seen that the more complex the radical the more easily does it decompose into simpler ones : thus ethyl disintegrates into methyl at about 800° C., whereas free propyl and butyl are apparently unstable at temperatures above 400° C.

Benzyl Radicals. Paneth and Lautsch (1935) heated the vapour

of tetrabenzyl tin and obtained clear evidence of the formation of benzyl radicals ; these attacked mirrors of selenium, tellurium and mercury. In the last instance the product was identified as dibenzyl mercury, and with tellurium yellow oily drops, apparently of dibenzyltelluride, were observed. The benzyl radicals resemble those of methyl and ethyl, in the fact that under the experimental conditions generally employed they have a longer half-life period at higher than at lower temperatures. In the absence of a carrier gas this was found, by observing the rate of removal of tellurium mirrors, as already described, to be 6×10^{-3} sec. at 200° C., assuming a unimolecular decomposition. In a cold tube the life of a benzyl radical is much shorter than that of methyl, possibly because of the greater accommodation coefficient of the tube for the former, but at higher temperatures they attain a similar order of stability.

Thermal Decomposition of Organic Compounds. A large variety of organic compounds, quite apart from metal alkyls, yield free radicals, generally methyl, on passing through a tube heated at a suitable point to a temperature of 800° to 1000° C. Hydrocarbons, alcohols, ketones, acids, esters and aldehydes have all been found to produce fragments capable of removing mirrors of lead, antimony or zinc, and which react with mercury to give alkyls identifiable by means of the corresponding alkyl mercuric bromides (Rice, Johnston and Evering, 1932). In order to detect the free radicals it is necessary to have the vapour at low pressure, about 1 to 2 mm. of mercury, and a rapid flow of gas ; under these conditions butane when heated at 800° to 1000° C. readily gives radicals, but if the pressure is increased to 40 to 70 mm. the decomposition products are unable to attack metallic mirrors placed within a few millimetres of the heated portion of the tube. At the higher pressures the number of collisions in the gas phase is increased ; the rate at which the free radicals are removed is then high, and their detection is not possible. Mention has already been made of the relative stability of the benzyl radical ; this can be obtained, and its presence confirmed, by heating dibenzyl ketone in a red-hot silica tube (Paneth, 1935).

Energy of Formation of Radicals. Before going on to describe

other methods, whereby free radicals have been obtained, mention will be made of an attempt to determine the activation energy of the process which results in the production of the radicals by heating (Rice and Johnston, 1934). Vapours of various organic substances were passed through the usual tube, the furnace being kept at a definite temperature, and the times taken to remove antimony mirrors at various distances from the furnace were measured. Extrapolation of these results to zero distance gave an approximate measure of the concentration of free radicals leaving the furnace, and consequently of their rate of formation at the particular temperature employed. By repeating the observations at another temperature, it is possible, by the familiar Arrhenius equation (p. 270), to calculate from the two rates the energy of activation for the production of free radicals. This method is, of course, highly approximate, since the radicals formed in the primary dissociation undoubtedly take part in other reactions besides the removal of metallic mirrors, but the results at least should be of the right order. Some of these are recorded in Table LXXIV., which gives the compounds heated, the linkage assumed to be broken in the production of the radicals, the experimentally determined activation energy, and finally the strength of the broken linkage as known from other sources.

TABLE LXXIV

Apparent Activation Energies for Formation of Free Radicals.

Compound Heated.	Linkage Broken.	Energy of Activation.	Bond Energy.
Methane . .	C—H	100,000 cals.	100,000 cals.
Ethane . .	C—C	75,900	85,000
Dimethyl ether .	C—O	81,100	85,000
Trimethylamine .	C—N	50,800	65,000

The close parallelism between the results in the last two columns suggests that the bond energy gives at least the order of the activation energy for the breaking of a particular link and the formation of free radicals. In view of the uncertainty with regard

to the decomposition of methane (*vide infra*) the result in this case may not be reliable, and the agreement of the apparent activation energy with the bond energy may be fortuitous.

Free Radicals by Photochemical Decomposition. By streaming the vapours of acetone, methyl ethyl ketone, or diethyl ketone at pressures of 0·5 to 2·5 mm. of mercury through a tube exposed to ultra-violet radiation from a mercury-vapour lamp, free methyl and ethyl radicals are produced (Pearson, 1934); these can be detected by their action on mirrors of lead, tellurium or antimony placed up to 25 cm. from the irradiated portion of the tube. The half-life period of the molecular fragments obtained from acetone, which proved to be methyl radicals, was measured by the method of Paneth and Hofeditz (p. 381) and found to be $5{\cdot}3 \times 10^{-3}$ sec. The graph of log A against t was almost exactly a straight line, indicating that the disappearance of the radicals was a first-order reaction. It is not certain whether $CH_3{\cdot}CO{\cdot}$ radicals are produced in addition to $CH_3{\cdot}$, by the photolysis of acetone, or whether both methyl groups split off simultaneously, but if the acetyl radicals are obtained as the first result of the absorption of radiation they probably decompose rapidly to give carbon monoxide and free methyl. It may be observed that ethane and carbon monoxide are the chief reaction products, the hydrocarbon resulting presumably from the combination of pairs of methyl radicals.

The fragments obtained from diethyl ketone, and identified as free ethyl by the corresponding alkylarsine mercurichloride, have a somewhat shorter half-life period, $3{\cdot}3 \times 10^{-3}$ sec., than those resulting from the photochemical decomposition of acetone; this result is in agreement with the work of Paneth and Lautsch (1931), who found the ethyl radical to be somewhat less stable than methyl. It is important to record the important claim that exposure of di-*n*-propyl ketone to the light from a mercury-vapour arc results in the formation of free *n*-propyl radicals, since all other methods to prepare them had previously failed (Pearson and Purcell, 1936). The half-life period of these radicals was found to be $2{\cdot}3 \times 10^{-3}$ sec. under the same conditions as those employed for ethyl and methyl, for which the results have been mentioned above. The products of photolysis of methyl butyl ketone failed to remove a

standard mirror, although signs were observed of the removal of a very thin deposit.

In the initial experiments, it appeared that no free radicals were produced by exposing acetaldehyde to ultra-violet light, but later work (Purcell and Pearson, 1935) showed this to be due to the deposition of a film of a polymer of the aldehyde on the metal mirror employed to indicate the presence of the radicals. By keeping a tellurium film warm, the condensation of the polymer was prevented and attack of the deposit was observed. The amount of methyl radicals formed by the irradiation of acetaldehyde is approximately only one-sixth that obtained from acetone for an equivalent extent of decomposition. The observations on the production, or otherwise, of free radicals by thermal or photo-

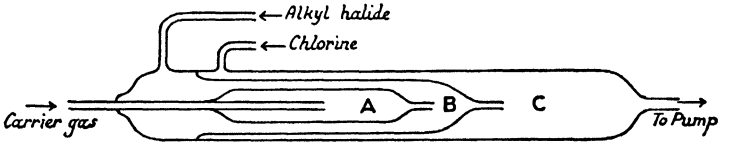


FIG. 25.—Diagrammatic representation of apparatus used by Polanyi and his co-workers to demonstrate the production of free radicals in "dilute" flames.

chemical action are of great importance in connection with the study of the particular reaction mechanisms, and the subject will be discussed subsequently in some detail.

Exposure of the vapours of tetraethyl lead or of dimethyl mercury to the radiation from a condensed spark, wavelength about 2000 Å., gives free radicals capable of removing metallic mirrors (Prileshajeva and Terenin, 1935); and similar evidence has been secured for the production of free methyl groups, by the exposure of tetramethyl lead to the light from a mercury-arc (Leighton and Mortensen, 1936). It is possible that a photochemical method of this kind may find some application in the production of the less stable radicals.

Free Radicals in Dilute Flames. The observations of Polanyi and his co-workers ("Recent Advances in Physical Chemistry," Chapter V.) on the reaction of sodium vapour with alkyl and aryl halides and other applications of the so-called "highly dilute"

flame, led them to suppose that free radicals were produced ; thus

$$R{\cdot}X + Na = NaX + R{\cdot}$$

where R is an alkyl radical and X a halogen atom. In order to verify this view the arrangement shown diagrammatically in Fig. 25 was employed (Polanyi, Horn and Style, 1934). The carrier gas, hydrogen, methane or nitrogen, at a pressure of 4 to 7 mm. of mercury, is passed at a rate of flow of 15 metres per sec. over liquid sodium in a container, *A*, heated to about 200° C. The alkali metal vapour, at a partial pressure of about 10^{-3} mm. of mercury, emerging through the nozzle meets with the alkyl halide and reaction occurs in the space *B*. If free radicals are produced by this interaction, then the rapid stream of carrier gas should carry them through the second nozzle into the space *C*, where they might be detected. When chlorine was introduced into *C*, by the side-tube shown, considerable quantities of hydrogen chloride were found if hydrogen was the carrier gas, and methyl bromide was the halide used to react with the sodium vapour : this must have resulted from the initial reaction

$$Na + CH_3Br = NaBr + CH_3{\cdot} ,$$

followed by the chain, set up by the methyl radicals,

$$CH_3{\cdot} + Cl_2 = CH_3Cl + Cl$$
$$Cl + H_2 = HCl + H$$
$$H + Cl_2 = HCl + Cl, \text{ etc.}$$

It is true that similar chains can be initiated by sodium atoms, but examination of the reaction tube, by means of a sodium resonance lamp, showed that no detectable quantity of these atoms entered the space *C* ; further, increasing the pressure of methyl bromide reduced markedly the length of the " flame " containing sodium, emerging from the first nozzle, but the effect on the production of hydrogen chloride was hardly noticeable. A more direct test for the presence of free radicals was applied by replacing the chlorine with iodine vapour borne by part of the carrier gas, in this case nitrogen or methane ; the radicals reacted with the iodine, thus

$$CH_3{\cdot} + I_2 = CH_3I + I,$$

and methyl and ethyl iodides were obtained and identified when employing methyl and ethyl bromides, respectively, to react with the sodium. The direct thermal reaction between the bromide and iodine was studied to see if the alkyl iodides arose in this way. No appreciable interaction was detected below 320° C., although in the actual experiments with sodium the highest yields of alkyl iodide were obtained when working at temperatures 100° lower. From the amount of methyl or ethyl iodide obtained the yield of free radicals, calculated on the basis of the quantity of sodium reacting, was of the order of 10 per cent. Although it has been stated that free phenyl radicals are obtainable in the same manner, by the action of sodium vapour on bromobenzene, Paneth (1935) failed to secure positive results, using the removal of metallic mirrors as a test for the presence of free radicals. With benzyl chloride, however, the sodium vapour being carried in a stream of helium, benzyl radicals were obtained and detected, 15 cm. from the reaction space, by their attack on tellurium mirrors.

Free Radicals in Discharge Tubes. It has been previously mentioned that positively charged fragments are found in discharge tubes : it has also been observed that in the passage of several organic compounds, as, for example, methyl and ethyl alcohols, acetaldehyde, acetone and acetic acid, through an electrical discharge tube—10,000 volts were used—particles capable of removing lead and antimony mirrors were obtained. The product of the discharge through acetone was shown to contain methyl radicals by their action on mercury, and subsequent identification by melting point and X-ray diffraction of methyl mercuric bromide. It was noted that the radicals resulting from the electrical discharge did not remove mirrors of zinc and cadmium ; this result was somewhat unexpected, since zinc, in particular, is generally easily attacked (Rice and Whalley, 1934). Attention may be called again to the fact that the fragments in the discharge tube may well carry an electrical charge, in which case they are not really identical with the free radicals obtained by thermal or photochemical decomposition.

The Methylene Radical. As far back as 1912 Staudinger and Kupfer allowed carbon monoxide, after passing through an

ethereal solution of diazomethane, CH_2N_2, to stream through a tube heated at 400° to 500° C., and so obtained the compound keten, $CH_2{:}CO$. This result suggests the primary decomposition of diazomethane into nitrogen and methylene,

$$CH_2N_2 = N_2 + CH_2{:}\ ,$$

followed by combination of the latter with the carrier gas to yield keten; thus,

$$CH_2{:} + CO = CO{:}CH_2.$$

This observation indicated the possibility of obtaining free methylene radicals from diazomethane, and successful experiments were carried out by Rice and Glasebrook (1934). The diazomethane was dissolved in dibutyl phthalate at − 80° C. and butane or ether served as carrier gas for passage through the furnace in a manner similar to that used for the preparation of free methyl and ethyl radicals. At temperatures between 350° and 550° C. the decomposition product is able to remove mirrors of tellurium, selenium, antimony and arsenic, but not those of zinc, lead or cadmium; it is probable that free methylene radicals are formed in the range of temperature specified, for methyl radicals attack all the metals mentioned. The product of the action on tellurium is a red, non-volatile solid, which deposits on the walls of the tube just beyond the mirror, having the composition $(CH_2Te)_n$; it is apparently a polymeric form of telluroformaldehyde, and is readily distinguishable from dimethyl-ditelluride, $CH_3Te{\cdot}TeCH_3$, the product from methyl radicals, which passes over into a liquid-air trap. The methylene radicals are said to be very reactive and have a half-life period of a few thousandths of a second. If the temperature of the furnace, through which the diazomethane is passed, is raised above 650 °C. methylene is no longer detectable, its place being taken by methyl radicals. It is possible that the methylene radicals attack the carrier gas under these conditions.

When diazoethane, $CH_3{\cdot}CHN_2$, is heated in a quartz tube at low pressures decomposition occurs but no free radicals have been detected, although under the same conditions the fragments obtained from diazomethane readily remove an antimony mirror.

The identifiable products in the former case are mainly ethylene, together with nitrogen, and so it appears that if the ethylidine radical, $CH_3 \cdot CH:$, is formed it must have a very short life, as it evidently rearranges itself immediately to give ethylene, $CH_2:CH_2$. No butylene is obtained, so it is evident that the ethylidine particles do not exist long enough for them to combine in pairs to any appreciable extent. Similar results have been found with acetaldazine, $CH_3 \cdot CH:N \cdot N:CH \cdot CH_3$, for on heating in a quartz bulb at 450° C. and a pressure of 450 mm. of mercury, about 60 per cent. of the product is ethylene; most of the remainder is a non-volatile oil of uncertain composition. The very low stability of the ethylidine radical is indicated by the fact that when carbon monoxide carrying diazoethane vapour is passed through a heated tube, no methyl keten is detected; this means that the reaction

$$CH_3 \cdot CH: + CO = CH_3 \cdot CH:CO$$

does not occur, although as previously mentioned the corresponding combination does take place with methylene radicals from diazomethane.

THERMAL DECOMPOSITION OF HYDROCARBONS

Thermal Decomposition of Methane. The possibility of the production of methylene as the first stage in the thermal decomposition of methane has been the subject of much controversy. Kassel (1933) studied the kinetics of the process in quartz bulbs at 700° to 800° C., and found the reaction to be homogeneous and of the first order; the energy of activation was determined as 79,000 cals. To account for the observations, it was suggested that the primary thermal process is

$$CH_4 = CH_2: + H_2 - 47{,}000 \text{ cals.},$$

which would not be incompatible with the observed activation energy; decomposition into $CH_3 \cdot$ and H would have required a much larger energy, since the process would have been endothermic to the extent of about 102,000 cals. Hence the first stable product of the decomposition of methane is apparently ethane (Storch, 1933), formed by the reaction

$$CH_4 + CH_2: = C_2H_6 + 36{,}000 \text{ cals.},$$

which being exothermic will probably occur with very little activation energy. Other reactions, such as the formation of ethylene, acetylene, carbon and hydrogen by the decomposition of ethane, etc., probably also occur.

Detection of Methylene Radicals. With the object of obtaining more definite information as to the primary products of the breakdown of methane, Belchetz and Rideal (1934, 1935) streamed the gas, at a pressure of 0·1 mm. of mercury, rapidly past either platinum or carbon filaments heated to high temperatures, and allowed the products to impinge on deposits of tellurium or iodine, placed 3 mm. away ; this short distance was adopted as being the probable mean free path of radicals under the experimental conditions, so that it was hoped to identify them before they had any opportunity of colliding with themselves or with other particles. With the platinum filament, at temperatures between 1100° and 1400° C., an iodine mirror was attacked and the product was identified as methylene iodide, indicating the presence of methylene radicals resulting from the primary decomposition of methane. No formation of either of the two methyl tellurides was observed at any temperature up to 1400° C., although atomic hydrogen was produced when the filament was hotter than 1200° C. Methylene iodide was also detected when methane was streamed past a carbon filament at 1745° C., and the fragments allowed to fall on iodine : no evidence was obtained for the formation of methyl iodide. Further proof that methylene radicals were present is the observation that the condensate on a cooled glass surface at − 80° C., reacts with bromine to give ethylene dibromide so that the liquid is ethylene formed by the union of two methylene groups.

Detection of Methyl Radicals. On the other hand, Rice and Dooley (1934) obtained only the characteristic dimethyl ditelluride as a consequence of the action of the radicals resulting from the passage of methane through a quartz tube, a portion of which was heated in a furnace to 1150° to 1200° C. No indication of the polymeric telluroformaldehyde was obtained. The presence of a piece of platinum foil in the heated part of the tube made no difference to the results. According to these authors, therefore,

not methylene but methyl radicals are the primary products of the thermal decomposition of methane. Belchetz and Rideal (1935) have confirmed the formation of methyl tellurides at a cold tellurium mirror, from methane after passage by a carbon filament at 1745° C., but this is considered to be a secondary product; for when the mirror was maintained at 100° C., so that the organic tellurium compound volatilised as it was formed, a polymer of telluroformaldehyde collected in a cooler part of the apparatus, but only a mere trace of methyl telluride resulted. With the filament at 1850° C. a large quantity of the telluroformaldehyde polymer was obtained, but the two methyl tellurides were also present in identifiable amounts. It is suggested, therefore, that the results are best interpreted by assuming that methylene radicals are first formed; these give with tellurium the compound $(TeCH_2)_n$: if this is not removed from the sphere of action it may be reduced by atomic hydrogen, or even by hot molecular hydrogen to give the methyl tellurides. At higher temperatures methyl radicals might result directly from the reaction between methylene and atomic hydrogen, or in another manner, since, as already mentioned, Rice and Glasebrook found that methylene at temperatures above 700° C. reacts with butane or ether to yield methyl radicals.

Kassel (1935) has considered the consequences of the two possibilities for the primary decomposition of methane from the standpoint of the reaction kinetics, and concludes that the experimental observations made by him in quartz bulbs, at about 800° C., cannot be reconciled with the formation of methyl radicals, although they can be explained by a mechanism involving methylene. It appears, therefore, that the balance of evidence favours the view that methylene results from the disintegration of methane at high temperatures, and considering their reactivity it is not surprising that Rice and Dooley failed to detect them under the experimental conditions they employed. The free methylene radicals would have an extremely short life at high temperatures, over 1000° C., and their detection is possible only within a very short distance of their place of origin.

Nature of the Methylene Radical. There are two other points

of interest in connection with the decomposition of methane which bear on the properties of methylene radicals. Kassel's measurements, as well as those of Storch, indicated an activation energy for the decomposition process of about 80,000 cals., Belchetz and Rideal obtained a value of 95,000 cals. using a carbon filament, and Rice and Dooley report 100,000 $\pm$ 6000 cals., for observations with methane flowing through a quartz tube. It is, therefore, not impossible that different reactions occur under the different experimental conditions, although the final products, mainly ethylene and hydrogen, appear to be the same. The following considerations may perhaps have some bearing on the subject. Under normal conditions the atom of carbon has two unpaired electron spins, its state being designated, from the spectroscopic standpoint, by the symbol ^3P : in this state carbon should be bivalent. In order to have a valency of four, that is, with four electrons having unpaired spins, it must be excited into the ^5S state, the excitation energy being approximately 37,000 cals.* If two hydrogen atoms, in the form of a molecule, are stripped from methane, without the carbon changing its energy state, the heat required would be about 100,000 cals. ; thus,

$$(a)\ CH_4 = CH_2(^5S) + H_2 - 100{,}000 \text{ cals.};$$

but if the carbon atom were able to change to the bivalent ^3P state the energy change would be 37,000 cals. less ; thus,

$$(b)\ CH_4 = CH_2(^3P) + H_2 - 63{,}000 \text{ cals.}$$

The energies of activation for the two processes would be of the order of the heat absorbed in the reactions, and consequently (*b*) would require less activation energy, and would take place more readily at low temperatures than would the alternative decomposition. It is possible that this may account for the different energies of activation observed under different conditions. The methylene derived from the ^3P carbon atom is strictly speaking not a free radical, but a relatively stable molecule, although the possibility of change of the carbon to the ^5S state would make it

* According to Van Vleck (1934) the energy difference between the carbon atoms taking part in bivalent and quadrivalent compounds is very much larger than this value.

much less stable than methane, yet more stable than the methyl radical. The methylene radical containing carbon in the ^5S state would, of course, be very reactive. The possibility of the existence of methylene in normal and excited states may perhaps account for the apparently conflicting observations made by different authors.

Thermal Decomposition of Ethane. The nature of the thermal decomposition of ethane, and of higher paraffins, is clearly related to that of methane disintegration; Rice and Dooley (1933) state that if pure ethane is passed through a quartz tube, a portion of which is heated in a furnace at 850° to 950° C., active particles, believed to be free methyl radicals, are produced; the energy of activation for the process yielding the radicals was found to be about 80,000 cals. The passage of ethane past a carbon filament at 1450° to 1800° C. gave Belchetz and Rideal (1935), on the other hand, no evidence for the formation of either methylene, ethylidine or methyl radicals; ethylene and hydrogen were, however, obtained in quantity. From observations at several temperatures the energy of activation of the decomposition process was calculated as 94,000 cals.; but since the normal value for the reaction

$$C_2H_6 = C_2H_4 + H_2$$

is accepted as about 73,000 cals., it appears that the heated carbon filament was playing some part in the reaction. The different experimental conditions may well be responsible for the divergence in the reported results. The strength of a C—C bond is of the order of 80,000 cals.; hence the observations of Rice and Dooley are not incompatible with the process

$$CH_3{\cdot}CH_3 = 2CH_3{\cdot}$$

It has been seen previously that the ethylidine radical tends to rearrange spontaneously to ethylene, and if, by analogy with the formation of methylene from methane, the aforementioned radical were the primary product of the decomposition of ethane, the production of ethylene is readily explained,

$$CH_3{\cdot}CH_3 = H_2 + CH_3{\cdot}CH{:} \rightarrow CH_2{:}CH_2.$$

If the carbon in the ethylidine radical is in the ^3P state the heat absorbed, and consequently the energy of activation of the primary process, would be of the order of 70,000 cals., in agreement with the observed results at low temperatures. The production of the alternative form of the radical, with the ^5S carbon atom, would require an activation energy of the order of 100,000 cals.; it may be significant that this is close to the figure obtained at a heated carbon filament over the temperature range of 1480° to 1730° C.

Thermal Decomposition of Propane and Butane. A disagreement, similar to that existing in connection with the decomposition of both methane and ethane, exists over the thermal disintegration of propane; the Rice technique, at temperatures about 900° C., is said to give methyl radicals almost exclusively, whereas the employment of a carbon filament is stated to yield no free radicals at 1650° C., although methylene radicals, detected by their action on a *warm* tellurium mirror, were observed when the filament temperature was raised to 1750° C. When a cold tellurium mirror or mercury was employed to react with the free radicals, *methyl* derivatives were formed in both cases: these are considered, as in the case of methane, to be secondary. It has also been shown that methylene radicals result from the decomposition of propylene; this is probably a rearrangement product of the propylidene radical formed initially. The stages in the decomposition of propane may then be formulated

$$CH_3{\cdot}CH_2{\cdot}CH_3 = H_2 + CH_3{\cdot}CH_2{\cdot}CH: \rightarrow CH_3{\cdot}CH{:}CH_2$$

$$CH_3{\cdot}CH{:}CH_2 = CH_2: + CH_3{\cdot}CH: \rightarrow CH_2{:}CH_2.$$

The combination of methylene with hydrogen would give methane, which constitutes an important proportion of the decomposition products of propane at temperatures about 700° C.; the formation of the other substances, viz., propylene, ethylene and hydrogen, is of course readily explained by the mechanism postulated; further reference to this subject will be made later. The thermal decomposition of butane gives methyl, and some ethyl, radicals according to Rice, Johnston and Evering (1932), but Belchetz and Rideal (1935) have detected only methylene:

the difference in the experimental conditions may once more account for the discrepancy. The observations, as far as the analysis of the reaction products is concerned, appear to favour a mechanism similar to that proposed for the decomposition of propane : at present, however, the matter is too speculative and uncertain to merit further discussion here.

FATE OF FREE RADICALS

Fate of Methyl Radicals : Decomposition of Tetramethyl Lead. Apart from the controversial instances just discussed, there are a number of cases in which the formation of free methyl and ethyl is not in doubt, and it is of interest to examine the products of these processes in order to obtain some information concerning the reactions of the radicals. Tetramethyl lead was kept in a closed vessel at atmospheric pressure and at a number of different temperatures ; the gases which accumulated were analysed, and the results obtained (Simons, McNamee and Hurd, 1931) are given in Table LXXV.

TABLE LXXV

Products of Decomposition of Tetramethyl Lead at Atmospheric Pressure.

Temp.	Percentage Composition of Gas.			
	265°	340°	440°	550° C.
Hydrogen . .	small	small	small	28·2
Methane . .	65·1	86·1	51·9	22·6
Ethane . .	21·7	7·8	38·9	22·6
Ethylene . .	small	small	small	25·6

These figures indicate that the methyl radicals, the primary decomposition products, are removed by at least two alternative processes. At low temperatures, large amounts of carbon, firmly deposited on the walls of the reaction vessel, are formed, and this suggests that decomposition is occurring at the walls. Such a

reaction may be an attack of the methyl radicals on the tetramethyl lead itself, yielding methane together with carbon and other solid products. Methane may also be formed by the interaction of methyl with other hydrocarbons in the gas, and also, together with carbon and other products, by a process involving mutual destruction of the radicals (Paneth, Hofeditz and Wunsch, 1935); thus

$$2CH_3\cdot = CH_4 + (C + H_2).$$

The formation of ethane, from two methyl radicals, must also occur either as a wall-reaction or as a result of a three-body collision in the gas phase; increase of temperature will diminish the former, but favour the latter to some extent. The ethylene probably arises from the process

$$2CH_3\cdot = C_2H_4 + H_2,$$

which can occur in a binary collision; this reaction apparently becomes effective only at about 500° C.

When tetramethyl lead vapour is passed through a heated zone, as in the Paneth method for preparing free radicals, the final reaction products are somewhat different; if the temperature of the tube is 550° C. the gas obtained contains 82·8 per cent. of ethane and 10·4 per cent. of methane, when the pressure of the organic lead compound is 0·5 mm. of mercury. At a pressure of 1·5 mm. the proportion of ethane is decreased and that of methane increased; raising the temperature, as far as 820° C., produces changes of the same type, and simultaneously appreciable quantities of ethylene and hydrogen make their appearance. It is evident that at the lower temperatures ethane results by the combination of ethyl radicals at the walls and, as is to be expected, this decreases as the temperature is raised: in view of the low pressure, the union in the gas phase, requiring a three-body collision, occurs only to a minute extent. The methane, ethylene and hydrogen increase with increasing temperature, as might be anticipated when the very small time which the radicals spend in the heated zone is taken into consideration.

When hydrogen is used as the carrier gas for tetramethyl lead the proportion of methane is much increased, especially if the radicals are kept at a relatively high temperature; in the experi-

ments of Paneth, Hofeditz and Wunsch (1935) the hydrogen, at 1·4 to 1·6 mm. of mercury pressure, charged with the vapour of the organic lead compound, was first passed through a section of the tube heated to about 900° C., and then through a length kept either at 20° or at 350° C. The ratio of the lead compound to hydrogen was varied in different experiments—the larger the ratio the greater the concentration of methyl radicals—and the resulting gases were collected. From the analysis of these gaseous products the proportions of the radicals disappearing as ethane and methane were determined; the results are recorded in Table LXXVI.

TABLE LXXVI

Products of Decomposition of Tetramethyl Lead with Hydrogen as Carrier.

Tube at 20° C.			Tube at 350° C.		
Ratio $Pb(CH_3)_4$ to H_2.	Ethane, per cent.	Methane, per cent.	Ratio $Pb(CH_3)_4$ to H_2.	Ethane, per cent.	Methane, per cent.
444	65·3	31·6	392	60·0	37·0
75	64·4	34·2	168	51·5	46·3
13	54·5	45·5	58	42·7	56·1
8·5	44·8	55·2	10·3	18·9	81·1

These results are most readily interpreted (cf. p. 383) by supposing that ethane is mainly formed at the walls, and that methane is the result of reaction of the radicals with hydrogen; the rate of the latter process should increase as the temperature is raised, whereas that of the former should decrease.

Fate of Ethyl Radicals : Decomposition of Tetraethyl Lead. The decomposition of tetraethyl lead has also been studied under various conditions, but unfortunately different from those employed for the methyl compound. When tetraethyl lead boils, at 220° C., it decomposes giving a gas containing 50 per cent. of ethane, 40 per cent. of ethylene and 4 per cent. of butane, but when the vapour is allowed to flow through a heated tube different

results are obtained, as indicated by the approximate figures given in Table LXXVII. (Meinert, 1933).

TABLE LXXVII

Products of Decomposition of Flowing Tetraethyl Lead Vapour.

Pressure, mm.	Temp.	Percentage Composition of Gas.			
		Ethane.	Ethylene.	Butane.	Hydrogen.
760	300° C.	46	12	35	6
760	425°	18	32	35	12
0·5	500°	18	33	34	14

A number of static experiments were also made in glass bulbs at different temperatures with the tetraethyl lead at various pressures. The general effect of temperature is much the same as in the flow method : increase of pressure, however, brings about a marked rise in the ethane concentration, with a corresponding fall in that of butane and of ethylene. Packing the bulbs with glass, so as to increase the surface area, also tends to increase the ethane at the expense of the butane and ethylene. The proportion of hydrogen, which did not exceed 10 per cent., was found to be greater the higher the temperature and the lower the pressure. The high yield of butane always present indicates that the main process for the removal of ethyl radicals primarily formed is the wall reaction, or three-body process,

$$2C_2H_5\cdot = C_4H_{10}.$$

It may be noted that when gas carrying ethyl radicals is passed through a liquid-air trap in order to condense the latter, the condensate contains at least 25 per cent. of *n*-butane.

At low temperatures and high pressures ethane probably results mainly from interaction of ethyl radicals with unchanged tetraethyl lead, or with hydrogen ; this might also be expected to be a wall reaction, and hence occurs more readily in a packed bulb. Ethylene can result in two ways, thus

$$2C_2H_5\cdot = 2C_2H_4 + H_2$$

and

$$2C_2H_5\cdot = C_2H_6 + C_2H_4 ;$$

the extent of both processes increases as the temperature is raised, and so they probably occur in the gas phase.

Tetraethyl lead has also been decomposed in benzene solution enclosed in a bomb at 260° to 275° C. (Cramer, 1935); ethane is then the main product together with appreciable amounts of ethylene, some butane and unsaturated liquid hydrocarbons. The predominant reaction is evidently the disproportionation

$$2C_2H_5\cdot = C_2H_4 + C_2H_6,$$

and a large fraction of the ethylene is evidently induced to polymerise by the ethyl radicals. Such induced polymerisation, to form higher unsaturated hydrocarbons, has been observed as a result of the decomposition of diethyl mercury in the presence of ethylene (Taylor and Jones, 1930): the mechanism of the process is by no means clear.

Decomposition of Other Metal Alkyls. The homogeneous decomposition of tetraethyl germanium vapour, at 440° C. and at a pressure slightly below atmospheric, is unimolecular and the gaseous products consist of 30 to 40 per cent. of ethane, about 10 per cent. each of hydrogen and methane, about 20 per cent. of ethylene, 14 per cent. of higher olefines, mainly propylene and butylene, and a small amount of propane. These results are not difficult to understand in view of those already discussed, and they suggest that ethyl radicals are formed in the primary stage of decomposition and that the hydrocarbons detected are derived from them (Geddes and Mack, 1930).

The products of decomposition of sodium ethyl might have been expected to bear some relationship to those from other metal-ethyls, but the position appears to be rendered complicated by the reactivity of the sodium. At temperatures of 90° to 100° C. the gas obtained consists of 85 per cent. of ethylene and 15 per cent. of ethane, there being a residue of sodium hydride, NaH; as a result of spontaneous decomposition at ordinary temperatures, however, there is relatively more ethane than ethylene, and the solid $Na_2C_2H_4$ remains (Carothers and Coffman, 1929).

Products of Electrolysis. In certain electrolyses it appears highly probable that free alkyl radicals are liberated primarily

at the anode and the nature of the gases evolved is therefore of some interest. Zinc ethyl is a non-conductor, but a solution in it of sodium ethyl conducts electricity, presumably because of the presence of the ions Na^+ and $C_2H_5^-$; if an attackable anode, *e.g.*, zinc, lead, antimony, bismuth, etc., is employed, then organo-metallic compounds are formed: thus, lead gives the tetraethyl compound. The electrical process therefore appears to be the discharge of ethyl ions, with the consequent formation of the free radicals. At anodes of platinum, copper or iron, which are not attacked, the resulting gases consist mainly of ethane and ethylene, so that the disproportionation reaction, already noted to occur under other conditions, is the main process by which the ethyl radicals disappear. A solution of the Grignard compound ethyl magnesium bromide, C_2H_5MgBr, in ether, when electrolysed yields at the anode a gas containing almost equal amounts of ethane and ethylene, together with a little hydrogen (about 1 per cent.). It seems that here also ethyl radicals are liberated; they react mainly in the manner already described, and to a small extent by the alternative process which yields ethylene and hydrogen (p. 405). Propyl magnesium bromide behaves similarly on electrolysis, and the anode gases consist of almost equal parts of propane and propylene; thus the propyl radicals, presumably formed at the electrode, react in the following manner

$$2C_3H_7\cdot = C_3H_8 + C_3H_6.$$

The products from methyl magnesium bromide are especially interesting: at low concentrations of the Grignard reagent, mostly methane (80 per cent.) and some unsaturated hydrocarbons, mainly *iso*-butylene, are obtained, but from more concentrated solutions the anode gases consist of almost pure ethane. In the latter case the main process is evidently the combination of methyl radicals in pairs. When dilute solutions are electrolysed the methyl radicals are presumably removed by the process

$$2CH_3\cdot = CH_4 + CH_2:,$$

followed by the polymerisation of the CH_2: radicals to yield *iso*-butylene. Since the latter compound contains four methylene groups, the theoretical composition of the gas should be 80 per cent.

methane and 20 per cent. *iso*-butylene, very close to that actually observed (Evans and Lee, 1934). It may be noted here that up to 5 per cent. of *iso*-butylene has been obtained in the gas from the low temperature decomposition of tetramethyl lead; this substance appears to be a definite product of the recombination of methyl radicals.

Electrolysis of Fatty Acids. Some analogy may be drawn between the gases obtained when simple free radicals combine with those resulting from the electrolysis of aqueous solutions of the salts of the lower fatty acids (Kolbe reaction). At low current densities the hydrocarbons obtained from sodium acetate solution contain a large proportion of methane, but as the current is increased ethane becomes the main product. It is reasonable to suppose, therefore, that acetate radicals, which are first formed, immediately decompose, possibly with the intermediate formation of acetyl peroxide, to yield carbon dioxide and methyl radicals, and the latter then unite to give either methane or ethane, as just explained, according to the conditions. The absence of *iso*-butylene from the gas rich in methane might well be due to its oxidation at the anode. When an aqueous solution of sodium propionate is electrolysed the anode gas generally contains a large proportion of ethylene: this is not unexpected if the ethyl radical is an intermediate stage in the process. The products of electrolysis of the salts of butyric, valeric and other acids, also contain quite a large proportion of unsaturated hydrocarbons, the presence of which could be readily explained by the decomposition of free radicals.

REACTIONS INVOLVING FREE RADICALS

Having considered the production and properties of simple free radicals it will be of interest to examine a number of reactions, thermal and photochemical, in which they probably play some part. As the results at present available in connection with the latter type of process appear to be capable of more simple interpretation, they will be considered first.

Photochemical Decomposition of Alkyl Iodides. The absorption

spectrum of ethyl iodide is continuous at wavelengths shorter than about 3000 Å. (Iredale, 1929), indicating that decomposition of the iodide is occurring; the energy of the absorption limit (see "Recent Advances in Physical Chemistry," Chapter VI.) corresponds to that required to break the C—I bond, about 68,000 cals., but is insufficient for breaking any of the other bonds in the molecule. Apparently the primary photochemical process brought about by light of wavelength less than 3000 Å. is to be represented by

$$C_2H_5I + \text{radiation} \rightarrow C_2H_5\cdot + I,$$

followed by

$$2I = I_2.$$

The quantum efficiency of the process, as measured by the production of molecular iodine, was found to be unity, in agreement with the mechanism proposed. It seems, therefore, that free ethyl radicals are formed. These react to some extent to reform ethyl iodide, but the production of a gas, consisting probably of ethane and ethylene, suggests that some, at least, combine in pairs in the familiar manner. The products and kinetics of the photochemical oxidation of ethyl iodide are also best explained by supposing that free ethyl radicals are involved (L. T. Jones and Bates, 1934). Methyl iodide shows similar behaviour on photochemical decomposition, and some confirmation of the intermediate formation of free methyl is indicated by the fact that on illuminating a mixture of the iodide and oxygen with the radiation from a mercury-vapour lamp, the chief reaction products (Bates and Spence, 1931) are water, methylal, *i.e.*, $CH_2(OCH_3)_2$, and a polymer of formaldehyde, viz., $(CH_2O)_n$. The essential oxidation reactions, following the primary decomposition of methyl iodide into methyl radicals and iodine, are

$$CH_3\cdot + O_2 = HO\cdot + CH_2O \rightarrow (CH_2O)_n$$
$$CH_3I + HO\cdot = CH_3OH + I$$
$$2CH_3OH + CH_2O = CH_2(OCH_3)_2 + H_2O.$$

Methyl iodide, after exposure to ultra-violet radiation, is able to expedite the ortho–para-hydrogen conversion; thus indicating

the presence of free radicals (West, 1935), as already explained (p. 124).

It appears that the presence of hydrogen molecules does not appreciably affect the photochemical decomposition of methyl iodide at 0° C., so that at this temperature the reaction

$$CH_3\cdot + H_2 = CH_4 + H$$

is inappreciable. In view of the conclusion already recorded (p. 385), that the velocity of this process increases as the temperature is raised, it must require an appreciable activation energy, and consequently it is not surprising to find it to be so slow at 0° C. as to be undetectable under the experimental conditions employed.

Photochemical Decomposition of Ketones. The photolysis of ketones with radiation of wavelength of 2200 to 3200 Å. has attracted considerable interest in recent years. The most straightforward case is that of methyl ethyl ketone: the products of photochemical decomposition indicate that the breakdown of the molecule occurs in two distinct ways, represented in the following manner.

$$CH_3\cdot CO\cdot C_2H_5$$

70 to 80 % | 20 to 30 %

$$\tfrac{1}{3}(C_2H_6 + C_3H_8 + C_4H_{10}) + CO \qquad \text{(probably) } C_2H_4 + CH_3\cdot CHO$$

It is evident that the most important primary process, in which about three-quarters of the ketone molecules eventually decomposed are involved, is

$$CH_3\cdot CO\cdot C_2H_5 + \text{radiation} \rightarrow CH_3\cdot + C_2H_5\cdot + CO.$$

This process may possibly occur in two stages, thus

$$CH_3\cdot CO\cdot C_2H_5 + \text{radiation} \rightarrow CH_3\cdot + C_2H_5\cdot CO\cdot$$

and

$$C_2H_5\cdot CO\cdot = C_2H_5\cdot + CO,$$

the decomposition of the $C_2H_5\cdot CO\cdot$ radical, requiring little, if any, activation energy, occuring almost simultaneously. The absorption of ultra-violet radiation by a ketone molecule takes place

almost exclusively at the C=O bond, and hence it is probable that the primary act of absorbed energy is to convert the carbonyl group into a carbon monoxide molecule ; thus

$$>C=O \rightarrow C\equiv O,$$

so that the two alkyl radicals are detached simultaneously. If the energy required for this process is 101,000 cals., and the energy of each of the C—C links, attaching $CH_3\cdot$ and $C_2H_5\cdot$ to the $>C=O$ group, is 90,000 cals., the energy absorbed in the complete process of decomposition of methyl ethyl ketone into carbon monoxide and methyl and ethyl radicals is only 79,000 cals. per gm.-mol. No matter how the radicals are formed, their production is not in doubt, as is shown by the observation that methyl ethyl ketone, after exposure to suitable radiation, is able to remove metallic mirrors, as already recorded (p. 391) ; the formation of equivalent amounts of methyl and ethyl radicals also readily accounts for the presence of ethane ($2CH_3\cdot$), propane ($CH_3\cdot + C_2H_5\cdot$) and butane ($2C_2H_5\cdot$) in almost equivalent amounts in the final products of photolysis. Simultaneously with the disintegration considered above, a relatively small proportion of the ketone yields acetaldehyde, presumably, and ethylene : the mechanism of this process is not clear.

Acetone. The products of the photochemical decomposition of acetone vapour according to Norrish and his co-workers are 46 per cent. carbon monoxide, 44 per cent. ethane and 9 per cent. methane, although Damon and Daniels (1933) found somewhat less ethane, but more methane, together with about 4 per cent. each of hydrogen and carbon dioxide. Theoretical consideration of the results suggests a primary decomposition, in one or two steps * according to the mechanism considered for methyl ethyl ketone, yielding methyl radicals ; thus

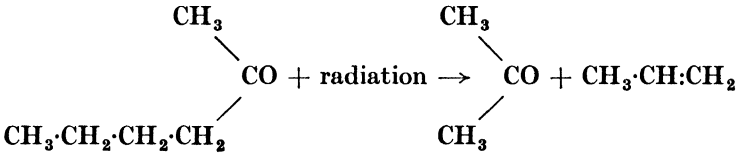
$$CH_3\cdot CO\cdot CH_3 + \text{radiation} \rightarrow 2CH_3\cdot + CO,$$

the combination of which gives mainly ethane and some methane. This result is in agreement with others mentioned previously : the

* The presence of diacetyl amongst the non-gaseous products of photolysis of acetone suggests that the $CH_3\cdot CO\cdot$ radical has appreciable stability, and that the splitting off of the $CH_3\cdot$ radicals occurs in two steps (Barak and Style, 1935).

proportion of methane to ethane formed is known to depend on the conditions, and this may account for the small discrepancies in the results obtained by different workers. The formation of free radicals is also confirmed by the observations on the removal of metallic mirrors (p. 391), and by the influence of the system in which the photolysis of acetone is occurring on the conversion of para-hydrogen to the ortho-form (p. 124).

Methyl Butyl Ketone. Methyl butyl ketone behaves in a manner different from that of the ketones just considered; the products of photochemical decomposition are acetone and propylene, with ethane and carbon monoxide, and 1 to 2 per cent. each of hydrogen and methane. No free radicals have been detected as a result of the exposure of the vapour to ultra-violet light (p. 391), and so the primary act of disintegration certainly does not involve the formation of methyl or ethyl radicals. The energy absorbed by the C=O linkage is transferred to that between the α and β carbon atoms, so that the reaction



takes place. It is not impossible that a propylidine radical, $CH_3{\cdot}CH_2{\cdot}CH{:}$, may be formed as the result of the initial breaking of the C—C bond, but this would immediately rearrange itself to propylene (see p. 401). If the exposure to radiation is not prolonged, the acetone formed at the same time does not undergo decomposition and can be isolated from the reaction products in amounts similar to that of the propylene. The small quantities of ethane, carbon monoxide, etc., detected as a consequence of photolysis may result from decomposition of the acetone or from an alternative disintegration of the methyl butyl ketone into methyl and butyl radicals and carbon monoxide.

Di-Propyl Ketone. When di-*n*-propyl ketone is decomposed photochemically free propyl radicals are formed and can be detected by their action on metallic mirrors (p. 391). The amount

of hexane produced indicates that about 37 per cent. of the ketone undergoes primary dissociation according to the equation

$$\begin{matrix} CH_3{\cdot}CH_2{\cdot}CH_2 \\ \qquad\quad \diagdown \\ \qquad\quad CO \\ \qquad\quad \diagup \\ CH_3{\cdot}CH_2{\cdot}CH_2 \end{matrix} + \text{radiation} \longrightarrow 2CH_3{\cdot}CH_2{\cdot}CH_2{\cdot} + CO,$$

the remainder breaking at the bond between α and β carbon atoms, as is the case almost exclusively with methyl butyl ketone, so that the products are ethylene and methyl propyl ketone. Continued irradiation results in the decomposition of the latter in the same two alternative ways : one giving free methyl and propyl radicals, which combine to yield ethane ($2CH_3{\cdot}$), butane ($CH_3{\cdot} + C_3H_7{\cdot}$) and hexane ($2C_3H_7{\cdot}$), and the other giving ethylene and acetone (Bamford and Norrish, 1935). Further experiments on the photolysis of *cyclo*heptanone and of *cyclo*hexanone give results showing that the elimination of carbon monoxide is the primary process, but as these have no direct bearing on the production or properties of free radicals they need not be discussed here.

Photochemical Decomposition of Aldehydes. Decomposition of the vapour of aldehydes by light is in some ways different from that of ketones : for a number of aldehydes, *e.g.*, formaldehyde, acetaldehyde, propaldehyde, *iso*-butyric aldehyde and benzaldehyde, the products indicate that the essential reaction is

$$\begin{matrix} R \\ \diagdown \\ CO \\ \diagup \\ H \end{matrix} + \text{radiation} \longrightarrow RH + CO.$$

The R radical and hydrogen atom are evidently split off simultaneously : this process would require 92,000 cals., assuming as before the change from $>C=O$ to a carbon monoxide molecule necessitates 101,000 cals., and that the energies of the C—H and C—C bonds are 103,000 and 90,000 cals., respectively. Before the R and H particles can escape from the vicinity of one another, they combine to form the hydrocarbon RH. If, however, R and H

had an appreciable separate existence the substances R_2 and H_2, in addition to RH, might be expected amongst the decomposition products : actually only small amounts are obtained under suitable conditions (Leighton and Blacet, 1932, 1933), so that normally a relatively small amount of the aldehyde yields free radicals having a separate existence. The work of Pearson and Purcell (1935), already described (p. 392), shows the proportion of acetaldehyde decomposing to give the methyl radical to be actually only about one-sixth that of acetone for the same light absorption. At high temperatures, *e.g.*, at 300° C., it appears very probable, however, that much larger amounts of free methyl are present amongst the products of the photolysis of acetaldehyde : the quantum efficiency is then about 300, compared with a value of 0·03 at low temperatures. It is evident that a chain mechanism is operative and the following series of reactions leads to a kinetic expression in agreement with the experimental results (Leermakers, 1934).

$$\begin{aligned} CH_3{\cdot}CHO + \text{radiation} &\rightarrow CH_3{\cdot} + {\cdot}CHO \\ {\cdot}CHO &= CO + H \\ CH_3{\cdot} + CH_3{\cdot}CHO &= CH_4 + CH_3{\cdot}CO{\cdot} \\ H + CH_3{\cdot}CHO &= H_2 + CH_3{\cdot}CO{\cdot} \\ CH_3{\cdot}CO{\cdot} &= CH_3{\cdot} + CO. \end{aligned}$$

The regeneration of the methyl radical in the last step sets up the chain which leads to the high quantum efficiency. The main processes for the breaking of chains are

$$2CH_3{\cdot} = C_2H_6$$

and

$$CH_3{\cdot} + {\cdot}CHO = CH_3{\cdot}CHO,$$

both of which would probably have to be wall reactions or three-body collisions. It may be mentioned in conclusion that no free radicals have been detected in the photochemical decomposition of propaldehyde vapour, either by the Paneth method or by the effect on the conversion of para- to ortho-hydrogen.

Free Radicals in Thermal Reactions. The possibility of the existence of free radicals of appreciable life, as applied to the concepts of chain reactions, has led to some interesting results,

Suppose a molecule M_1 decomposes primarily into a simple radical R_1 and another molecule M_2, thus

$$(1)\ M_1 \rightarrow M_2 + R_1;$$

this process, since it involves the breaking of a bond, *e.g.*, C—C or C—O, will require a large activation energy, probably of the order of 90,000 cals., and hence will be relatively slow, except at very high temperatures. Suppose the radical R_1 reacts with a molecule of M_1, removing a hydrogen atom from the latter, and leaving another radical R_2; thus

$$(2)\ R_1 + M_1 \rightarrow R_1H + R_2.$$

The radical R_2 contains one hydrogen atom less than M_1, and so if the latter is a relatively large molecule, R_2 will also be large, and so it may easily decompose, splitting off the original radical R_1, and generating another molecule M_3, thus

$$(3)\ R_2 \rightarrow M_3 + R_1.$$

Since the radical R_1 used up in reaction (2) is regenerated in (3), the process will have a chain mechanism. The breaking of chains may occur in three ways:

$$(4)\ R_1 + R_2 \rightarrow M_4$$
$$(5)\ R_1 + R_1 \rightarrow M_5$$
and $$(6)\ R_2 + R_2 \rightarrow M_6.$$

Of these only (4) and (5) need be considered, for M_6 will be a complex molecule, since R_2 will generally be large, as seen above, and so will tend to dissociate into $2R_2$. The relative extents to which the processes (4) and (5) occur depend on the energies of activation of the stages involved in the chain, and two important cases must be considered. If the activation energy for the process (2) is relatively small, about 15,000 cals., and that of (3) relatively high, about 40,000 cals., then reaction (2) will tend to occur more rapidly than (3); hence the stationary concentration of R_2 radicals will be large relative to that of R_1 radicals, the latter being removed readily, but regenerated slowly in the chain process. The reaction chains will consequently be broken mainly by reaction (4), since (5) is likely to occur less frequently. In the early stages of the process a steady state will be reached when the R_1

radicals are formed by reactions (1) and (3), and removed by reactions (2) and (4) at the same rate : that is

$$k_1[M_1] + k_3[R_2] = k_2[R_1][M_1] + k_4[R_1][R_2] \quad . \quad . \quad . \quad \text{(i.)}$$

the k terms representing the velocity constants of the process denoted by the numerical suffix. Similarly, in the stationary state, the rate of production of R_2 by reaction (2) will be equal to the rate of removal by (3) and (4) ; hence,

$$k_2[R_1]\,[M_1] = k_3[R_2] + k_4[R_1][R_2] \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

By adding equations (i.) and (ii.) it is seen that

$$k_1[M_1] - 2k_4[R_1][R_2] = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

Returning to equation (i.) : if the chain is fairly long, then $k_1[M_1]$ and $k_4[R_1][R_2]$ may be neglected in comparison with the other terms, since k_1 is in any case small, because of the high activation energy required for reaction (1) ; and the fact that there is little tendency for the chains to be broken means that k_4 is also small. It is then possible to write

$$k_3[R_2] - k_2[R_1][M_1] = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv.)}$$

From the equations (iii.) and (iv.), it follows that

$$[R_1] = \sqrt{k_1k_3/2k_2k_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

and

$$[R_2] = [M_1]\sqrt{k_1k_2/2k_3k_4} \quad . \quad . \quad . \quad . \quad \text{(vi.)}$$

The total rate of decomposition of the molecules M_1 will depend on the reactions (1) and (2), and hence

$$-\frac{d[M_1]}{dt} = k_1[M_1] + k_2[R_1][M_1] \quad . \quad . \quad . \quad \text{(vii.)}$$

$$= k_1[M_1]\,(1 + \sqrt{k_2k_3/2k_1k_4}) \quad . \quad . \quad \text{(viii.)}$$

inserting the value of $[R_1]$ from equation (v.). Since k_1 and k_4 are both small, as already shown, the second term in the round bracket is greater than unity, so that equation (viii.) may be approximated to the form

$$-\frac{d[M_1]}{dt} = k[M_1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ix.)}$$

where k is a constant made up of k_1, k_2, k_3 and k_4. This is the equation for a reaction of the first order, and the surprising result is obtained that a chain process, involving free radicals, may apparently be kinetically unimolecular (Rice and Herzfeld, 1934). By following an exactly similar procedure, on the assumption that the energy of activation of reaction (2) is large, whereas that of (3) is smaller, so that the concentration of R_1 is greater than that of R_2, and process (5) is the chief chain-breaking reaction, it would have been found that

$$-\frac{d[M_1]}{dt} = k'[M_1]^{3/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (x.)$$

where k' involves k_1, k_2 and k_5. The order of the reaction would thus be apparently 1·5.

Free Radicals and Unimolecular Reactions. It would be of interest now to see to what extent some unimolecular decompositions might have chain mechanisms: the method applied is to introduce the free radicals, which may be expected to act as chain carriers, into the gas under consideration, and to study the results. The decomposition of azomethane is unimolecular and homogeneous, but its breakdown is only slight at 275° C. Unfortunately, it was not found possible to introduce methyl radicals at this temperature, but ethyl radicals might be expected to have the same chain-carrying properties, and these can be obtained by heating tetraethyl lead at 250° to 275° C. If this substance is mixed with azomethane there is still no appreciable reaction at 275° C., suggesting that in this case, at least, a chain mechanism is not operative, although free radicals are certainly formed in the decomposition when it does take place on heating to a higher temperature (Leermakers, 1933). In the unimolecular decomposition of dimethyl ether vapour, on the other hand, a chain reaction appears to occur. At temperatures below 400° C. the ether is stable and is not decomposed photochemically, but if some acetone is added and the mixture exposed to ultra-violet radiation, a first order decomposition of the ether sets in. The photolysis of acetone, which is not a chain reaction, produces methyl radicals, and these presumably start up the chain resulting

in the splitting up of the dimethyl ether (Leermakers, 1934). This chain may be represented :

$$CH_3\cdot + CH_3{\cdot}O{\cdot}CH_3 = CH_4 + CH_3{\cdot}O{\cdot}CH_2\cdot$$
$$CH_3{\cdot}O{\cdot}CH_2\cdot = CH_2O + CH_3\cdot$$

Formaldehyde, CH_2O, is known to be an intermediate product, but it finally breaks down to give carbon monoxide and hydrogen, which, together with methane, are the main results of the decomposition of dimethyl ether. The reaction mechanism proposed also accounts for the products being equivalent amounts of methane, carbon monoxide and hydrogen. The chains should be broken by the combination of two methyl radicals, but there appears to be no record of any ethane; as the reaction chains are long, about 200 molecules of ether being decomposed for every quantum of light absorbed by the acetone, its amount would be small. Although the results recorded and the speculations based on them are interesting, it must not be assumed that they prove the normal homogeneous thermal decomposition of dimethyl ether to be a chain reaction : there is a possibility, but by no means a certainty.

Staveley and Hinshelwood (1936) have recently made the important discovery that nitric oxide is able, in many instances, to react with free radicals and so break reaction chains in which they take part ; it is thus possible to determine whether a particular reaction involves a free radical chain mechanism by studying the influence on the velocity of the presence of small amounts of nitric oxide. Working in this way it has been shown that the unimolecular thermal decomposition of propaldehyde and of diethyl ether both involve reaction chains ; these are, however, apparently of short length and do not account for the whole of the decomposition.

The chain-reaction concept has been applied to calculate the proportions of various products that should be obtained with some ethers, *e.g.*, methyl ethyl, diethyl and methyl propyl ethers : in the former two cases the calculations agree, at least qualitatively, with the experimental results, but with the last mentioned ether there are considerable discrepancies (Rice, 1934).

Decomposition of Ethyl Nitrite. The passage of ethyl nitrite vapour at low pressure (about 1 mm.) through a heated tube results in decomposition, known from other work to be unimolecular, but the products have no action on cold metallic mirrors; if carbon dioxide is used as carrier gas, so that the partial pressure of the nitrite is reduced to one-hundredth part of its previous value, antimony mirrors are readily removed after the gas has passed through the furnace at 425° C. The energy of activation of the radical-forming process is about 35,000 cals., which is of the same order as that found for the over-all decomposition, 37,700 cals. (Steacie and Shaw, 1934). This low energy must mean the breaking of an N—O bond, so that the primary process is

$$CH_3{\cdot}CH_2{\cdot}ONO = CH_3{\cdot}CH_2{\cdot}O{\cdot} + NO$$

followed by

$$CH_3{\cdot}CH_2{\cdot}O{\cdot} + CH_3{\cdot}CH_2{\cdot}ONO = CH_3{\cdot}CH_2{\cdot}OH + CH_3{\cdot}CH(ONO){\cdot}$$

and

$$CH_3{\cdot}CH(ONO){\cdot} = CH_3{\cdot}CHO + NO,$$

which would account for the experimental products, nitric oxide, ethyl alcohol, and acetaldehyde, obtained by Steacie and Shaw at 270 mm. of mercury pressure. At low partial pressures, however, in the flow experiments, it appears that the second step is

$$CH_3{\cdot}CH_2{\cdot}O{\cdot} = CH_3{\cdot} + CH_2O$$

followed by $CH_3{\cdot} + CH_3{\cdot}CH_2{\cdot}ONO = CH_4 + CH_3{\cdot}CH(ONO){\cdot}$

and, as before, $CH_3{\cdot}CH(ONO){\cdot} = CH_3{\cdot}CHO + NO,$

so that in addition to the formation of free radicals, formaldehyde and methane should be produced instead of alcohol (Rice and Rodowskas, 1935).

It must be pointed out that although free radicals may result in the decomposition of ethyl nitrite there is no evidence of a chain reaction: it is presumably a homogeneous normal unimolecular process. The thermal decomposition of acetone, which is of the first order, produces free methyl radicals, and a chain mechanism was proposed by Rice and Herzfeld (1934): further experimental work has shown, however, that this suggestion is probably incorrect (Winkler and Hinshelwood, 1935). The introduction of

methyl radicals, from dimethyl mercury, into acetone at 350° to 400° C., which is well below the usual decomposition temperature, does not result in the production of any keten, the normal primary product from acetone. Acetonylacetone is formed in amounts corresponding to the amounts of dimethyl mercury added (Rice, Rodowskas and Lewis, 1934). Similarly, although methyl radicals are produced in the photochemical decomposition of acetone, this is also not a chain reaction.

Decomposition of Acetaldehyde. The thermal decomposition of acetaldehyde presents a case of some interest: the process is homogeneous, and has an apparent order of 1·5, suggesting a chain reaction of the type of which mention has been already made (p. 417); thus, using analogous numbers for the various stages,

$$(1) \qquad CH_3{\cdot}CHO = CH_3{\cdot} + {\cdot}CHO$$
$$(2) \quad CH_3{\cdot} + CH_3{\cdot}CHO = CH_4 + CH_3{\cdot}CO{\cdot}$$
$$(3) \qquad CH_3{\cdot}CO{\cdot} = CO + CH_3{\cdot}$$

The energy of activation for process (2) is probably greater than for (3), so that the chains are broken by the combination of $CH_3{\cdot}$ radicals; thus

$$(5) \quad 2CH_3{\cdot} = C_2H_6.$$

Making the assumptions previously indicated, this series of reactions would make the rate of decomposition of acetaldehyde proportional to the 1·5 power of the concentration (Rice and Herzfeld, 1934).

Although the aldehyde is quite stable at 300° C. the introduction of azomethane brings about decomposition, presumably as the result of a chain reaction set up by methyl radicals; each chain appears to involve about thirty molecules (Allen and Sickman, 1934). The rate of the process is proportional to the acetaldehyde concentration and to the square-root of that of the azomethane, which is in agreement with the requirements of a chain mechanism set up by the radicals produced from the latter compound. Packing the reaction vessel with glass tubing reduces the rate of reaction, since the chains are more readily broken. The decomposition of acetaldehyde induced by methyl radicals is evidently a

chain process, but this does not prove the normal thermal decomposition at 550° C. also to be a chain reaction. Winkler and Hinshelwood (1935) found no appreciable change in the rate of decomposition as a result of a sixteen-fold increase of the surface area of the reaction vessel: they conclude, therefore, that under the experimental conditions employed, namely, 562° C. and 240 mm. of mercury initial pressure, there is no appreciable chain process.* The acetaldehyde decomposition reaction is notoriously complicated (Travers, 1935), and for the present an open mind must be preserved on the subject, especially as the photolytic decomposition is believed to involve chain propagation, at least at temperatures above 300° C. It may be noted that the introduction of azomethane into propaldehyde has a very much smaller effect than with acetaldehyde: in the photochemical decomposition also, there is evidence, from the removal of metallic mirrors and the influence on the conversion of para- to ortho-hydrogen, that very few free radicals are present.

Thermal Decomposition of Hydrocarbons. The possibility that particles, such as CH, CH_2 or CH_3, having a transient existence, are produced in the thermal decomposition of hydrocarbons was considered as far back as 1908 (Bone and Coward), for only in this way was it reasonably possible to account for the nature of the reaction products. The question has been re-opened by F. O. Rice in recent years, who, by considering the strengths of various bonds in a hydrocarbon, and assuming that the activation energy required to break any particular bond is equal to the energy of the linkage, has been able to account both qualitatively and quantitatively for the thermal decomposition products of a number of paraffin hydrocarbons. The arguments are based on the assumption that the first stage in the disintegration is the splitting off of a methyl or an ethyl radical, or both, and that these then set up chain reactions; it is also postulated that the hydrocarbon residue, after removal of the simple radical, gives up a hydrogen atom, leaving an olefine. The hydrogen atom can then also set up

* Using the method involving nitric oxide (p. 418), Staveley and Hinshelwood (1936) have shown that at 560° C. the thermal decomposition of acetaldehyde does not involve free radical chains.

a chain of reactions. For example, with propane the first stages are

$$CH_3{\cdot}CH_2{\cdot}CH_3 = CH_3{\cdot}CH_2{\cdot} + CH_3{\cdot}$$

and

$$CH_3{\cdot}CH_2{\cdot} = CH_2{:}CH_2 + H,$$

followed by the chains

$$CH_3{\cdot}CH_2{\cdot}CH_3 + CH_3{\cdot} = CH_4 + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}$$

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot} = CH_2{:}CH_2 + CH_3{\cdot} \text{ etc.},$$

and

$$CH_3{\cdot}CH_2{\cdot}CH_3 + H = H_2 + CH_3{\cdot}\dot{C}H{\cdot}CH_3$$

$$CH_3{\cdot}\dot{C}H{\cdot}CH_3 = CH_3{\cdot}CH{:}CH_2 + H \text{ etc.}$$

Other secondary processes have been suggested, but these need not be considered here. By taking the probability of the breaking of any particular bond as $e^{-E/RT}$, where E is the bond strength, an empirical allowance being made for the differences when the same bond, *e.g.*, C—H, is in different positions, Rice has calculated the proportions of various compounds to be expected. The computations indicated, for example, that the products of decomposition of propane at 650° C. should consist of 19·5 per cent. of each of hydrogen and propylene, and 30·5 per cent. each of methane and ethylene: the experimental results of Pease and Durgan (1930) showed that 21 to 22 per cent. of hydrogen, 28 to 31 per cent. of methane, and a total of 47 to 50 per cent. of ethylene and propylene were obtained. The agreement between calculated and experimental results is very striking, but it must not be forgotten that the former depend to a great extent on the assumed bond energies, which may very well be in error. Further, it is not certain that the formation of methyl radicals is the primary stage of the decomposition of simple hydrocarbons (p. 401), and Kassel (1933) states that the nature and amounts of the various final products can be accounted for by assuming that two hydrogen atoms, either from the 1 : 4, 1 : 2 or 1 : 1 carbon atoms, are split off to varying extents, the process being the reverse of hydrogenation.

In concluding this chapter it is desirable to point out the necessity for caution in postulating the formation of free radicals as intermediates in many reactions, as has been frequently, and perhaps unjustifiably, done. The splitting off of a radical involves the breaking of a bond, such as C—C, C—O or C—N, the

energies of which are about 85,000, 85,000 and 65,000 cals., respectively: the activation energy of the process must consequently be of this order. The requisite energy can either be supplied by radiation, when short-wave light is necessary, or else it must be supplied thermally: in the latter case it can be readily shown that with such high activation energies there will be no appreciable reaction, resulting in radical formation, at temperatures below 700° C. For processes which are rapid well below this temperature it is unlikely that radicals are formed, unless the linkage which is broken happens to be a weak one, as is the case with the C—metal bond in the metallic alkyls, or if there is a rearrangement in the molecule when the radical splits off resulting in the liberation of energy and a gain of stability.

REFERENCES

BATES and SPENCE. *J. Amer. Chem. Soc.*, 1931, **53**, 1689.
BELCHETZ and RIDEAL. *Ibid.*, 1935, **57**, 1168, 2466; *Trans. Faraday Soc.*, 1934, **30**, 170.
BONE. *Ibid.*, 1934, **30**, 148.
BURAWOY, GIBSON and HOLT. *J. Chem. Soc.*, 1935, 1024.
CAROTHERS and COFFMAN. *J. Amer. Chem. Soc.*, 1929, **51**, 588.
CRAMER. *Ibid.*, 1934, **56**, 1234.
FREY. *Ibid.*, 1933, **55**, 3357; *Ind. Eng. Chem.*, 1934, **26**, 198.
EVANS and LEE. *J. Amer. Chem. Soc.*, 1934, **56**, 654.
GEDDES and MACK. *Ibid.*, 1930, **52**, 4372.
HEIN *et al.* *Z. anorg. Chem.*, 1924, **141**, 161; 1926, **158**, 153.
IREDALE. *J. Phys. Chem.*, 1929, **33**, 290.
JONES and BATES. *J. Amer. Chem. Soc.*, 1934, **56**, 2285.
KASSEL. *Ibid.*, 1932, **54**, 3949; 1935, **57**, 833.
LEERMAKERS. *Ibid.*, 1933, **55**, 4508; 1934, **56**, 1537, 1899.
LEIGHTON *et al.* *Ibid.*, 1932, **54**, 3165; 1933, **55**, 1766; 1936, **58**, 448.
MEINERT. *Ibid.*, 1933, **55**, 979.
NORRISH *et al.* *Trans. Faraday Soc.*, 1931, **27**, 391, 404; 1934, **30**, 103; *J. Chem. Soc.*, 1932, 1518; 1933, 119; 1934, 874, 1456; 1935, 455, 1504.
PANETH *et al.* *Berichte*, 1929, **62**, 1335; 1931, **64**, 2702, 2708; *Z. Elektrochem.*, 1931, **37**, 577; *Trans. Faraday Soc.*, 1934, **30**, 179; *J. Chem. Soc.*, 1935, 366, 372, 380.
PEARSON. *Ibid.*, 1934, 1718; 1935, 1151; 1936, 253; *Ann. Reports Chem. Soc.*, 1934, **31**, 251*.
PEASE and DURGAN. *J. Amer. Chem. Soc.*, 1930, **52**, 1262.
POLANYI *et al.* *Trans. Faraday Soc.*, 1934, **30**, 187, 189*.
PRILESHAJEVA and TERENIN. *Ibid.*, 1935, **31**, 1483.
RICE *et al.* *J. Amer. Chem. Soc.*, 1931, **53**, 1959; 1932, **54**, 3529; 1933, **55**, 3035, 4245, 4329; 1934, **56**, 284, 741, 1311, 2105, 2381, 2472, 2497, 2747; 1935, **57**, 350, 1384; *Trans. Faraday Soc.*, 1934, **30**, 152*; *Chem. Reviews*, 1935, **17**, 53*; "Aliphatic Free Radicals," 1935*.

SICKMAN and ALLEN. *J. Amer. Chem. Soc.*, 1934, **56**, 1251, 2031.
SIMONS *et al.* *Ibid.*, 1933, **55**, 2696, 3898 ; *J. Physical Chem.*, 1933, **36**, 939.
STAVELEY and HINSHELWOOD. *Proc. Roy. Soc.*, 1936, [*A*], **154**, 335 ; *J. Chem. Soc.*, 1936, 812, 818.
STORCH. *J. Amer. Chem. Soc.*, 1932, **54**, 4188.
TAYLOR. *Trans. Faraday Soc.*, 1925, **21**, 560 ; *J. Amer. Chem. Soc.*, 1930, **52**, 111.
TRAVERS *et al.* *Proc. Roy. Soc.*, 1932, [*A*], **126**, 1 ; *J. Soc. Chem. Ind.*, 1934, **53**, 321T.
WEST. *J. Amer. Chem. Soc.*, 1935, **57**, 1391.
WILLIAMSON. *Ibid.*, 1934, **56**, 2216.
WINKLER. *Trans. Faraday Soc.*, 1935, **31**, 761.
WINKLER and HINSHELWOOD. *Proc. Roy. Soc.*, 1935, [*A*], **149**, 340, 355.

* Review papers and books, wherein further references can be found, are marked with an asterisk.

INDEX

Accommodation coefficient, 384
Acetaldehyde, photochemical decomposition, 414
thermal decomposition, 420
influence of free radicals, 420
Acetanilide, solubility, 266
Acetone, enolisation, 334
photochemical decomposition, 411
Acetone–iodine reaction, 287, 334, 337 *et seq.*, 365
Acid–base catalysis, 328 *et seq.*
Acid, definition, 330
Acidity function, 371
Activated complex, or state, 307 *et seq.*
theory of reaction velocity, 307–318
and steric restriction, 315
and the Brønsted-Bjerrum equation, 362
and the collision theory, 314, 318
and the probability factor, 313
and unimolecular reactions, 316, 324
atomic reactions, 311
molecular reactions, 312
molecule–ion reactions, 313
reactions in solution, 322–326
zero-point energy of, 170
Activation energy, 269 *et seq.*, 289, 311
in hydrogen and deuterium reactions, 166–169
variation in a series, 303 *et seq.*
viscosity correction, 289, 292
Activity, in velocity equations, 355 *et seq.*
Aldehydes, photochemical decomposition, 408
Alpha-particles, disintegration by, 1, 5, 33
production of, 19, 21, 22
in artificial radioactivity, 45
radioactivity induced by, 30, 33
Ammonia, photochemical decomposition, 182
Ammonium cyanate, isomeric change, 370
salt formation, 284, 302, 303
solvent effects, 318–321
Anti-neutrino, 18
Arrhenius equation, 270, 289
Artificial radioactivity. *See* Radioactivity.
Association and solubility, 250
Asymmetric-top molecules, 80
Atomic radii, 212. *See also* Inter-atomic distances.
reactions, 311
weights, 28
Azo-group configuration, 223

Balmer spectra, 137
Base, definition, 320
Beckmann change, kinetics, 286, 295
Benzoic acid, solubility, 263
Benzyl radicals, 388, 389
Bimolecular reactions, catalysed, 284
in solution, 284, 297
solvent effects, 318–321, 324
Bond distances. *See* Inter-atomic distances.
Boron amide, structure, 221
Bose-Einstein statistics, 57, 132–134
Brønsted-Bjerrum equation, 361 *et seq.*
tests of, 367–370
Butane, thermal decomposition, 401
Butyl radicals, 387

Cane sugar. *See* Sucrose.
Carbon dioxide, structure, 219
disulphide, structure, 219
–carbon bond distances, 217
–halogen bond distances, 216
monoxide, entropy, 88
–nitrogen bond distances, 220
–oxygen bond distances, 218–219

Carbon suboxide, structure, 219
–sulphur bond distances, 219
tetrachloride, electron diffraction, 192, 198, 200, 207
Catalysis, acid–base, 328 *et seq.*
by ions and molecules, 333, 337 *et seq.*
dual theory, 329
salt effects, 363–375
primary, 364
secondary, 373
Catalytic catenary, 346–351
coefficients, 337 *et seq.*
and dissociation constant, 351–355
Chain reactions, 415–423
Chlorine monoxide, decomposition, 273
Chloroacetanilide, isomeric change, 356–359
Cis- and **Trans-** compounds, 223
Cloud-tracks, 2, 13, 23
Cohesive energy, 249
Collision number, 268, 311
in solution, 276, 288
solvent–solute, 292, 300
ternary, with solvent, 297
theory of reaction, 268, 281
Compound formation and reaction velocity, 326
and solubility, 252
Conservation of energy and mass, 3, 19, 21, 25
Critical complex, 307. *See also* Activated complex.
Critical solution temperature, 253, 257
Cyanide radical, partition function, 67
Cyanogen, structure, 220

Degrees of freedom, 269, 271, 295, 312
Deuterium, 136 *et seq.*
analysis of mixtures, 140–143
atomic spectra, 137, 154
compounds, melting and boiling points, 165
properties, 164 *et seq.*
spectra, 166
zero-point energies, 150, 151
concentration by electrolysis, 138, 143–153
by evaporation, 137
discovery of, 136–137
dissociation, 162
heat of, 158
entropy, 161
Deuterium, heat capacity, 160
molecular spectra, 155
molecule, partition function, 66, 73
zero-point energy, 157
ortho–para inter-conversion, 159, 169
ratio, 158
oxide, density, 141
freezing point, 143
preparation, 138, 145
properties, 163
reactions in, 185
physical properties, 154
reactions with ammonia, 182
with ethylene, 182
with halogens, 177–179
with hydrogen, 171–174
with nitrous oxide, 181
with oxygen, 179
with water, 174–177
zero-point energy in, 166 *et seq.*
separation by chemical methods, 153
by electrolysis, 144–152
theory of, 149
" tunnel " effect in, 150
by other methods, 143, 152–153
factor, 146
spectroscopic constants, 156
" tunnel " effect in reactions, 150, 169
Deuterons, disintegration by, 22
production of, 4
radioactivity induced by, 34
Diacetone alcohol, decomposition, 359
Diazo-group, configuration, 223
Dibromobenzene, solubility, 262, 266
Dibromosuccinic acid, decomposition, 295
Diffraction by electrons. *See* Electron diffraction.
Disintegration by alpha-particles, 1, 5
by deutrons, 22
by neutrons, 10, 11, 12
by protons, 19, 21
simultaneous, 26
Double-bond distances, 218

Electron diffraction, or scattering, 189 *et seq.*
by atoms, 202

Electron diffraction, coherent, 191
equation for, 191, 193, 203
experimental study, 195
incoherent, 194
intensity curves, 197
inter-atomic distances from, 209 *et seq.*
maxima and minima, 194, 200
molecular configuration from, 221 *et seq.*
radial distribution, 206
valency angles from, 224 *et seq.*
positive. *See* Positron.
waves, 189
Electronic partition function, 62
Energy, free, 59
functions, 59, 91
internal, 55, 57
levels in nucleus, 5
of activation. *See* Activation.
total, 59
translational, 54
values from spectroscopic data, 69
zero-point energy, 57, 59, 60, 157
Entropy, calculation of, 84
change and reaction velocity, 316–318
internal, 57
rotational, 85
total, 58
translational, 54
vibrational, 86
virtual, 75
Equilibrium constant and reaction velocity, 309 *et seq.*
calculation, 59–61, 89–95
Esterification, catalysed, 299, 305
mechanism of, 306
steric hindrance in, 306
Esters, hydrolysis. *See* Hydrolysis.
solubility, 254, 258
Ethane, thermal decomposition, 400
Ethers, decomposition, 417–418
Ethylene iodide, decomposition, 275
Ethylidine radicals, 396, 400
Ethyl nitrite, decomposition, 419
radicals, fate of, 404
identification, 385
production, 385
reactions, 386, 404
Exchange reactions, 94, 174–179, 185

Fermi-Dirac statistics, 57, 132–134
Free radicals, 377 *et seq.*
Free radicals, activation energy of formation, 389
and chain reactions, 414–423
by thermal decomposition, 378, 385, 389, 417–420
fate of, 402–408
in decomposition of hydrocarbons, 396–402, 421
in dilute flames, 392
in discharge tubes, 394
in electrolysis, 406–408
in photochemical reactions, 391, 408–414
in thermal reactions, 414–423
in unimolecular reactions, 417–420
reactions involving, 408–423

Gas reactions, kinetics, 269, 273–277
Gases, solubility. *See* Solubility.
Geiger-Müller counter, 32
Glucose, mutarotation. *See* Mutarotation.

Halides, structure of, 213
Halogen bond distances, 210, 213–215, 216
Heat capacity, calculation, 81–83
internal, 57
of reaction, calculation, 95
Helium, in disintegration, 11
mass 3 isotope, 20
atomic weight, 21
Hydrocarbons, thermal decomposition, 396–402, 421
Hydrogen atoms, partition function, 63
detection, 121
dissociation, 89, 116
heat of, 158
entropy, 84–85, 111
equilibrium, 100, 107
forms of, 98
heavy. *See* Deuterium.
ortho- and para-, analysis of mixtures, 116
discovery, 98–101
free energy changes, 114
heat capacities, 108
inter-conversion, 117–130
energy of, 113
heterogeneous, 126
applications, 130
high temperature, 128

Hydrogen, ortho- and para-, interconversion, heterogeneous, low temperature, 127
homogeneous, 117
applications, 121, 123
by atomic hydrogen, 119
by electrical discharge, 120
by paramagnetic substances, 122
catalysed, 122
high temperature, 118
in liquid and solid, 124
photo-sensitised, 121
magnetic properties, 106
ratios, at equilibrium, 106
spectra, 103–104
vapour pressure, 105
para-, preparation, 101
stability, 102
Hydrolysis, 299, 304, 335, 336
salt effects in, 374
Hydroxyl radicals, partition function, 68

Ideal systems, 231, 235, 238
Induced radioactivity. *See* Radioactivity.
Internal heat of vaporisation, 247, 249
Internal pressure, 243
and reaction velocity, 320, 324
and solubility, 243
measurement, 245–247
tables, 248, 265
Iodine, dissociation, 92
solubility, 260
Ionic reactions, 369, 372
strength, 363
Ions, catalytic action, 337 *et seq.*
Iso-catalytic systems, 344
Iso-molecular reactions, 93
Isotopes, bombardment of, 20
effect in partition function, 75
Isotopic exchange equilibria, 94

Ketones, photochemical decomposition, 391, 410–413
Kinetic-activation theory, 269
-activity factor, 362

Liquids, solubility. *See* Solubility.
Lyman bands, 103

Mass and energy equivalence, 4
reduced, 156, 309
–spectroscopic atomic weights, 29
estimation of deuterium, 140
Maxwell-Boltzmann law, 55
Metal alkyls, decomposition, 378, 385, 387, 389, 392, 402–406
Methane thermal decomposition, 396
Methyl radicals, fate of, 402–404
from methane, 397
half-life, 381
identification, 380
production, 378, 392
reactions, 383, 386
Methylene radicals, 394
from methane, 397
identification, 395
nature of, 398
Miscibility of liquids, partial, 236
Molecular configurations, 221 *et seq.*
Mutarotation, of beryllium benzoyl camphor, 285
of glucose, 285, 331
of tetramethyl glucose, 332

Naphthalene, solubility, 261
Negative proton, 18
Neutrino, 17
Neutron, 5 *et seq.*
constitution of, 9
discovery of, 5
disintegration by, 10
mass, 8, 9, 28
production, 7, 8, 25–27
radioactivity induced by, 41
velocity, 6
Nickel carbonyl configuration, 224
Nitramide, decomposition of, 336
Nitric oxide, dissociation, 90
entropy, 88
heat capacity, 81
partition function, 64, 68
Nitrogen pentoxide, decomposition, 276, 360
valency angle, 227
Nitrous oxide, entropy, 87
structure, 220

Nuclear energy levels, 5
spin factors, 66, 67, 72–75
functions, 62
spins, 98, 131
reversal, 99
Nucleus, constitution of, 9
stability of, 47

Orientation effects in reaction velocity, 280, 372
Ortho- and **Para-states,** 83, 131. *See also* Hydrogen and Deuterium.
distribution of, 133
Oxygen atoms, partition function, 63
molecules, heat capacity, 83
partition function, 66
nuclear spin, 66, 134
valency angle, 225
Ozone, decomposition, catalysed, 274
unimolecular, 294

Partition function, and reaction velocity, 309–314
defined, 57
electronic, 62, 71
internal approximate, 71, 92
isotope effect in, 75
nuclear spin, 62
factor in, 66, 67, 72–75
of atoms, 62
of diatomic molecules, 64
of monatomic molecules, 62
of polyatomic molecules, 76
rotational, 65 *et seq.*, 71, 77–80, 312, 313
translational, 61, 309, 312, 313
vibrational, 64, 71, 77, 86, 312, 313
Photochemical reactions, and free radicals, 391, 408–414
in solution, 277
Pinene, isomerisation, 277
Polarity and solubility, 257
Positron, discovery, 12–13
mass, 14
production by cosmic rays, 13
by γ-rays, 14
in artificial radioactivity, 31 *et seq.*
theory of formation, 15
Potential energy curves, 167, 308
Probability factor and entropy, 316
in reaction velocity, 313–318, 324–325
variation, 303
Propane, thermal decomposition, 401
Propyl radicals, 387, 401, 412
Protium, 139
Proton, acceptors and donors, 333
in acid–base equilibria, 330
Protons, disintegration by, 19, 21
formation in disintegration, 1, 24
negative, 18
radioactivity induced by, 34
Pseudo-ideal systems, 254

Radioactivity, applications, 49–51
artificial, 30–51
by alpha-particles, 30, 33
by deuterons, 34
by neutrons, 41
by protons, 34
discovery of, 30
emission of alpha-particles in, 45
of γ-rays in, 39
of electrons in, 33, 48
of positrons in, 31, 33, 47
in organic compounds, 44
rate of decay, 32
Radio-aluminium, identification, 40
-carbon, identification, 37
-chlorine, identification, 33
-elements, separation by electrical field, 32
by γ-ray recoil, 44
short life, 40
-fluorine, identification, 39
-iodine, applications, 50
-nitrogen, identification, 32, 35
-oxygen, identification, 38
-phosphorus, application, 51
identification, 31
-sodium, identification, 39
Raoult equation, 229, 230
and solubility, 231
deviations from, 234, 236, 242, 250
Reactions in solution, 269 *et seq.*
and activated complex theory, 322 *et seq.*
and gas, comparison, 273–276, 323
bimolecular, 282
molecule–ion, 283

Reactions in solution, photochemical, 277
slow, 278, 283, 325
solvent influence, 318 *et seq.*
and cohesion, 320
and polarity, 320
and solubility, 325
unimolecular, 276, 290
Rotational energy of polyatomic molecules, 77–80
partition function, 65
statistical weight, 65

Sackur-Tetrode equation, 54
St. John effect, 201
Salt effects in catalysis, 363–375
primary, 364
secondary, 373
Scattering of electrons. *See* Electron.
Separation coefficient, or factor, 146
Slow reactions, 278, 283, 313–318, 325
Solid state, orientation in, 87
rotation in, 112
Solids, solubility. *See* Solubility.
Solubility and association, 250
and compound formation, 252
and critical temperature, 233
and melting point, 240
and Raoult's equation, 231, 235, 238
and reaction velocity, 325, 360
and temperature, 33, 241
and vapour pressure, 229, 232
calculation of, 249
of gases, 231, 254
of liquids, 235, 257
of solids, 238, 259
prediction, 263
theory of, 243 *et seq.*
Solutions, ideal, 235
irregular, 250–254
regular, 248–250, 259
Solvent, choice of, 266
effect in reaction velocity, 318 *et seq.*
Spherical rotator, 78
State sum. *See* Partition function.
Statistical methods, 53 *et seq.*
weight, defined, 56
rotational, 65
Steric hindrance in esterification, 306
restriction, 315
Sucrose, inversion, 328
kinetics, 371
Sulphur, solubility, 260
Summation methods, 70, 71
of state. *See* Partition function.
Symmetrical-top molecules, 79
Symmetry number, 73, 74

Ternary collisions, 297
Thermal reactions and free radicals, 414 *et seq.*
Transition state. *See* Activated complex.
Translational energy. *See* Energy.
entropy, 54
partition function, 61, 309
Trans-uranium elements, 45
Triazo-group, configuration, 222
Trichloroacetate ion, decomposition, 322
Triethylsulphonium bromide, decomposition, 295
Trinitrobenzoic acid, decomposition, 295, 322
Triple-bond distances, 288
Tritium, atomic weight, 27
concentration by electrolysis, 186
formation in disintegration, 10, 26

Unimolecular reactions, and the activated complex theory, 316, 324
in gases, 271
and free radicals, 417–423
in solution, 276, 290–297
effect of solvent, 276, 324
with solvent as reactant, 296
Unstable species, 12, 30. *See also* Radioactivity.
Uranium, neutron bombardment of, 45
Urea, kinetics of formation, 370

Van't Hoff-Dimroth equation, 359
Velocity constant calculation of, 309

Walden inversion, mechanism, 50
Water, heavy, 138–139. *See also* Deuterium oxide.

X-ray diffraction, 189–191

Zero-point energy. *See* Energy.
factor, 61, 309, 310

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