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THE KINETICS OF
REACTIONS
IN
SOLUTION

THE KINETICS OF REACTIONS IN SOLUTION

BY

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PREFACE

I HAVE written this book to show that reactions in solution, that is to say, the phenomena of chemical change in general, can profitably be examined in the light of the kinetic theory —an hypothesis which seven years ago was focused upon, but believed to be restricted to, the comparatively few reactions which occur in gases. It will be observed that the theory brings coherence to a large number of diversified phenomena, and can therefore be said to have stood the pragmatic test.

In a book of this scope, reference can be made to but a relatively small number of chemical reactions. The examples selected are, however, sufficiently representative to portray a miniature, but not too distorted a picture of the whole field of inquiry. I have purposely applied the kinetic theory in a simple manner, partly on account of the inherent difficulties which the problem obviously presents, and partly because the task is primarily to decide whether the principle underlying its application is valid. It may prove to be otherwise: I have made every effort to indicate clearly what are the theoretical explorations, and what the actual facts.

The willing assistance given by my friends and colleagues has turned what might be tedium into joy. Mr. C. N. Hinshelwood has been my guide on all matters that perplexed me. My indebtedness to him is great. To acknowledge it is my pleasant duty; to assess it would be difficult, and is fortunately not necessary. Dr. N. V. Sidgwick kindly read the manuscript and made valuable suggestions. I have also had the advantage of discussing certain problems with Professor T. M. Lowry and Professor M. Polanyi, and with Professor W. C. M. Lewis at almost terminal intervals since I left his laboratory. Mr. E. J. Bowen, Dr. R. O. Griffith,

and Dr. A. McKeown have kept me from erring in matters photochemical. Finally I wish to thank Professor J. N. Brönsted, Professor H. M. Dawson, Professor V. K. La Mer, and Dr. Hermann Schmid for enlightenment on obscure points and for permission to reproduce various diagrams.

E. A. M.-H.

OXFORD, 1933.

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I

THE COLLISION THEORY

CANE sugar dissolved in water may be kept almost indefinitely at room temperatures. In the presence of decinormal acid, however, the sugar is split up at a measurable velocity into glucose and fructose, and the chemical change is virtually complete at the end of one day. These well-known facts raise two questions. Why does the reaction not take place in the absence of acid? Why does the reaction in its presence end in a day rather than in a second or a century? The science of chemical kinetics sets out to answer these and similar questions by a formal treatment of all the factors which may determine or influence the velocity of chemical change. In the development of the subject, the inversion of cane sugar occupies a prominent position as the first chemical change to be timed* and one of the first reactions in the study of which the importance of temperature was realized.† This reaction has attracted the attention of hundreds of investigators, and several publications dealing with its kinetics have appeared annually since the days of Wilhelmy.‡ That its precise mechanism is not yet fully understood will serve as a sufficiently illuminating comment upon the difficulties attending the problem in general.

Although chemical dynamics had its origin in the study of reactions in solution, its growth, except along empirical lines, was disappointingly slow until the advantages of investigating gaseous reactions were realized. For these, the kinetic theory of gases furnishes precise information about the various types of motions executed by the reacting molecules. Within the last fifteen years, the advancement of knowledge concerning chemical change in general has been

* Wilhelmy, *Pogg. Annalen*, **81**, 413, (1850).

† Arrhenius, *Z. physikal. Chem.*, **4**, 226, (1889).

‡ 140 papers had appeared by 1906 (Caldwell, *British Association Reports*, p. 351).

quite startling. Most of the phenomena relating to gaseous reactions have received ample interpretation in the light of the few simple hypotheses which form the basis of the collision theory of chemical reaction rate. It is the object of this book to show that chemical changes in solution also offer every prospect of being understood from the same standpoint. Fundamentally there can be no difference between the essential facts of chemical changes in the two systems. Recent experiments upon reactions studied in the presence and in the absence of a solvent bear striking testimony to the truth of this statement. In general, however, the solvent exerts a definite influence upon the velocity at which molecules dissolved in it undergo chemical transformation. The real problem, therefore, resolves itself into an application of the general principles of chemical kinetics to reactions in solution, and the discovery of logical means of extending such principles when in their unmodified form they prove to be insufficient to account for the facts.

DEVELOPMENT OF THE COLLISION THEORY OF CHEMICAL REACTION RATE

The rate at which any chemical change proceeds is denoted by its velocity constant (k), which simply defines the number of molecules reacting per unit time when the concentration of each reactant is unity. Arrhenius observed that the variation with temperature of the velocity constant for a number of reactions could be represented by an equation of the type:

$$\ln k = B - \frac{A}{T},$$

in which T is the absolute temperature, and the constants A and B are specific for each reaction. He recognized the similarity of this equation with the van 't Hoff isochore, which connects the equilibrium constant (K) of a chemical reaction with the increase ($+U$) in internal energy:

$$\ln K = \text{const.} - \frac{U}{RT},$$

and by analogy suggested the existence of an equilibrium between 'passive' molecules of the reacting species and 'active' molecules formed from normal molecules by the absorption of energy. It had hitherto been difficult to understand why only a few molecules—rather than all of them—reacted at any given time. The answer given by Arrhenius is that only that small fraction of the total number of molecules which is active at any instant can react; chemical changes are not instantaneous because the special distribution of energy required takes a finite time. The general correctness of this view has since received overwhelming confirmation.

The superiority of the Arrhenius equation over a number of similar empirical relations which were advanced almost simultaneously with it lay in the fact that it not only fulfilled the object for which it was created—i.e. to summarize in convenient mathematical form the relation between the velocity constant and temperature—but also threw light on the actual mechanism of chemical change. By putting $B = \ln Z$ and $A = E/R$, the equation can be rewritten in the form

$$k = Ze^{-E/RT}.$$

The fraction $e^{-E/RT}$ according to the Maxwell-Boltzmann distribution law is proportional to the number of molecules possessing energy E in excess of the average energy characteristic of all the molecules at the temperature T. The Arrhenius equation, therefore, implies that the number of molecules reacting per unit time is proportional to the number of molecules which are in a suitably activated condition. Other processes are known besides chemical transformation which obey the same law, for example:

number of molecules of a liquid evaporating per second $= \text{const.} \times e^{-\lambda/RT}$ (λ is the latent heat of vaporization),

number of electrons emitted by incandescent solids per second $= \text{const.} \times e^{-W/RT}$ (W is the thermionic energy),

number of molecules undergoing chemical change per second $= \text{const.} \times e^{-E/RT}$.

E is termed the critical increment of energy, or simply the critical increment, and is determinable experimentally by plotting the logarithm of the velocity constant against the reciprocal of the absolute temperature: the slope of the line, multiplied by the gas constant R (1·985 calories per degree) gives the value of E in calories per gram molecule. It will become clear subsequently that E is not always equal to the energy of activation, and has to be corrected in various ways. The necessity for introducing such modifications in no way detracts from the general truth of the Arrhenius hypothesis. Activation of some kind is a necessary step in almost all chemical changes which proceed with measurable velocity. This is the foundation of chemical dynamics.

After the introduction of the Arrhenius hypothesis, the most important contribution to the subject is the calculation in absolute measure of velocity constants in gaseous systems. This was achieved by Lewis,* who showed that the rates observed by Bodenstein† for the decomposition of hydrogen iodide and for the reverse reaction are in agreement with those calculated by means of the relation:

number of molecules reacting per second
$= \text{number of molecules colliding per second} \times e^{-E/RT}$.

It was at that time believed that the molecules became activated by radiation, but in the light of subsequent work Lewis's conclusion can best be re-stated as follows: the rate at which molecules decompose in gaseous bimolecular reactions is equal to the rate at which they collide with critical energies. These considerations thus give a physical meaning to the term Z of the Arrhenius equation: for bimolecular reactions it is simply the collision frequency. Before, however,

* *Trans. Chem. Soc.*, **113**, 471, (1918). Lewis's calculations were independently confirmed by Herzfeld (*Z. Elektrochem.*, **25**, 301, (1919)), Christiansen (*Kgl. Danske Videnskab. Selskab. Math. fys. Med.*, **1**, 14, (1919)), and Polanyi (*Z. Elektrochem.*, **26**, 50, (1920)). † *Z. physikal. Chem.*, **29**, 295, (1899).

the calculation can be regarded as absolute in the strict sense, the value of the heat of activation must be independently determined from data other than those of reaction velocity. Attempts in this direction have already been made by Villars,* Eyring,† and others, adopting the valency theory of Heitler‡ and London.§

The next phase in the development of the collision theory centres round the problem of unimolecular reactions. It is neither possible nor desirable to enter into a full discussion here, but the following brief account is required before the true nature of reactions in solutions can be understood. Perrin,‖ accepting the definition of a unimolecular process as one possessing a rate independent of the pressure (or concentration) of the reactant, argued that an isolated molecule should decompose at the same rate as a large number of molecules. The velocity of a unimolecular reaction appeared to be independent of collisions. Lewis, believing the velocity of reaction to be governed by the rate of interaction of radiant energy with the molecules,** developed a radiation hypothesis of chemical change. Both theoretical considerations relating to equilibria between radiation and matter as well as experimental investigations on the effect of irradiation on systems undergoing chemical reaction showed that the hypothesis, even in an amended form, was untenable. Lindemann,†† commenting on Perrin's argument, pointed out that molecules decomposing unimolecularly could still be activated by collisions provided the activated molecules persisted as such for a finite time, during which most of them reverted to their normal conditions by loss of energy while others decomposed. This mechanism, while offering the possibility of explaining unimolecularity in a manner consistent with the collision theory, carried with it two important

* *J. Amer. Chem. Soc.*, **52**, 1773, (1930).
† *Z. physikal. Chem.*, **B, 7**, 244, (1930).
‡ *Z. Physik*, **51**, 805, (1928).
§ *Z. Elektrochem.*, **35**, 552, (1929).
‖ *Ann. de Phys.*, **11**, 1, (1919).
** *Phil. Mag.*, **39**, 26, (1920).
†† *Trans. Faraday Soc.*, **17**, 598, (1922).

conditions: (1) at low pressures, when the supply of molecules activated by collisions becomes insufficient to maintain a stationary concentration of active molecules, the unimolecular constant should fall; (2) at higher pressures, the number of molecules activated per second should always exceed the number reacting per second. At the time of Lindemann's suggestion, only one instance of a homogeneous gaseous unimolecular reaction was known—the decomposition of nitrogen pentoxide—and this appeared to fulfil neither of these conditions. Judged upon the facts of this one reaction the collision theory would have been doomed. Much more secure evidence was, however, forthcoming in a number of new reactions discovered and investigated fully by Hinshelwood and his collaborators, who found that acetone,* propionic aldehyde,† dimethyl ether,‡ and diethyl ether§ decomposed unimolecularly at fairly high temperatures in the homogeneous gas phase. The most noteworthy feature of these reactions is that at fairly low pressures the unimolecular velocity constant falls off, but can be maintained at its normal value by the introduction of hydrogen. These two facts were rightly interpreted as evidence that the Lindemann mechanism was actually at work. Further experimental support was advanced by Ramsperger, who found the same behaviour to be exhibited by dimethyldiimide,‖ diisopropyldiimide,** and methylisopropyldiimide.†† At the present time over twenty gaseous unimolecular reactions have been studied, all of which have this feature in common. The work of Ramsperger and Tolman‡‡ and of Schumacher and Sprenger§§ enables us to include in this number the case of nitrogen pentoxide. It is thus quite evident that even in

* Hinshelwood and Hutchison, *Proc. Roy. Soc.*, **A, 111**, 245, (1926).
† Hinshelwood and Thompson, *ibid.*, **A, 113**, 221, (1926).
‡ Hinshelwood and Askey, *ibid.*, **A, 115**, 215, (1927).
§ Hinshelwood, *ibid.*, **A, 114**, 84, (1927).
‖ *J. Amer. Chem. Soc.*, **49**, 1495, (1927). ** *Ibid.*, **50**, 714, (1928).
†† Ramsperger and Leermakers, *ibid.*, **53**, 2061, (1931).
‡‡ *Proc. Nat. Acad. Sci.*, **16**, 6, (1930).
§§ *Ibid.*, **16**, 129, (1930).

unimolecular reactions molecules become activated by collisions. Experiment shows, however, that the number of molecules decomposing per second even in the low pressure region is usually very much greater than the number of molecules which according to the equation of Lewis are activated per second.

The elucidation of the problem presented here coincided with the introduction of the idea that contributions towards the energy of activation could be made by certain internal degrees of freedom of the reacting molecule as well as by their translational energy. Its first application is due to Polanyi* who estimated that 7 internal degrees of freedom come into play when bromine molecules dissociate. The theory has been discussed also by G. N. Lewis and Smith,† and by Christiansen,‡ but its first systematic presentation was made by Hinshelwood§ who had paved the way for its acceptance by the experiments to which reference has just been made. Hinshelwood showed that the chance of two molecules in collision possessing total energy E in excess of the average energy is given approximately by the expression

$$e^{-E/RT}\left(\frac{E}{RT}\right)^{\frac{1}{2}n-1}\frac{1}{(\frac{1}{2}n-1)!},$$

n is the total number of quadratic terms by means of which the energy is defined. The same relation has been independently deduced by Fowler and Rideal.‖ The total kinetic energy of a molecule can be expressed in three square terms. For collisional purposes, however, only the components of the velocity in one particular direction, i.e. along the line of centres, need be considered. One square term defines the contribution made by the translational energy of each molecule. For two molecules in collision, the kinetic energy may be expressed in two square terms. If we denote by F the number of internal degrees of freedom concerned,

* *Z. Physik*, **1**, 337, (1920). † *J. Amer. Chem. Soc.*, **47**, 1508, (1925).
‡ *Proc. Camb. Phil. Soc.*, **23**, 438, (1926).
§ *Proc. Roy. Soc.*, **A, 113**, 230, (1926). ‖ *Ibid.*, **A, 113**, 570, (1927).

and assume that each internal vibration is simple, involving two square terms (one defining the potential energy and one the kinetic energy of vibration), the total number n of square terms contributing to the energy of activation is $n = 2+2F$. Thus $F = \frac{1}{2}n-1$. The above expression may thus be written as

$$e^{-E/RT}\left(\frac{E}{RT}\right)^F \frac{1}{F!},$$

where F is the number of *internal* degrees of freedom.

Within certain limits, the fractional number of molecules with critical energy E increases rapidly as F is increased. When F is raised beyond a certain value, the number becomes small, since the quantity $F!$ may then exceed the quantity $(E/RT)^F$. For every value of E/RT there will therefore be a certain value of F which will correspond to the maximum number of activated molecules. The method of evaluating F in the case of gaseous reactions depends on the assumption that, at the pressure which corresponds to a diminution in k, the rate of activation is just equal to the rate of reaction. This method is clearly not available in the case of reactions in solution, but it can be replaced by another one. The number of internal degrees of freedom thus found is generally no greater than can be imagined as accommodated by the chemical bonds of the reacting molecules.

The elucidation by Hinshelwood of the problem of unimolecular reactions ranks in importance with the contributions of Arrhenius and of Lewis, and clearly marks the third stage in the development of chemical dynamics since its inception by Wilhelmy.

It transpired from the systematic study of gaseous reactions that simple molecules decompose bimolecularly, and more complex molecules decompose unimolecularly.*

* The distinction between these two kinetic types of chemical change is naturally not abrupt. Instances are known of molecules which decompose by both bimolecular and unimolecular mechanisms (e.g. nitrous oxide, Musgrave and Hinshelwood, *Proc. Roy. Soc.*, **A, 135**, 23, (1932)). As a general rule,

This fact must now be linked with the observation that in bimolecular changes activation coincides with reaction, whereas in unimolecular changes there is a definite time interval between the two. The idea that internal degrees of freedom play a part in unimolecular reactions suggests that this interval is associated with the time required for the redistribution of energy within the activated molecule, and possibly its localization in a vulnerable spot. Before the velocity of a unimolecular reaction can be predicted it is therefore necessary to know not only what fraction of the total number of molecules possess the right energy, but what the probability of transformation of the activated molecules amounts to. This has not yet been achieved, but the study of the dynamics of activated molecules is growing rapidly. By postulating that the rate of reaction is proportional to the number of activated molecules, it is implied that the probability of spontaneous transformation is independent of temperature, of the pressure, and of the distribution of the energy within the activated molecules. If it is assumed that a particular internal degree of freedom must acquire a certain minimum amount of energy before the molecule can react, the chance that energy will flow into this degree of freedom depends on the normal of energy which the molecule possesses over and above the critical energy.* These extensions to the simpler theory are of great interest and have been elaborated by Rice and Ramsperger† and by Kassel.‡ The experimental tests all depend on the manner in which the unimolecular constant alters with a change in pressure when this is relatively small. The inquiry consequently branches off into an aspect of the problem which has no counterpart in reactions in liquid systems.§

however, it is correct to say that simple molecules, or complicated molecules undergoing simple changes, will decompose bimolecularly.

* Sir J. J. Thomson, *Phil. Mag.*, **3**, 241, (1927).

† *J. Amer. Chem. Soc.*, **49**, 1617, (1927). ‡ *J. Physical Chem.*, **32**, 225, (1928).

§ According to the principles of wave mechanics, it becomes possible for a certain fraction of the molecules to undergo chemical transformation while

The collision theory has been amplified in another way, by incorporating the hypothesis of chain reactions originally advanced by Nernst* in an attempt to explain the rate of the photochemical union of hydrogen and chlorine. Resultant molecules at the instant of formation contain the energy of activation, and, if the reaction is exothermic, the heat of reaction also. The essential postulate of the theory (p. 259) is that these 'hot' molecules can activate fresh reactant molecules by colliding with them. It has been shown by Christiansen and Kramers† that a unimolecular velocity would then result, provided each activated molecule of product hands on its energy to a fresh molecule of reactant. This provision is equivalent to the assumption that the efficiency of energy transference is 100 per cent. between activated products and normal reactants, and zero between activated products and all other molecules. The assumption is not unreasonable, for it is known that the transference of energy during collisions is highly specific. Oxygen molecules, for example, are about 3,000 times as efficient as helium atoms in quenching the resonance radiation of mercury. Experiments on the influence of foreign gases upon the velocity of unimolecular reactions have shown, however, that the explanation given by the chain theory cannot be true in general. The modern tendency is to accept the theory of the internal degrees of freedom as the correct one unless there are definite experimental indications to the contrary. In the hands of Semenov‡ and of Christiansen§ the reaction-chain theory has provided a simple interpretation of the

possessing energy which is actually lower than the energy of activation (see, for example, Bourgin, *Proc. Nat. Acad. Sci.*, **15**, 357, (1929); Roginsky and Rosenkewitsch, *Z. physikal. Chem.*, **B, 12**, 279, (1931)). It is quite clear, however, that in the case of reactions with which we have to deal, where the potential energy barrier and the molecular weights are high, the number of molecules which escape through the non-classical 'tunnel' is unimportant. But if the rate is governed by the passage of a proton through the molecule (p. 236), there exists the possibility of an appreciable tunnel effect.

* *Z. Elektrochem.*, **24**, 335, (1918).
† *Z. physikal. Chem.*, **104**, 451, (1923).
‡ *Z. Physik*, **46**, 109, (1927).
§ *J. Physical Chem.*, **28**, 145, (1924).

phenomena of gaseous explosions and of negative catalysis. Explosive reactions in solution are not known. Photochemical measurements show, however, that long reaction chains, sometimes exceeding 10,000 cycles, can be propagated in solution, the length of the chain being in some cases dependent on the nature of the solvent (Chapter III). The existence of thermal reaction chains in solution has also been established, and the marked inhibitive action of traces of foreign bodies has been explained by Bäckström* in terms of Christiansen's theory of negative catalysis. Chain reactions in solution, however, are not prevalent.

The salient points of the collision theory may now be summarized in the following manner. Only molecules in a suitably activated state can undergo chemical change, the rate of which must therefore be closely connected with the number and stability of the activated molecules. In bimolecular reactions, the molecules react immediately upon acquiring the necessary energy, so that the rate of activation is equal to the rate of reaction. The energy is shared between two square terms only, and the chemical changes involved are usually simple. In unimolecular reactions, the activated molecules have a definite lifetime, which is terminated either by a reversal into the normal, unactivated state or by chemical transformation. The critical energy is distributed among a number of internal degrees of freedom, and the chemical changes concerned may be very complicated.

INTRODUCTION TO THE KINETICS OF REACTIONS IN SOLUTION

The extended collision theory is now universally accepted as the correct explanation of the kinetics of gaseous reactions.† In applying the theory to liquid systems there are two distinct lines of approach.

* *J. Amer. Chem. Soc.*, **49**, 1460, (1927).

† The full force of this statement can best be realized from a study of *The Kinetics of Chemical Change in Gaseous Systems*, Hinshelwood, *3rd Edition*, Oxford, (1933).

The rates and energies of activation for certain reactions may be determined experimentally in solution and compared with the corresponding quantities for the gaseous reactions. If these quantities happen to be the same in the two systems it is clear that the solvent exerts no influence on the mechanism of the reaction and can therefore be regarded as inert or 'ideal'. On the other hand, should the two quantities prove to be different, the solvent acts either as a catalyst or an anticatalyst, and knowing the magnitude of the effect in either case we can inquire into its cause. Conclusions of this nature drawn from the direct comparison of rates of reactions in the gaseous phase and in solution are independent of any hypotheses concerning the mechanism of the reactions and would still be valid in the unlikely event of our having to abandon the collision theory altogether. It is therefore a matter for regret that only a limited number of reactions have, up to the present, been investigated in this manner. These are dealt with in Chapter III.

The numerical predictions of the collision theory, sometimes in a duly modified form, may be compared with the observed velocities of reactions studied in solution under various conditions. Before this step can be taken, we must acquaint ourselves with the relevant information afforded by the kinetic theory.

Molecular Velocities.

The velocity of a gas molecule will in general be altered after each successive collision with another molecule. Its speed will be increased or decreased according as the molecule which it meets is travelling in the same or in the opposite direction. At any particular instant, a few of the molecules in a system containing a large number will be at rest: some will move very rapidly: most of the molecules will have a speed not very different from the average velocity (v) or from the root mean square velocity (c), which is the hypothetical velocity which each molecule

would possess if the total kinetic energy were equally distributed among all the molecules. The following simple derivation shows how these quantities may be calculated. In a cube of length l containing n molecules travelling with velocity c, the molecules may be imagined as divided into three groups, each group moving to and fro in directions parallel with the sides of the cube. The number of molecules striking one side of the cube in one second is $\frac{1}{3}n.c/2l$. The change of momentum due to each impact is $2mc$, hence the rate of change of momentum, or the force P acting on the wall, is $\frac{1}{3}n(c/l)mc$. The pressure

$$p = \frac{P}{l^2} = \frac{1}{3}\frac{mnc^2}{l^3} = \frac{1}{3}\frac{mnc^2}{V};$$

hence $pV = \frac{1}{3}mnc^2$. For one gram molecule of a perfect gas, $pV = RT$, and $mn = M$, the molecular weight; so that $RT = \frac{1}{3}Mc^2$. The root mean square velocity may thus be determined from the molecular weight and the temperature:

$$c = \sqrt{\frac{3RT}{M}}. \tag{1}$$

When R is given the value of $8{\cdot}315\times10^7$ ergs/degree, c has the units of cm./second. It can be shown that the average velocity $v = c\sqrt{\frac{8}{3\pi}}$, hence

$$v = \sqrt{\frac{8RT}{\pi M}}. \tag{2}$$

Maxwell's distribution law tells us how many of the molecules have velocities and positions lying within specified limits. It states that the number dN of molecules of a perfect gas which have positions lying between x and $(x+dx)$, y and $(y+dy)$, z and $(z+dz)$, and velocity components along the three rectangular coordinates lying within the limits u and $(u+du)$, v and $(v+dv)$, w and $(w+dw)$ is

$$dN_{xyzuvw} = Ae^{-\beta(u^2+v^2+w^2)}\,dxdydzdudvdw.$$

A and β are constants, and are related to the molecular

weight (M), the temperature (T), and the volume (V) containing N molecules:

$$\beta = \frac{1}{2}\frac{M}{RT} \qquad A = \frac{N}{V}\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}}.$$

To find the number with velocities lying within these limits, without regard to their positions, we have

$$\begin{aligned} dN_{uvw} &= \left\{\iiint dxdydz\right\} Ae^{-\beta(u^2+v^2+w^2)}\, dudvdw \\ &= VAe^{-\beta(u^2+v^2+w^2)}\, dudvdw \\ &= N\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} e^{-\beta(u^2+v^2+w^2)}\, dudvdw. \end{aligned}$$

Considerations of symmetry allow us to calculate the number with velocity components between u and $(u+du)$, irrespective of the components in the other two directions, as

$$dN_u = N\left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} e^{-\beta u^2}\, du, \text{ etc.}$$

Substituting $\frac{1}{2}(M/RT)$ for β,

$$\left.\begin{aligned} dN_u &= N\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\frac{Mu^2}{RT}}\, du \\ \text{Similarly,} \quad dN_v &= N\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\frac{Mv^2}{RT}}\, dv \\ \text{and} \quad dN_w &= N\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\frac{Mw^2}{RT}}\, dw \end{aligned}\right\}. \qquad (3)$$

Molecular Diameters.

In order to calculate collision frequencies in liquid systems, the diameters of the molecules must be known. This is not necessary in gaseous systems, where the collision number may be determined directly from a knowledge of the density and viscosity of the gas at any given temperature. The dimensions of some organic molecules have been determined from measurements of the viscosity of vapours by Lowry and Nasini.* For most of our purposes an accurate

* *Proc. Roy. Soc.*, **A, 123,** 686, (1929).

evaluation of the diameter of molecules is not required, and a round figure of 5×10^{-8} cm. may be assumed as a sufficiently good approximation to hold in the majority of cases. When a closer estimate is required, it may be assumed that the molecules in a liquid or a solid at low temperatures are closely packed spheres. n molecules will then occupy $n\sigma^3/\sqrt{2}$ c.c. The diameter is then related to the molecular volume (in c.c. per gram molecule) by the equation

$$\sigma = 1{\cdot}33\times10^{-8}\times V_m^{\frac{1}{3}}. \qquad (4)$$

Values found in this manner are in quite good agreement with those determined by the more accurate methods afforded by the study of surface films and the reflection of X-rays from crystal surfaces. The calculation of the diameter of a molecule of propyl iodide may be taken as an example. From surface tension measurements a length of 4·70 Å. can be ascribed to the chain of carbon atoms.* The radius of the iodine atom, determined by the X-ray analysis of its crystal lattice, is 2·19 Å. We may therefore take 9·08 Å. as the approximate length of the molecule. Its breadth at the hydrocarbon end is $\sqrt{20{\cdot}7} = 4{\cdot}55$ Å.† At the iodine end, the breadth is 4·38 Å. The molecule of propyl iodide has thus an almost uniform thickness of 4·47 Å. and a length of 9·08 Å. The geometric mean of these is 6·37 Å., which corresponds to the hypothetical diameter which the molecule would possess if it were perfectly symmetrical. The diameter calculated from the density and the molecular weight by means of equation (4) is 6·12 Å.

The advantage of a precise method of calculating σ is that it enables us to judge how the relative diameters of homologous molecules vary with their masses. This will be needed in the study of series of similar reactions.

It has been assumed here that the radius of an atom in a crystal is identical with that of the corresponding ion in

* Kosakewitsch and Uschakowa, *Z. physikal. Chem.*, **A, 157,** 188, (1931).

† 20·7 Å.^{2} is the effective cross-section of the CH_2 chain (Adam, *The Physics and Chemistry of Surfaces*, Oxford, (1929)).

solution. In the absence of solvation this is probably true. In hydroxylic solvents, however, the radius of an elementary ion appears, from a study of its mobility, to be not only somewhat greater in solution than in the crystal, but to vary in magnitude from solvent to solvent.* These results are consistent with the view that most ions are solvated in solution.

Molecular Collisions.

1. *The Number of Collisions between Molecules of Solute.* An approximate expression for the number of collisions occurring between gas molecules may be derived by imagining all the molecules except one to be stationary. If the mobile molecule be regarded as having an effective radius equal to its diameter, the other molecules may be treated as point particles.† The number of stationary molecules encountered in one second will then be the number of point particles contained in a parallelepiped with cross-section $\pi\sigma^2$ and length equal to the average velocity v. If there are n molecules per c.c., the number of collisions made per second by the mobile molecule is $\pi\sigma^2 vn$. The total number of collisions Z is $\pi\sigma^2 vn^2$, or since $v = \sqrt{\frac{8RT}{\pi M}}$, $Z = n^2\sigma^2\sqrt{\frac{8\pi RT}{M}}$. A more rigid derivation‡ shows that this is too large by a factor of $\sqrt{2}$, hence,

$$Z = \sigma^2 n^2 \sqrt{\frac{4\pi RT}{M}}. \qquad (5)$$

When chemical reactions depend on collisions between two similar molecules, it is sometimes open to question whether one or both of the colliding molecules is transformed in a suitable collision. With one exception, however, all the bimolecular reactions with which we have to deal in solution

* Hartley and Raikes, *Trans. Faraday Soc.*, **23**, 394, (1927).

† See, for example, Bloch, *The Kinetic Theory of Gases*, p. 27, (1924).

‡ See, for example, Jeans, *The Dynamical Theory of Gases*, p. 259, Cambridge (1925).

occur between unlike molecules. The correct expression to use in that case is

$$_1Z_2 = \sigma_{1,2}^2 n_1 n_2 \sqrt{\left\{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}}. \qquad (6)$$

This gives the total number of collisions occurring per c.c. per second in a gaseous system at temperature T, containing per c.c. n_1 molecules of molecular weight M_1 and n_2 molecules of molecular weight M_2. $\sigma_{1,2}$ is the sum of the molecular radii.*

The frequency of collisions is governed by the velocities and the diameters of the colliding molecules. Unless the presence of a solvent influences either of these, the number of collisions suffered by solute molecules in a dilute solution in an inert solvent must be the same as the number of collisions in the gaseous phase. It is known from measurements on osmotic pressure in aqueous and non-aqueous† solutions that the velocity is the same in the two systems, and from dielectric constant measurements‡ that the extent to which the molecules are deformed after dissolution is not great. This argument forms the basis for assuming that equation (6) gives the collision frequency in solution with quite considerable accuracy. Recent experiments which will be described in Chapter III prove that this assumption cannot be far wrong. That equation (6) gives the number of collisions correctly as far as order of magnitude is concerned

* There has been some confusion about the exact formula since the earliest presentation of the collision theory. Slightly inaccurate forms of this equation have been freely used. It is to be noted that equation (5) leads to a value of Z equal to one-half of that found by putting $M_1 = M_2$ in equation (6). Jeans points out that $_1Z_2$ is in fact the number of mean free paths of the n_1 molecules of the first type in unit volume which are terminated per unit time by molecules of the second type. When the molecules are of different types, this equals the collision rate: when they are similar, it equals twice the collision rate.

† Cf. Eichelberger, 'The Osmotic Pressure of Tetraphenylethylene in Benzene Solution' (*J. Amer. Chem. Soc.*, **53**, 2025, (1931)).

‡ Cf. Fairbrother, 'The Dipole Moment of Hydrogen Chloride in the Gaseous Phase and in Carbon Tetrachloride Solution' (*Trans. Chem. Soc.*, 43, (1932)).

has never been in doubt.* In the present work the gas collision formula is invariably used without correction of any kind. The number of collisions between ions may be determined by its use, but since electrostatic forces alter the distribution of the solute molecules, n_1 and n_2 can no longer be regarded as equal to the bulk concentration of the solute (Chapter VII).

Jowett† expresses the view that the collision frequency in a liquid system exceeds that in a gaseous system by a factor of $1/v_F$, where v_F represents the free space. Now v_F for various liquids at 20° C. ranges from 0·06 to 0·15, hence the collision number would, upon this supposition, be about 10 times greater than in the gas. Norrish and Smith‡ consider that the correction should involve a free-space term raised to the second power, but its magnitude as used by them is small. Polissar,§ on the other hand, argues that Z must be smaller for dilute solutions than for gaseous systems. The procedure which is adopted in this work will therefore not be free from criticism, but until there are proofs that a correction is necessitated and some kind of agreement about its magnitude and sign, there is clearly no optional course.

2. *The Number of Collisions between Molecules of Solute and Molecules of Solvent.* The frequency of collisions between solute and solvent molecules may be calculated in the following way.|| Einstein** has demonstrated that the mean displacement $\overline{\Delta x}$, measured along one axis, of a dissolved molecule in time t seconds, due to solvent bombardment is given by

$$\overline{\Delta x}^2 = \frac{2RTt}{CN_0},$$

* Christiansen, *Z. physikal. Chem.*, **113**, 35, (1924); Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, p. 242, (1927).

† *Phil. Mag.*, **8**, 1059, (1929).

‡ *Trans. Chem. Soc.*, 129, (1928).

§ *J. Amer. Chem. Soc.*, **54**, 3105, (1932).

|| Moelwyn-Hughes, *Trans. Chem. Soc.*, 95, (1932).

** *Z. Elektrochem.*, **14**, 235, (1908).

where N_0 is the Avogadro number; C, the resistance factor, is equal to $6\pi\eta r$ in the case of a molecule which is spherical and large compared with a solvent molecule. η is the viscosity of the solvent, and r is the radius of the solute molecule. Hence

$$\overline{\Delta x^2} = \frac{RTt}{3\pi N_0 \eta r}.$$

For the actual displacement $\overline{\Delta s}$ in three dimensions, we have as an average value

$$\overline{\Delta s^2} = 3\overline{\Delta x^2} = \frac{RTt}{\pi N_0 \eta r}.$$

The displacements measured by Perrin during his investigations of the Brownian movement were those corresponding to a time interval of 30 seconds, during which the solute molecule (or, more strictly, the colloid particle) had undergone several successive encounters with solvent molecules. If we take, however, as our value of t the time elapsing between two consecutive collisions, $\overline{\Delta s}$ reduces to λ, the mean free path, and t becomes λ/c, hence

$$\lambda = \frac{RT}{\pi N_0 \eta r c},$$

and

$${}_1Z_S = \frac{c}{\lambda} = \frac{\pi N_0 \eta r c^2}{RT} = \frac{3\pi N_0 \eta \sigma}{2M_1},$$

or

$${}_1Z_S = \frac{3\pi\eta\sigma}{2m_1}. \tag{7}$$

This enables us to calculate the number of collisions which one molecule of solute of mass m_1 and diameter σ makes during one second with solvent molecules in a medium of viscosity η.

${}_1Z_S$ may also be found from a knowledge of the diffusion coefficient. Interdiffusion in liquid systems may be treated in the same way as self-diffusion in gases, and the same equation has been shown to connect the diffusion coefficient

with the velocity and the mean free path in the two systems:*

$$D = \tfrac{1}{3}\lambda v.$$

In the absence of ternary collisions, the total number of solvent molecules encountered per second by one solute molecule will be

$${}_1Z_S = \frac{v}{\lambda} = \frac{v^2}{3D} = \frac{8RT}{3\pi M_1 D}.$$

To allow for the tendency of the velocity to persist after collision, a term $\frac{1{\cdot}051}{(1-\theta)}$ must be introduced.† θ is dependent on the masses of the colliding molecules and is approximately equal to $M_1/(M_1+M_S)$, where M_1 is the molecular weight of the solute molecule and M_S that of the solvent molecule. Hence, neglecting the factor 0·051,

$${}_1Z_S = \frac{8RT}{3\pi D}\left(\frac{M_1+M_S}{M_1 M_S}\right). \qquad (8)$$

Jowett (loc. cit.), who deduced this equation and employed it to calculate the collision frequencies in aqueous solutions from a knowledge of the diffusion coefficients, emphasized the important fact that Z diminishes rapidly with increase in temperature, and indicated the possible bearing of this conclusion upon the kinetics of chemical reactions which possess rates dependent upon collisions between solute and solvent molecules.

The similarity with equation (7) becomes apparent when we substitute for D the value given by the Sutherland expression

$$D = \frac{RT}{3\pi N_0 \eta \sigma}.$$

The theories of diffusion and of the Brownian movement both point to the conclusion that the collision rate is proportional to the viscosity of the solvent. The absolute values of the collision frequencies given by equations (7) and (8)

* Riecke, *Z. physikal. Chem.*, **6**, 564, (1890).

† Jeans, *The Dynamical Theory of Gases*, p. 260, (1925).

differ by a factor of $0{\cdot}57(1-\theta)$, the magnitude of which depends on the relative masses of solute and solvent molecules and will not generally be large. Unlike the collision frequency between two gas molecules or between two solute molecules, the collision frequency between solute and solvent molecules will decrease with a rise in temperature.

This difference is a consequence of the fact that, whereas in both solutions and gases Z depends on the velocity of translation of the molecules, it is only in the liquid system that the variation with temperature of the free space becomes considerable. Raising the temperature of a dilute solution will influence the rate of collisions between solute and solvent molecules in two ways: (1) the increased velocity of the molecules will favour the collision frequency, and (2) the increased separation of the molecules—due to thermal expansion—will affect the collision rate adversely. Physically interpreted, therefore, equations (7) and (8) mean that the effect of temperature on the free space is the important factor. There is much evidence that the free space in liquids increases rapidly with a rise in temperature; the rate of increase is, furthermore, almost equal to that of the fluidity, and is thus sufficient to explain the diminution in the collision frequency.*

Lindemann† in a treatment of ionic migration draws a similar conclusion. The variation of the velocity of migration of an ion with the temperature appears to be due to the increase in the mean free path resulting from thermal expansion.

3. *The Number of Collisions between Molecules of Solute and a Solid Surface.* In order to find the number of molecules

* Reverting to the question of the possible correction required for the expression giving the frequency of collisions between two solute molecules, it is likely that the significance of a free-space correction in that connexion also may be not so much in the change it may produce in the absolute value of Z as in the variation of Z with the temperature.

† *Z. physikal. Chem.*, **110**, 394, (1924); see also, Herzog, *Z. physikal. Chem.*, **B, 10**, 337, (1930).

which strike a solid surface in unit time, we may regard $\frac{1}{6}$th of the total number as moving towards the surface with the average velocity v at any instant. The number reaching unit area of the surface in one second will then be $\frac{1}{6}$th of the total number of molecules in a parallelepiped of cross-section 1 sq. cm. and length v cm. This number is $\frac{1}{6}vn$, where n is the number of molecules in 1 c.c. Substituting the value of v given by equation (2), $Z = \frac{1}{6}n\sqrt{(8RT/\pi M)}$. A more rigid derivation, taking into account the distribution of velocities,* shows that this expression is too low by a factor of $\frac{3}{2}$, hence

$$Z = n\sqrt{\frac{RT}{2\pi M}}. \qquad (9)$$

The equation will be required in connexion with the velocities of reactions catalysed by solids, and in certain cases of enzyme reactions.

Molecular Energies.

Molecules possess energy in virtue of their motion (translatory energy), of their rotation (rotatory energy), and of vibrations between the constituent units (vibratory energy). During collisions, there is in general a redistribution of energy in a manner which is governed by the principles of the quantum theory. Translational energy may be converted into energy of rotation or of vibration, and so on. An increase in the vibrational energy of diatomic molecules drives the constituent atoms farther and farther apart until finally complete dissociation results. The activation necessary for these reactions, which are among the simplest of chemical changes, may be derived at high temperatures from the kinetic energy of the molecules, or at low temperatures from radiant energy in the form of quanta corresponding to light of short wave-length. In the majority of thermal reactions, however, the formation of free atoms does not take place; internal stimulation to an extent smaller than

* See, for example, Tolman, *Statistical Mechanics with Applications to Physics and Chemistry*, p. 206, (1927).

that required for the production of free atoms is usually sufficient to permit the occurrence of those atomic rearrangements which constitute chemical change. The evidence for this conclusion is to be found in the magnitudes of the heat terms involved. If, for example, the combination of hydrogen and iodine took place only between atoms, an energy of activation of some 118,500 calories would be required for the formation of two gram molecules of the halide. Actually, about a third of this energy is sufficient to bring about the required change. The mental picture which we accordingly draw of the union of hydrogen and iodine is that both molecules absorb energy, which is accommodated in the form of vibrations between the constituent atoms until the atomic separations are such that an exchange of partners becomes possible with the greatest facility. Eyring and Polanyi* have shown how it is possible to calculate in very simple cases the energy of activation of a chemical reaction from a consideration of the interatomic forces involved in critical nuclear separations of this kind.

It is unnecessary here to pursue any farther the problem of calculating in absolute measure the energy of activation of chemical changes. In the present work, this quantity is regarded simply as a property characteristic of each chemical reaction and derivable from the results of kinetic experiments. The remaining problem is to indicate from a knowledge of the energy of activation what velocity the chemical change can be expected to have. Before this can be achieved, it is essential to possess more precise information concerning the manner in which the energy is distributed among the various molecules, and to derive expressions showing what fraction of the total number of molecules have at any instant energies equal to or greater than the energy of activation. This is of course the same as the probability that any one molecule at any given instant should possess the energy of activation.

* *Z. physikal. Chem.*, **B, 12,** 279, (1931); also Eyring, *J. Amer. Chem. Soc.*, **53,** 2537, (1931).

Maxwell's distribution law (equation (3)) tells us that the fractional number of molecules with velocity components (measured along one coordinate axis) lying between u and $(u+du)$ is

$$\frac{dN}{N} = \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}Mu^2/RT}\, du. \qquad (3)$$

If we require the number of molecules with kinetic energy lying between E and $(E+dE)$, we must take into account those molecules with velocities between $-u$ and $-(u+du)$, so that the total number within the required energy limits is

$$\frac{dN}{N} = \left(\frac{2M}{\pi RT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}Mu^2/RT}\, du.$$

Since $E = \frac{1}{2}Mu^2$, this expression can be rewritten in the form

$$\frac{dN}{N} = \frac{E^{-\frac{1}{2}}}{(\pi RT)^{\frac{1}{2}}} e^{-E/RT}\, dE.$$

This equation gives the fractional number of molecules possessing energy values between E and $(E+dE)$ when the energy is expressible in one quadratic term. It may therefore be applied not only to translational energy, but to rotational energy, to kinetic energy of vibration, as well as to potential energy of vibration when this is simple harmonic.* Suppose that two square terms only are involved. The chance that a molecule may possess an energy between Q and $(Q+dQ)$ in one square term is

$$\frac{Q^{-\frac{1}{2}}}{(\pi RT)^{\frac{1}{2}}} e^{-Q/RT}\, dQ.$$

The chance that simultaneously the energy in one term is between Q_1 and (Q_1+dQ_1) and in another term between Q_2 and (Q_2+dQ_2) is

$$\frac{1}{\pi RT} Q_1^{-\frac{1}{2}} e^{-Q_1/RT}\, dQ_1 \times Q_2^{-\frac{1}{2}} e^{-Q_2/RT}\, dQ_2.$$

Suppose $Q_1+Q_2 = E$. To determine the chance that a total energy lying between E and $(E+dE)$ may be possessed by

* We are here following Hinshelwood's treatment, which is to be found in *Proc. Roy. Soc.*, **A, 113,** 230, (1926) and more fully in *The Kinetics of Chemical Change in Gaseous Systems*, Chapter I, Oxford, (1933).

the molecule without reference to how it is shared between them, the term $(E-Q_1)$ may be substituted for Q_2 in the above expression, which is then integrated with respect to Q_1 from 0 to E. Thus

$$\frac{dN}{N} = \frac{1}{\pi RT}\int_0^E Q_1^{-\frac{1}{2}} e^{-Q_1/RT}\, dQ_1 (E-Q_1)^{-\frac{1}{2}} e^{-(E-Q_1)/RT}\, dE$$

$$= \frac{e^{-E/RT}\, dE}{\pi RT}\int_0^E Q_1^{-\frac{1}{2}}(E-Q_1)^{-\frac{1}{2}}\, dQ_1$$

$$= \frac{e^{-E/RT}\, dE}{RT}.$$

The fractional number of molecules with energies greater than E in the two terms jointly is

$$\frac{dN}{N} = \frac{1}{RT}\int_E^\infty e^{-E/RT}\, dE = e^{-E/RT}.$$

This is the familiar Maxwell-Boltzmann expression, derived in a novel manner. It is the exact form of the distribution law in all cases where only two square terms are concerned, and it therefore represents the chance of an energy greater than E where the relative motions of two colliding molecules is considered (one translational term for each), or where one internal harmonic vibration (one term representing kinetic energy, and the other potential energy) is involved.*

In a similar way the fractional number of molecules for which the total energy in n terms lies between E and $(E+dE)$ is

$$\frac{1}{(\pi RT)^{\frac{1}{2}n}}\int_0^E\int_0^E \ldots Q_1^{-\frac{1}{2}} e^{-Q_1/RT}\, dQ_1 \times Q_2^{-\frac{1}{2}} e^{-Q_2/RT}\, dQ_2 \ldots$$

$$\ldots\{E-(Q_1+Q_2+\ldots)\}^{-\frac{1}{2}} e^{-\{E-(Q_1+Q_2+\ldots)\}/RT}\, dE,$$

where $$Q_1+Q_2+\ldots = E.$$

* In the previous reference to the rates of evaporation and thermionic emission, it was stated that the velocities are proportional to $e^{-E/RT}$. The chance that the energy exceeds λ or W in these cases is not exactly $e^{-\lambda/RT}$ or $e^{-W/RT}$as it would be if only two square terms were involved, but it still is proportional to this factor.

The integral is $$\frac{e^{-E/RT}E^{(\frac{1}{2}n-1)}\,dE}{\Gamma(\frac{1}{2}n)(RT)^{\frac{1}{2}n}}.$$

The chance that a molecule possesses energy greater than E is

$$\frac{1}{\Gamma(\frac{1}{2}n)(RT)^{\frac{1}{2}n}}\int_E^\infty e^{-E/RT}E^{(\frac{1}{2}n-1)}\,dE.$$

The integral is

$$e^{-E/RT}\left\{\frac{1}{(\frac{1}{2}n-1)!}\left(\frac{E}{RT}\right)^{\frac{1}{2}n-1}+\frac{1}{(\frac{1}{2}n-2)!}\left(\frac{E}{RT}\right)^{\frac{1}{2}n-2}+\ldots+1\right\}. \quad (10)$$

When E/RT is large, as in most chemical reactions, the first term only need be considered:

$$\frac{e^{-E/RT}(E/RT)^{\frac{1}{2}n-1}}{(\frac{1}{2}n-1)!}.$$

If we now assume that of the total n terms, two represent the relative motions of colliding molecules, and F is the number of internal degrees of freedom, each degree of freedom involving two quadratic terms, then the chance that a molecule in collision possesses energy greater than E is

$$e^{-E/RT}\left(\frac{E}{RT}\right)^F\frac{1}{F!}. \quad (11)$$

For a given value of (E/RT) the fractional number of molecules with energy greater than E will increase rapidly as the number of degrees of freedom among which E is shared increases. Suppose, for example, we require to find the fractional number of molecules at a temperature of 300° absolute which possess energy greater than 21,000 calories per gram molecule, the following figures are found for various values of F.

The first value ($6{\cdot}3\times10^{-16}$) is simply $e^{-E/RT}$, and is the simplified form of equation (10), but not of the approximate expression (11), found when $n = 2$ or $F = 0$. The tabulated values show clearly the extent of the approximation made by omitting all but the first term of the series in equation (10).

$E = 21{,}000$ calories. $T = 300°$.

F	$\frac{dN}{N} = e^{-E/RT}\left(\frac{E}{RT}\right)^F \frac{1}{F!}$.
0	$6{\cdot}3 \times 10^{-16}$
1	221×10^{-16}
2	$3{,}864 \times 10^{-16}$
3	$45{,}080 \times 10^{-16}$
4	$394{,}500 \times 10^{-16}$
5	$2{,}761{,}000 \times 10^{-16}$
6	$16{,}100{,}000 \times 10^{-16}$

If the velocity of chemical reaction is assumed to be proportional to the number of molecules with energy greater than E distributed in n terms, it can be shown that the energy of activation (E) is related in the following manner to the critical increment (E_A) of the Arrhenius equation

$$E = E_A + (\tfrac{1}{2}n - 1)RT \quad \text{or} \quad E = E_A + FRT. \qquad (12)$$

This equation implies that the value of n and the probability of transformation of the activated molecules are both independent of temperature.

Summary of Equations.

The following equations will be repeatedly used in subsequent chapters. They are summarized here for convenient reference.

I. Root mean square velocity:

$c = \sqrt{(3RT/M)}$ (M = molecular weight);

$R = 8{\cdot}315 \times 10^7$ ergs/degree.

II. Average velocity:

$v = \sqrt{(8RT/\pi M)}$.

III. Diameter of molecule:

$\sigma = 1{\cdot}33 \times 10^{-8} \times V_m^{\frac{1}{3}}$; V_m is the molecular volume of the pure liquid or solid at low temperatures.

IV. Number of collisions per c.c. per second between

molecules of molecular weights M_1 and M_2, and diameters σ_1 and σ_2:

$$_1Z_2 = \sigma_{1,2}^2 n_1 n_2 \sqrt{\left\{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}}$$

where $\sigma_{1,2} = \left(\frac{\sigma_1+\sigma_2}{2}\right)$. n_1 and n_2 are the number of molecules of types 1 and 2 per c.c.

V. Number of collisions per second between 1 molecule of mass m_1 (diameter $= \sigma$) and molecules of solvent in terms of the viscosity (η) of the solvent:

$$_1Z_S = \frac{3\pi\eta\sigma}{2m_1}.$$

VI. Number of collisions per second between 1 molecule of solute of molecular weight M_1 and molecules of solvent in a dilute solution, in terms of the diffusion coefficient D of the solution:

$$_1Z_S = \frac{8RT}{3\pi M_1 D}.$$

VII. Correction for the persistence of velocity is $1/(1-\theta)$, where θ is approximately $M_1/(M_1+M_S)$. M_S is the molecular weight of the solvent. The collision frequencies of equations V and VI must therefore be multiplied by the factor $(M_1+M_S)/M_S$.

VIII. Number of molecules striking unit area of solid in one second:

$$Z = n\sqrt{\frac{RT}{2\pi M}}.$$

n is the number of molecules per c.c.

IX. Fractional number of molecules with energy greater than E in two quadratic terms: $e^{-E/RT}$.

X. Fractional number of molecules with energy greater than E in n quadratic terms:

$$e^{-E/RT}\left(\frac{E}{RT}\right)^{\frac{1}{2}n-1}\frac{1}{(\frac{1}{2}n-1)!}.$$

II

THE ARRHENIUS EQUATION

ACCORDING to the general theory of activation, the rate at which molecules undergo chemical transformation is proportional to the number of molecules in an appropriately activated condition. This number, in turn, is an exponential function of the temperature and of the energy of activation, and usually determines the order of magnitude of the

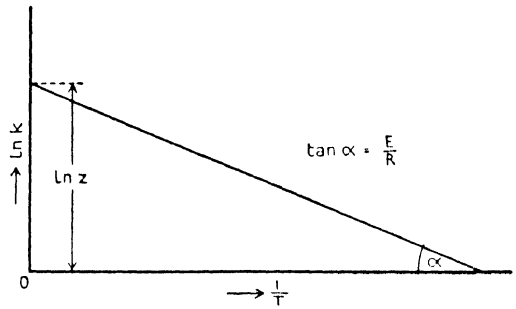


FIG. 1.

reaction velocity. The satisfactory investigation of the kinetics of any chemical change must consequently include as accurate an evaluation of the critical increment as experiment will permit. As we have seen, the variation with temperature of the velocity constant for a thermal reaction occurring in solution may be expressed in the form

$$k = Zc^{-E/RT}$$

or

$$\ln k = \ln Z - \frac{E}{RT}.$$

The constants Z and E, which are specific for each reaction, may thus be determined by plotting $\ln k$ against $1/T$; the slope of the curve is $-E/R$, and the intercept on the $\ln k$ axis is $\ln Z$ (Fig. 1). In practice, it is more convenient to obtain the value of E only from the graph, when Z can be

found by inserting into the equation the values of k and T corresponding to any point on the curve.* The precision with which the quantities E and Z can be determined clearly depends on the range of temperature within which measurements are possible, on the sensitiveness of the temperature control, as well as on the numerical accuracy assignable to the velocity constants.

Methods of Measuring the Velocity of Reaction.

The most usual procedure for following the course of a chemical reaction entails the removal of samples of the reaction mixture, and the arrest of chemical change either by quickly cooling or by running into a suitable chilling preparation. The composition of the system from time to time can then be determined by the ordinary methods of analysis. Reactions involving a change in the concentration of acids, bases, halides, and so forth may conveniently be followed by titrations. Organic radicals may also be estimated by the usual means.† It is advantageous, wherever possible, to use two independent methods of estimation. For example, in the case of the union of triethylamine with ethyl iodide

$$N(C_2H_5)_3 + C_2H_5I \rightarrow (C_2H_5)_4NI$$

the rate may be measured by titrating samples against standard acid, to determine the amount of amine left, and against standard thiocyanate to determine the amount of iodide produced. The hydrolysis of sucrose has been studied by measuring the decrease in optical rotation and the increase in reducing power. Both methods give the same result. When this is not so, there is some side reaction.

Reactions in solution which are attended by the formation

* When velocity constants have been obtained at two temperatures only, E may be evaluated from the integrated expression: $E = \frac{RT_2T_1}{T_2 - T_1} \ln \frac{k_2}{k_1}$.

† e.g. amino nitrogen by the van Slyke method.

of slightly soluble gases, such as nitrogen,* oxygen,† carbon dioxide‡ or carbon monoxide,§ may be investigated manometrically.

Several physicochemical properties of the reacting system are often available as a means of measuring the rate of reaction, provided the properties in question are additive. Blank experiments should always be performed to make certain that there exists a strict proportionality between the concentrations of the participants and the physicochemical quantity which is measured. Some of the properties of solutions which have been utilized kinetically are: colour,‖ viscosity,** thermal expansion,†† optical rotation,‡‡ electrical conductivity,§§ refractive index,‖‖ freezing-point,*** coagulation power,††† and extinction coefficient.‡‡‡

* e.g. from diazoacetic ester (Bredig and Fraenkel, *Z. physikal. Chem.*, **60**, 207, (1907)), nitrosotriacetonamine (Goodall and Lewis, *ibid.*, **137**, 45, (1928)) and diazonium salts (Cain and Nicoll, *Trans. Chem. Soc.*, **81**, 1412, (1902)).

† e.g. from hydrogen peroxide (Harned, *J. Amer. Chem. Soc.*, **40**, 1461, (1918)).

‡ e.g. from acetonedicarboxylic acid (Wiig, *J. Physical Chem.*, **32**, 961, (1928)).

§ e.g. from formic acid (Meyer, *Z. Elektrochem.*, **15**, 506, (1909)).

‖ The addition of hydrocyanic acid to camphorquinone (Lapworth, *Trans. Chem. Soc.*, **83**, 995, (1903)); the reduction of ferric chloride by stannous chloride (Harcourt, *Phil. Trans.*, **A, 212**, 187, (1913)); the conversion of creatine into creatinine (Edgar and Wakefield, *J. Amer. Chem. Soc.*, **45**, 2242, (1923)).

** Numerous reactions studied by Schroeder (*Z. physikal. Chem.*, **45**, 75, (1903)) and by Dunston and Mussell (*Trans. Chem. Soc.*, **99**, 565, (1911)).

†† Decomposition of diacetone alcohol (Koelichen, *Z. physikal. Chem.*, **33**, 129, (1900)); hydrolysis of dimethyl acetal (Brönsted and Grove, *J. Amer. Chem. Soc.*, **52**, 1394, (1930)).

‡‡ Mutarotation of optically active substances; hydrolysis of disaccharides, trisaccharides and glykosides generally. For the modern improvements in polarimetric methods, the papers of Lowry should be consulted.

§§ The hydration of acetic anhydride (Rivett and Sidgwick, *Trans. Chem. Soc.*, **97**, 732, (1910)); the saponification of esters (Walker, *Proc. Roy. Soc.*, **78**, 157, (1907)). Refinements in electrical conductivity determinations are described in the papers of Sir Harold Hartley.

‖‖ Hydrolysis of sucrose (Duane, *Am. J. Sci.*, **11**, 349, (1901)). The measurement of the dielectric constant should nowadays prove helpful, since this can be made with great accuracy.

*** Isomerization of phenylbenziminophenyl ether in the fused state (Chapman, *Trans. Chem. Soc.*, **127**, 1992, (1925)).

††† Conversion of *cis*dichlordiethylenediaminechromchloride into an aquoderivative (Freundlich and Pape, *Z. physikal. Chem.*, **86**, 458, (1914)).

‡‡‡ The reaction between iodine and ethyl alcohol (Batley, *Trans. Faraday Soc.*, **24**, 438, (1928)).

The selection of the most suitable method depends upon the nature of the reaction and upon other circumstances. Preference should be given to a method which allows the same reaction system to be examined continuously, without the removal of samples. With the polarimetric, dilatometric, or manometric technique, for example, the same volume of reaction mixture is kept in a vessel from start to finish, suitably jacketed by thermostat liquid or vapour.

The probable error in any reliable work seldom exceeds 2 per cent. and is often much less.*

Unimolecular Reactions.

A reaction is said to be unimolecular when the number of molecules decomposing at any instant is proportional to the total number of molecules present at that instant. If a is the initial concentration of the reactant, and x the amount which has been transformed in time t, then

$$\frac{dx}{dt} = k_1(a-x).$$

k_1 thus denotes the constant fractional number of molecules which undergo chemical change in an infinitesimally short time interval. Integration gives

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x}. \qquad (1)$$

The unimolecular constant has therefore the dimensions of a frequency, and an absolute value which is independent of the unit in which the concentration is expressed.

Acetonedicarboxylic acid decomposes unimolecularly in aqueous solution, with the elimination of carbon dioxide:

$$CO(CH_2COOH)_2 \rightarrow CO(CH_3)_2 + 2CO_2.$$

By titrating the amount of acid remaining at various time intervals, after removing the carbon dioxide in a stream of

* The sources of error are fully dealt with by Rice and Urey, Reaction Velocity in Homogeneous Systems, *A Treatise of Physical Chemistry* (edited by H. S. Taylor), p. 949, (1931).

nitrogen, Wiig* determined the velocity constants given in Table 1. The Arrhenius equation takes the form $\ln k_1 = 32{\cdot}26 - 23{,}200/RT$ (Fig. 2).

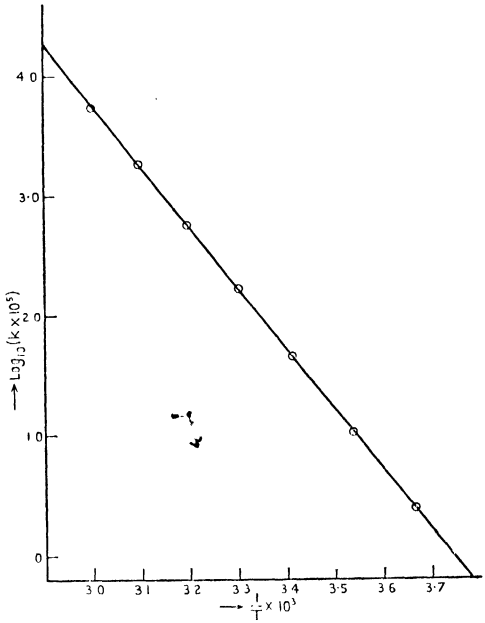


FIG. 2.—Decomposition of acetonedicarboxylic acid in aqueous solution. Unimolecular. E = 23,200 calories.

Table 1

Decomposition of acetonedicarboxylic acid in aqueous solution

	$k_1 \times 10^5$ (seconds^{-1})	
$t°$ C.	Observed	By the Arrhenius equation
0	2·46	2·41
10	10·8	10·8
20	47·5	44·9
30	163	167
40	576	565
50	1,850	1,830
60	5,480	5,400

* *J. Physical Chem.*, **34**, 596, (1930).

The rate of this reaction is uninfluenced by changing the material of the vessel in which the reaction is carried out, so that the decomposition proceeds entirely in the homogeneous liquid phase. This is generally, although not always, true of reactions which are measured in solution; the ease with which velocity constants can be reproduced without discriminating between reaction vessels of different material and dimensions indicates the absence of any heterogeneous decomposition on the walls, and renders it unnecessary to carry out special experiments in this direction. The hydrolysis of sucrose, however, and a few other reactions have been investigated in vessels packed with glass beads, but the increased surface thus afforded does not influence the rate of inversion.* The decomposition of hydrogen peroxide, on the other hand, in aqueous and in alkaline solution, is definitely influenced by the walls of the reaction vessel, the catalytic activity of glass being less than that of silica and greater than that of a wax-lined surface. In quartz vessels the reaction is apparently homogeneous.† Traces of dust catalyse the reaction.‡ Instances of this kind of behaviour are rather exceptional. A solute molecule will not usually increase its chances of decomposing by leaving the bulk of the solution to take up a position on the wall. Certain reactions are known which proceed in solution by a chain mechanism; the discovery that such reactions show a pronounced wall effect would not be surprising.

Bimolecular Reactions.

The velocity with which methyl iodide and sodium ethoxide react in ethyl-alcoholic solution is proportional to the number of molecules of each of the two reactants.

$$CH_3I + C_2H_5ONa \rightarrow CH_3OC_2H_5 + NaI$$

Starting with concentrations of a and b respectively, the rate

* Speranski, *Z. physikal. Chem.*, **5**, 607, (1890).
† Robertson, *J. Amer. Chem. Soc.*, **53**, 382, (1931).
‡ Pana, *Trans. Faraday Soc.*, **24**, 486, (1928).

after time t, when x gram molecules of products have been formed per litre, is

$$\frac{dx}{dt} = k_2(a-x)(b-x)$$

or

$$k_2 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}. \qquad (2)$$

By titration methods, Hecht and Conrad* found the following values for the bimolecular constant at various temperatures. They are seen to be in good agreement with the equation $\ln k_2 = 26{\cdot}21 - 19{,}490/RT$ (Fig. 3).

Table 2

Formation of methylethyl ether in ethyl-alcoholic solution

	$k_2 \times 10^5$ (litres/gram molecule-second)	
$t°$ C.	Observed	By the Arrhenius equation
0	5·60	5·50
6	11·8	11·9
12	24·5	24·5
18	48·8	50·1
24	100	100
30	208	193

If the initial concentrations of the two types of molecules participating in a bimolecular reaction are equal, we have

$$\frac{dx}{dt} = k_2(a-x)^2,$$

which on being integrated gives

$$k_2 = \frac{1}{ta} \frac{x}{(a-x)}. \qquad (3)$$

The rate at which ammonium cyanate is converted into urea in aqueous solution is proportional to the square of the concentration of the salt.

$$NH_4CNO \rightarrow (NH_2)_2CO$$

The velocity of reaction is thus dependent on the number of collisions between ammonium cyanate molecules, or—as is

* *Z. physikal. Chem.*, **3**, 450, (1889).

more probable from a study of the effects produced by the addition of electrolytes—between other entities present in amounts proportional to $[NH_4CNO]$. The actual mechanism of the reaction is not known* beyond that it is definitely

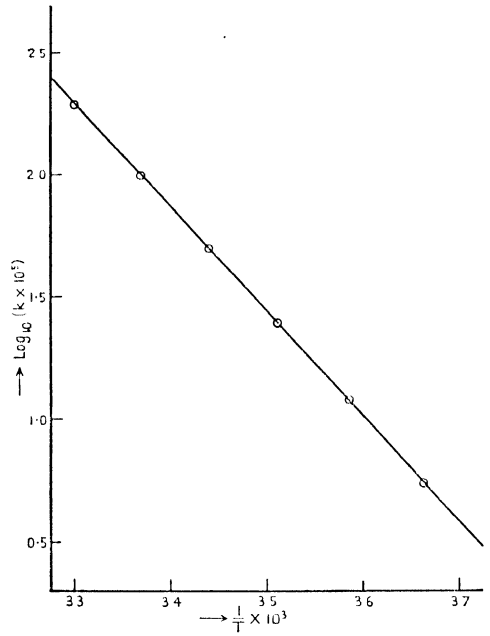


FIG. 3.—Reaction between methyl iodide and sodium ethoxide in ethyl-alcoholic solution. Bimolecular. E = 19,490 calories.

bimolecular, as will be shown presently. The data of Walker and Hambly† conform closely with the equation

$$\ln k_2 = 29{\cdot}08 - 23{,}170/RT.$$

This is the only known instance of a dissolved molecule decomposing bimolecularly while being capable on purely chemical grounds of decomposing unimolecularly. It is

* The addition of ammonium sulphate or potassium cyanate causes an increase in k, compared with which the effect produced by potassium sulphate is negligible. This is consistent with the view that the reactants are the ions NH_4^+ and CNO^-; but other explanations are possible (cf. Chattaway, *Trans. Chem. Soc.*, 170, (1912)).

† *Trans. Chem. Soc.*, **67**, 746, (1895).

Table 3

The conversion of ammonium cyanate into urea in aqueous solution

	$k_2 \times 10^5$ (litres/gram molecule-second)	
$t°$ C.	Observed	By the Arrhenius equation
25·0	3·78	3·78
39·0	23·5	22·2
50·1	86·7	80·0
59·7	240	228
64·5	380	378
69·2	666	608
74·7	1,030	1,040
80	1,660	1,750

interesting to note that the reverse transformation of urea into ammonium cyanate appears to be unimolecular.* Thus a slight increase in molecular complexity from the salt with its electrovalent linkage to the organic molecule with its co-valent bonds is sufficient to lower the kinetic order of the reaction. This affords an interesting comparison with the observation that acetaldehyde in the gaseous phase decomposes bimolecularly,† whereas propionic aldehyde decomposes unimolecularly.‡ The largest molecules known to decompose bimolecularly in the two systems are NH_4CNO and CH_3CHO.

Termolecular Reactions.

The vast majority of reactions in solution belong to the first or second kinetic order. Of reactions involving concentrations raised to higher powers, the reduction of ferric chloride by stannous chloride may be mentioned.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

This was believed by Noyes§ to be termolecular (see, however, p. 220). If the initial concentration of ferric chloride be twice as great as that of stannous chloride, then the

* Burrows and Fawsitt, *ibid.*, **105**, 609, (1914).
† Hinshelwood and Hutchison, *Proc. Roy. Soc.*, **A, 111**, 380, (1926).
‡ Hinshelwood and Thompson, *ibid.*, **A, 113**, 221, (1926).
§ *Z. physikal. Chem.*, **16**, 546, (1895).

instantaneous rate of reaction after t seconds is

$$\frac{dx}{dt} = k_3(a-x)^3;$$

whence

$$k_3 = \frac{1}{2t}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\}. \qquad (4)$$

Velocity constants were determined by chilling samples of the reaction mixture in solutions of mercuric chloride; this oxidized the remaining stannous chloride without affecting the ferrous chloride, which could be estimated by titrating against potassium dichromate. The influence of temperature on the value of k_3 has been investigated by Timofeew, Muchin, and Gurewitsch,* whose results are given in Table 4 along with those calculated by means of the equation $\ln k_3 = 36{\cdot}76 - 21{,}520/RT$.

Table 4

Reduction of ferric ion by stannous chloride in aqueous solution

	$k_3 \times 10^2$ (seconds^{-1}(gram mol./litre)$^{-2}$)	
$t°$ C.	Observed	By the Arrhenius equation
0	5·08	5·08
12	31·5	27·3
15	41	40·4
21	87·5	88·3
25	142	143

At the dilution employed in these experiments (16 litres per gram molecule) the reaction is almost entirely ionic.

Determination of the Order of Reaction.

By substituting the value of $\frac{1}{2}a$ for x in equations 1, 3, and 4, the times of half-completion for the various reactions are:

Unimolecular $$t_{\frac{1}{2}} = \frac{\ln 2}{k_1}$$

Bimolecular $$t_{\frac{1}{2}} = \frac{1}{k_2 a}$$

Termolecular $$t_{\frac{1}{2}} = \frac{3}{2k_3 a^2}.$$

* *Z. physikal. Chem.*, **115**, 161, (1925).

In general, for a reaction of the nth order,

$$t_{\frac{1}{2}} \propto \frac{1}{a^{n-1}}, \tag{5}$$

so that a study of how the time of half-completion varies with the initial concentration enables us to determine to which kinetic order any reaction belongs. The bimolecular character of the conversion of ammonium cyanate into urea, established by Walker and Hambly, was confirmed in this manner by Doyle* whose results are given in Table 5.

Table 5

Conversion of ammonium cyanate into urea at 35° C.

a (gram molecule per litre)	$t_{\frac{1}{2}}$(hours)	$k_2 = 1/t_{\frac{1}{2}}a$ (10^4 litres/gram mol. second)
0·05	37·03	1·50
0·10	19·15	1·45
0·20	9·45	1·47

This is the most reliable method of ascertaining the order of a chemical reaction in solution, and is applicable in the majority of cases. Occasionally, however, an alternative method depending on the change in the initial rate with the concentration is more expedient although less trustworthy.† Frequently it is found that the value of n is not quite a whole number—a consequence of the fact that while the initial concentration is altered the magnitude of the factors determining the rate of reaction is not changed proportionally on account of the slight variation in the properties of the medium. It should be remarked that conformity of the results for a given reaction with one of the well-known velocity constant equations is no evidence that the order of the reaction in question is the same as that for which the equation was deduced (see pp. 209 and 219).

Catalysed Unimolecular Reactions.

A catalyst is a substance which, while undergoing no ultimate change in itself, is able to accelerate the rate at

* *Thesis*, Liverpool, (1922).

† van 't Hoff, *Studies in Chemical Dynamics*, p. 101, (1896).

which other substances undergo chemical transformation. Diazoacetic ester is relatively stable in aqueous solution at ordinary temperatures. In the presence of very small concentrations of hydrogen ion, however, the ester decomposes rapidly:

$$\begin{matrix} N \\ \| \\ N \end{matrix}\!\!\diagdown\!\!\diagup CH.COOC_2H_5 + H_2O \xrightarrow{H^+} CH_2OH.COOC_2H_5 + N_2$$

By measuring the rate at which nitrogen was evolved from well-stirred solutions, Bredig and Fraenkel* found the velocity of reaction at any instant to be proportional to the concentration of ester present at that instant and to the (constant) concentration c_{H^+} of hydrogen ion; hence

$$\frac{dx}{dt} = k_2 c_{H^+}(a-x)$$

or

$$k_{obs} = k_2 c_{H^+} = \frac{1}{t} \ln \frac{a}{a-x}.$$

The reaction is thus essentially bimolecular, the rate depending on the number of encounters between hydrogen ions and ester molecules, although the data for any given concentration of catalyst will conform to the unimolecular law. The value of k_2—sometimes referred to as the catalytic coefficient of the reaction—should thus be independent of the concentration of hydrogen ion and of the nature of the acid from which it is produced. Table 6 shows how adequately these conditions are fulfilled in dilute solutions.

The reaction is the classical instance of hydrogen ion catalysis, and has often been utilized in estimating the concentration of hydrogen ion in systems where the commoner methods are not applicable. The discovery that anions and undissociated molecules can catalyse reactions which had previously been considered to be sensitive to hydrogen ion only cast doubt for a time on the validity of this method. Subsequent work, however, has failed to

* *Z. Elektrochem.*, **11**, 525, (1905).

Table 6

Decomposition of diazoacetic ester in aqueous acidic solutions at 25° C.

Catalysing acid	$c_{H^+} \times 10^4$ (gram ion/litre)	$k_{obs} \times 10^4$ (seconds^{-1})	$(k_2 - k_{obs}/c_{H^+}) \times 10$ (litres/gram mol. second)
Nitric	18·2	11·7	6·45
	9·09	5·77	6·33
Picric	9·09	5·93	6·53
	3·64	2·33	6·38
m-Nitrobenzoic	16·8	9·52	6·28
Fumaric	14·6	10·5	6·52
Succinic	7·24	4·75	6·42
Acetic	5·63	3·63	6·45

detect the catalytic influence of other ions towards this reaction, and many others, which restores the kinetic method of hydrogen ion determinations.* Fraenkel's data† are seen to accord well with the equation $\ln k_2 = 29{\cdot}17 - 17{,}480/RT$.

Table 7

Catalytic decomposition of diazoacetic ester

	$(k_2 = k_{obs}/c_{H^+}) \times 10$ (litres/gram mol. second)	
t° C.	Observed	By the Arrhenius equation
15	2·28	2·33
25	6·42	6·41
35	16·9	16·5
45	41·4	41·4

Pseudo-unimolecular Reactions.

A bimolecular reaction of the type $A + B \rightarrow$ Products, proceeding under such conditions that the concentration of A is greatly in excess of that of B, will appear to be unimolecular. Reference to equation (2) shows that, since $a \gg b$, the maximum value of x is b, so that $(a-x)$ can be regarded as constant and equal to a; hence

$$\frac{dx}{dt} = k_2 a(b-x)$$

* Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59, (1929).

† *Z. physikal. Chem.*, **60**, 202, (1907).

and $$k_{obs} = k_2 a = \frac{1}{t} \ln \frac{b}{(b-x)}.$$

The combination of ethyl iodide and dimethylaniline, when carried out at low concentrations in an inert solvent, is bimolecular:

$$C_2H_5I + C_6H_5N(CH_3)_2 \rightarrow C_6H_5N(CH_3)_2C_2H_5I.$$

If dimethylaniline be used as a solvent, the reaction is unimolecular with respect to the iodide. Hirniak's data* for the reaction under these conditions agree with the equation $\ln k_{obs} = 11{\cdot}79 - 14{,}000/RT$ (Fig. 4).

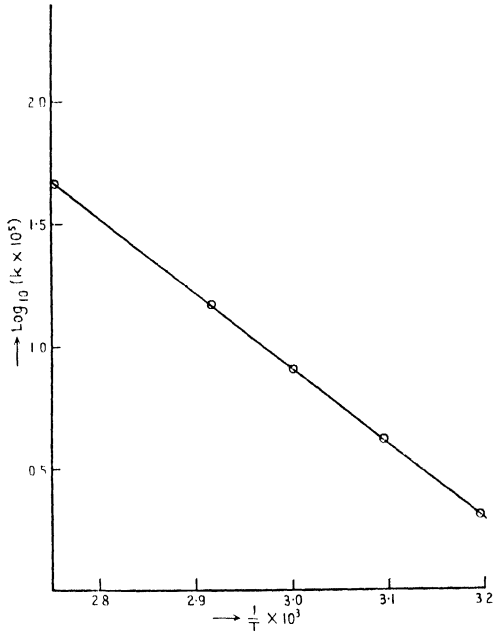


FIG. 4.—Combination of ethyl iodide with dimethylaniline, in dimethylaniline as solvent. Pseudo-unimolecular. E = 14,000 calories.

Had ethyl iodide been used as a solvent, the reaction would have been unimolecular with respect to the other reactant: the change must thus be of the second order. This method

* *Tables Annuelles*, **2**, 508, (1911).

of determining the order of reaction is known as Ostwald's 'isolation' method.

Table 8

Unimolecular constants for the combination of ethyl iodide with dimethylaniline in dimethylaniline as solvent.

	$k_{obs} \times 10^5$ (seconds^{-1})	
$t°$ C.	Observed	By the Arrhenius equation
40	2·05	2·04
50	4·09	4·12
60	7·93	7·94
70	14·7	14·7
90	46·0	45·9

The hydration of acetic anhydride is bimolecular in acetone and in acetic acid solutions,* but is unimolecular with respect to the anhydride in aqueous solution.†

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

The hydration of acid anhydrides in water and their esterification in alcoholic solution, as well as uncatalysed hydrolyses in aqueous solution belong to the class of pseudo-unimolecular changes.

Opposing Unimolecular Reactions.

When a chemical change proceeds not to completion but to an equilibrium stage, it becomes necessary to allow for this fact in deriving the kinetic equations. Relations of greater complexity result, their form depending on the order of the direct and reverse reactions. We shall deal here with the simplest case, i.e. when both changes are unimolecular. Let the initial concentrations of A and B be a and b respectively; x is the amount of change at time t.

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B.$$

$$(a-x) \quad (b+x)$$

* Philip, *Trans. Chem. Soc.*, **28**, 259, (1912).

† Rivett and Sidgwick, *ibid.*, **97**, 732, (1910); Orton and Jones, *ibid.*, **101**, 1708, (1912).

Then $$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_1(a-x) - k_2(b+x),$$

which gives on integration

$$(k_1+k_2) = \frac{1}{t}\ln\frac{S}{S-x}, \qquad (6)$$

where $$S = \frac{k_1 a - k_2 b}{k_1+k_2}.$$

If the initial reaction mixture contains only one reactant ($b = 0$), $S = \dfrac{a}{1+k_2/k_1} = a/(1+K)$. K is the equilibrium constant (Chap. V).

The interconversion of γ-hydroxybutyric acid and its lactone* and of *d*- and *l*-menthone† conform with this equation. So also does the mutarotation of glucose, and certain other sugars, which must be referred to in some detail.

α-Glucose, which has a specific optical rotation of $+113°$, when dissolved in water is converted into a mixture which has a stable rotation of $+52{\cdot}5°$. Similarly, β-glucose, with an initial rotatory power of $+19°$, is converted into the same mixture. Lowry‡ explained these changes in terms of dynamic isomerism, the final mixture in each case representing equilibrium amounts of α- and β-glucose, with possibly a minute quantity of an intermediate form. The changes are accelerated by acids, and to a much greater extent by bases. The temperature coefficient of the velocity of mutarotation of glucose in water was investigated by Hudson and Dale,§ who, supplementing their results with those of Lowry (*loc. cit.*), Trey,|| Osaka,** and others, have compiled the following table. As is to be expected, the observed velocity ($k_\alpha+k_\beta$), whether we examine pure α- or β-glucose, has the same value. Independent experiments

* Henry, *Z. physikal. Chem.*, **10**, 98, (1892).
† Vorländer, *Berichte*, **36**, 268, (1903).
‡ *Trans. Chem. Soc.*, **75**, 212, (1899).
§ *J. Amer. Chem. Soc.*, **39**, 320, (1917).
|| *Z. physikal. Chem.*, **18**, 193, (1895). ** *Ibid.*, **35**, 661, (1900).

Table 9

$t°$ C.	$(k_\alpha+k_\beta)\times 10^4$ (minutes^{-1}; $\log_{10}$)		
	α-glucose	β-glucose	By the Arrhenius equation
0·7	7·4	7·4	7·4
5	12·9	15·0	12·2
10	23·5	22·3	21·6
15	39·9	37·9	37·4
20	63·5	65·4	63·3
25	105	106	106
30	175	168	173
40	437	395	442

show the equilibrium constant K $\left(=\frac{[\beta\text{-glucose}]}{[\alpha\text{-glucose}]}=\frac{k_\alpha}{k_\beta}\right)$ to have a value of 0·554, which is independent of temperature, hence the heat of reaction is zero, and over the complete temperature range $k_\alpha = k_{\text{obs}}\times\frac{1\cdot8}{2\cdot8}$ and $k_\beta = k_{\text{obs}}\times\frac{1}{2\cdot8}$. The Arrhenius equation, in the units referred to, takes the form $\log_{10}(k_\alpha+k_\beta) = 11\cdot0198-3{,}873/T$. Converting the constants into the customary units, we have

$$\ln(k_\alpha+k_\beta) = 22\cdot12-\frac{17{,}660}{RT}.$$

Hitherto we have dealt with the reaction in water only. Hudson and Dale concluded that the temperature coefficient of the reaction catalysed by hydrogen ion is the same as for the uncatalysed reaction. At any given temperature $(k_\alpha+k_\beta) = A+B[\text{H}^+]$, where B is the catalytic coefficient. $\log_{10} B = 11\cdot435-3{,}873/T$, which, on being converted into natural logarithms and seconds^{-1}, may be written as $B = 1\cdot05\times10^{11}e^{-17{,}660/RT}$. It will be shown later (p. 232) that Hudson and Dale's critical increment for the uncatalysed reaction is probably reliable, but that E for the catalysed reaction is too low.

Autocatalysed Reactions.

A chemical change which is hastened by one of its own products is said to be autocatalysed. The interaction

between acetone and bromine in aqueous acidic solution affords an interesting example. Apart from the autocatalytic effect, the change proceeds by way of a fascinating mechanism which was elucidated by Lapworth.* For our present purpose, it will be expedient to consider first the reaction between acetone and iodine, which has been shown to have precisely the same mechanism.†

The net effect of the reaction between acetone and iodine in acidic solution is represented by the equation

$$CH_3COCH_3+I_2 \xrightarrow{H^+} CH_3COCH_2I+H^++I^-.$$

The rate at which acetone disappears is found to be directly proportional to the concentrations of acetone and hydrogen ion but to be independent of the concentration of iodine. If we denote by a and c the initial concentrations of hydrogen ion and acetone respectively, and by x the amount of acetone which has been converted in time t, we have

$$-\frac{d[CH_3COCH_3]}{dt} = k[CH_3COCH_3][H^+]$$

or

$$\frac{dx}{dt} = k(a-x)(c+x),$$

which on integration gives

$$k = \frac{1}{t(a+c)} \ln \frac{a(c+x)}{b(a-x)}. \qquad (7)$$

Lapworth's mechanism is consistent with all the facts known concerning the reaction. The measurable process consists of the enolization of acetone, the rate of which is proportional to $[H^+]$:

$$CH_3COCH_3 \overset{H^+}{\rightleftarrows} CH_3C(OH):CH_2;$$

normally, an equilibrium condition would be established between the keto and enol forms, but in the presence of

* *Trans. Chem. Soc.*, **85**, 30, (1904).
† Dawson, *ibid.*, **95**, 1860 (1909).

iodine the following reaction sets in immediately and completely:

$$CH_3C(OH):CH_2+I_2 \rightarrow CH_3COCH_2I+H^++I^-.$$

It is to be noted that, in spite of the slightly complicated nature of the reaction and the modified form which the expression for the velocity constant consequently assumes, k is simply a bimolecular coefficient denoting the rate at which acetone is enolized when its concentration and that of hydrogen ion are unity.

The influence of temperature on the value of k has been measured by Rice and Kilpatrick,* whose results are given in Table 10. On plotting $\ln k$ against $1/T$ in the usual way, we arrive at the expression $\ln k = 24{\cdot}41 - 20{,}580/RT$.

Table 10

The enolization of acetone in aqueous acidic solution

	$k \times 10^6$ (litres/gram molecule-second)	
$t°$ C.	Observed	By the Arrhenius equation
0	1·16	1·17
24	25·4	25·3
25	27·9	28·6
27	35·9	36·0
35	88·2	88·1

Rice, Fryling, and Wesolewski† found the temperature-coefficient for the velocity of this reaction to be independent of the nature of the catalysing acid and of the presence of a large number of electrolytes and non-electrolytes, although the actual velocity is affected. The average of 21 values for the ratio $k_{25° C.}/k_{23° C.}$, in close agreement with one another, is 1·2625; whence

$$E = \frac{2{\cdot}303\,RT_1T_2}{T_2-T_1}\log\frac{k_2}{k_1} = 20{,}350 \text{ calories.}$$

Generally, the evaluation of the critical increment from velocities determined at two temperatures only—especially

* *J. Amer. Chem. Soc.*, **45**, 1401, (1923). † *Ibid.*, **46**, 2405, (1924).

when these are in such close proximity—is inadmissible. In the present instance, however, there is fair agreement between the two values quoted although greater reliance is to be placed on the first.

The reaction of aldehydes with bromine and iodine follows the same course,* though a certain amount of oxidation occurs at the same time, especially with bromine. Strong evidence in favour of the view that the velocity actually measured is that of enolization is afforded by the identity in the velocity constants found for the two halogens.

Certain similar features are borne by a number of reactions which have been investigated by Stewart and Bradley.† Although the changes do not exhibit autocatalysis, they may conveniently be discussed at this stage. Disubstituted aminomethylsulphonic acids react in aqueous solution with three oxidizing agents—iodine, bromine, and hydrogen peroxide—at exactly the same rate:

$$R_2\overset{+}{N}H.CH_2.SO_3^- + I_3^- + H_2O \rightarrow R_2\overset{+}{N}{:}CH_2 + SO_4^{--} + 3I^- + 3H^+.$$

The velocity, moreover, is unimolecular with respect to the acid and independent of the concentration of the oxidizing agent, even when this is present in minute amounts. The authors point out that these facts indicate the measurable process to be the slow attainment of the equilibrium

$$R_2\overset{+}{N}H.CH_2.SO_3^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} R_2\overset{+}{N}{:}CH_2 + HSO_3^-,$$

which is followed by the rapid oxidation;

$$HSO_3^- + I_3^- + H_2O \rightarrow SO_4^{--} + 3I^- + 3H^+.$$

It may be mentioned that this last reaction, although rapid in comparison with the rate-determining step, has probably a measurable velocity, just like the oxidation of arsenite ions (p. 218) and sulphite ions (p. 261), and coordination reactions generally (p. 171).

* Dawson, Burton, and Ark, *Trans. Chem. Soc.*, 1275, (1914).

† *J. Amer. Chem. Soc.*, **54**, 4183, (1932).

Heterogeneous Reactions.

When a reaction occurs exclusively at the surface of a solid, the number of molecules decomposing per unit time is proportional to the number of adsorbed molecules. The amount (a) of substrate adsorbed depends on the area (A) of the surface and on the concentration (C) of the substrate in the bulk of the solution. These quantities are empirically related by the Freundlich isotherm $a = KAC^{1/n}$, where n and K are constants specific for each system, the latter representing a type of equilibrium between the surface concentration (a/A) and the bulk concentration of the substrate. Whether the reaction considered is of the bimolecular kind, possessing a rate determined by the number of suitable impacts made by dissolved molecules upon the surface, or of a unimolecular type with a rate governed by the stability of the activated, adsorbed molecule, we have for the velocity of reaction

$$-\frac{dC}{dt} = k'C^{1/n},$$

which gives on integration

$$k' = \frac{1}{t}\,\frac{n}{n-1}\{C_0^{(n-1)/n} - C_t^{(n-1)/n}\}. \qquad (8)$$

Sodium hypochlorite in aqueous solution at room temperatures is relatively stable, a slow decomposition of uncertain order setting in and reaching half completion in about three years. In the presence of small quantities of metallic oxides, however, a very rapid reaction takes place due to the catalytic decomposition of adsorbed hypochlorite ions; $ClO^- \rightarrow Cl^- + \frac{1}{2}O_2$. By measuring the volume of oxygen evolved, Chirnoaga* investigated the velocity of reaction under varying conditions. With nickel peroxide as catalyst, $1/n$ is found to be 0·47. Values of k' determined at various temperatures using 0·08 gram of catalyst per litre of well-stirred solution are given in Table 11, along with those calculated from the equation $\ln k' = 20{\cdot}94 - 16{,}580/RT$.

* *Trans. Chem. Soc.*, 1693, (1925).

Table 11

Decomposition of hypochlorite ion at the surface of nickel peroxide

	$k' \times 10^4$ (seconds^{-1}: concentration in gram molecules/litre)	
$t°$ C.	Observed	By the Arrhenius equation
25	8·12	7·83
30	12·4	12·4
35	19·4	19·7
40	29·3	30·5
45	45·2	45·1
50	69·2	68·2

It will be convenient at this stage to comment on the units conventionally adopted to express the quantities with which we have to deal in chemical kinetics. Confusion frequently arises from omitting to state the unit of time employed and from the arbitrary use of common and natural logarithms. A large amount of published material has been marred and rendered almost valueless from this neglect, although absolute magnitudes may occasionally be retrieved by graphical and other means. In the present work *all velocity constants, unless otherwise stated, are expressed in terms of gram molecules per litre, the time unit being the second, and logarithms being taken to the base e.* The critical increment has the usual unit of calories per gram molecule.

Of the vast number of reactions occurring in solution only a very small number fail to conform with the Arrhenius equation. Enzymic reactions are a notable exception. The importance of determining accurately the critical increment has here been stressed because it yields information—necessarily incomplete, it is true—concerning that factor which, among many others, is dominant in deciding the order of magnitude of the velocity of chemical change. This remains true although the equation of Arrhenius, except in simple cases of bimolecular reactions, has been deprived of a good deal of the physical significance originally attaching to it, and is now retained as the most convenient form of epitomizing experimental data.

III

A COMPARISON OF THE KINETICS OF REACTIONS IN THE GASEOUS PHASE AND IN SOLUTION

In general the rate of a chemical reaction is influenced by the medium in which the reaction takes place. The velocity of the combination of ethyl iodide and triethylamine at 100° C., for example, is 750 times as great in acetophenone as in hexane.* Trinitrobenzoic acid decomposes 2,050 times as fast in water at 60° C. as in toluene at the same temperature.† Both bimolecular and unimolecular reactions are thus subject to the influence of the solvent, although the mechanism is probably very different in the two cases.

There have been frequent and varied attempts at correlating the relative catalytic efficiency of different solvents—towards particular reactions—with certain physical properties of the solvent or of the solution. Mention may be made of the solubility,‡ the refractive index,§ the viscosity,‖ the dielectric constant,** and the cohesion.†† An alteration in the magnitude of some of these properties is undeniably accompanied by a change in the velocity of reaction, the parallelism in certain instances being quite striking. There is, moreover, theoretical significance attaching to such empirical observations, since the physical properties concerned, although not directly associated with the kinetic problem, reflect the presence of others which can reasonably be supposed, on certain hypotheses, to influence the rate of chemical change. Solubility, for example, is related to thermodynamic activity, and refractive index to the rate of absorption of radiation;

* Menschutkin, *Z. physikal. Chem.*, **6**, 41, (1890).

† Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **A, 131,** 186, (1931).

‡ Dimroth, *Annalen*, **377,** 127, (1910).

§ Cox, *Trans. Chem. Soc.*, **119,** 142, (1921).

‖ Hawkins, *ibid.*, **121,** 1170, (1922).

** Michael and Hibbert, *Berichte*, **41,** 1080, (1908); Hückel, *Leipziger Vorträge*, **83,** (1929).

†† Soper and Williams, *Trans. Chem. Soc.*, 2297, (1931).

viscosity is connected with the collision frequency, and dielectric constant with the electrical configuration of the molecules and the ionizing power of the solvent. Difficulties, however, arise as soon as semi-empirical formulae relating to a given reaction in a series of solvents are applied to a second reaction, of a different chemical character,* in the same series. It then becomes manifest that such regularities as are found are quite specific. In spite of persistent and ingenious efforts in this direction, the conclusion is unavoidable that all attempts at explaining the phenomena of solvent action on a purely physical basis have failed. Before a theory of sufficient generality can be found, attention will probably have to be redirected to van 't Hoff's view of chemical combination between solute and solvent as one of the prominent factors in the total solvent effect. The acceptance of such a theory in no way precludes the existence of certain molecular species which can be dissolved in suitable solvents without any interaction of this kind. In the absence of further interference these solute molecules should decompose at the same rate in the inert solvents as in the gaseous phase. The requirement which has to be fulfilled in an ideal case, therefore, is that the solute molecules shall be able to acquire sufficient energy to allow them to decompose, but that this amount of energy shall be insufficient to permit of any interaction with the solvent. That conditions of this kind are rarely met with is perhaps not surprising. Nevertheless, examples have been revealed of reactions of varying kinetic type possessing rates and energies of activation which are the same in the gaseous phase as in certain inert solvents. These bear an importance which is equalled only by their rarity, for they serve to establish the normal behaviour, by investigating departures

* Sometimes, even towards two similar reactions, the catalytic order of a series of solvents may be different. Thus, for the combination of bromacetophenone and aniline, the velocity of reaction increases with the dielectric constant of the solvent; but for the combination of allyl bromide and aniline, the reverse state of affairs is found.

from which the study of solvent action may rightly be said to commence.

The experimental comparison between the rates of reactions in solution and in the gaseous phase clearly offers the most direct course for examining the influence of the solvent, and is in principle very simple. The difficulties, in fact, lie almost entirely on the experimental side. It is clearly necessary for the reaction to proceed homogeneously and with measurable speed in the two phases. The solvent, moreover, while being able to dissolve the reactant in convenient proportions, must be incapable of reacting with it. Furthermore, the rate of reaction in solution must be such that it can be measured at temperatures below or not far above the boiling-point of the solvent. Of the reactions which have been examined in the homogeneous gas phase, few proceed with measurable velocity at temperatures round about the boiling-points of suitable solvents. On the other hand, of the reactions which have hitherto been investigated exclusively in solution, two have recently been studied in the gaseous phase.* These proved to be heterogeneous, a behaviour which is probably indicative of the majority of such reactions, particularly when one of the products is a solid. There exist at present six thermal reactions in all which have afforded direct comparison between the rates in the gaseous phase and the rates either in the pure liquid phase or in carbon tetrachloride solution.

THERMAL REACTIONS

The Decomposition of Nitrogen Pentoxide.

Nitrogen pentoxide in the homogeneous gas phase at room temperatures decomposes unimolecularly, except at very low pressures. Although the change is known to involve the transitory formation of other oxides of nitrogen, the net reaction is

$$N_2O_5 \rightarrow N_2O_4 + \tfrac{1}{2}O_2.$$

* Moelwyn-Hughes and Hinshelwood, *Trans. Chem. Soc.*, 230, (1932).

Unimolecular constants determined manometrically for the gaseous reaction by Daniels and Johnston,* and subsequently confirmed by the colorimetric measurements of White and Tolman,† are compared in Table 1 with the constants found by Lueck‡ for the reaction in carbon tetrachloride and in chloroform solution. Neither of these solvents alters the velocity to any very marked extent,

Table 1

	$k \times 10^5$ (seconds^{-1})		
$t°$ C.	In gas	In CCl_4	In $CHCl_3$
25	3·38	4·09	3·72
30	5·89	8·42	10·3
35	13·5	16·2	14·5
40	24·7	32·2	38·1
45	49·8	61·1	50·1
50	75·9	116	128
55	150	212	166
E (calories)	24,710	25,500	24,450

although the slight difference recorded is probably real. Eyring and Daniels§ found that bromine, nitrogen tetroxide, nitromethane, and three chlorine-substitution products of ethane also act as relatively inert solvents, but nitric acid and dichlorpropane reduce the rate about twenty-five-fold and cause the critical increment to increase to 28,300 calories. These deviations from the normal values characteristic of the gaseous reaction are attributed by the authors to the formation of definite complex molecules which are assumed to possess stabilities differing from the stability of free nitrogen pentoxide.

The Isomerization of Pinene.

At temperatures of about 200° C., *d*-pinene is converted slowly into di-pentene,‖ the reaction proceeding unimolecularly in the homogeneous gas phase. Velocity constants

* *J. Amer. Chem. Soc.*, **43**, 53, (1921).
† *Ibid.*, **47**, 1240, (1925).
‡ *Ibid.*, **44**, 757, (1922).
§ *Ibid.*, **52**, 1473, (1930).
‖ Conant and Carlson, *ibid.*, **51**, 3464, (1929).

determined polarimetrically by Smith* at six temperatures ranging from 184·6 to 237·1° C., and expressed in reciprocal seconds, are given by the equation

$$\ln k = 33{\cdot}77 - \frac{43{,}710}{RT}.$$

In the pure liquid phase and in petrolatum solution, the rate of reaction is again not very different from that of the gaseous reaction (Table 2). The small variation found for the

Table 2

$t°$ C.	Medium	$k \times 10^7$ (seconds^{-1})
184·6	Gas	3·66
184·5	Pure liquid	4·99
198·0	Gas	14·3
197·8	Petrolatum	21·3
217·9	Gas	88·5
217·9	Petrolatum	130

reaction in solution may not be genuine, for a slight optical activity possessed by the solvent indicated the presence of small quantities of impurity. The critical increment for the reaction in solution appears to be 41,210 calories. Experiments were performed, however, at two temperatures only, and at one of these without duplication, so that within the limits of a fairly wide experimental error this value must be regarded as equal to E for the gaseous reaction. Unfortunately no estimate can be formed for the energy of activation in the pure liquid phase.

The Decomposition of Chlorine Monoxide.

The thermal decomposition of chlorine monoxide ($2Cl_2O \rightarrow 2Cl_2+O_2$) in the homogeneous gas phase proceeds in consecutive stages.† The pronounced acceleration which follows the initial period of very slow change cannot be

* *Ibid.*, **49**, 43, (1927).

† Hinshelwood and Prichard, *Trans. Chem. Soc.*, **123**, 2730, (1923); Hinshelwood and Hughes, *ibid.*, **125**, 1841, (1924).

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attributed to autocatalysis since the introduction of oxygen or of chlorine does not influence the velocity. The rate of reaction at each stage responds to the effect of pressure in a manner characteristic of bimolecular changes. From the nature of the curves showing the percentage composition as a function of the time, it is concluded that the absolute velocity for each stage of the decomposition must be of the same order of magnitude, and, as would be anticipated under such conditions, the energy of activation is sensibly constant over the complete range. The foregoing explanation accounts in a consistent and satisfactory manner for the principal facts known concerning the reaction. An alternative mechanism in terms of reaction chains has been suggested by Beaver and Stieger.*

The kinetics of this reaction have also been examined in carbon tetrachloride solution.† In the absence of traces of water, which retards the reaction, and of light, which induces photochemical decomposition, the change corresponds closely to that occurring in the gaseous phase. There is an initial period of very slow change, followed by marked acceleration. By varying the initial concentration of chlorine monoxide, each stage in the reaction has been shown to be definitely bimolecular.

It is an unfortunate occurrence that separate values for the bimolecular constants for the consecutive stages cannot, on account of mathematical difficulties, be disentangled. A quantitative comparison between the rates in the two systems becomes possible, however, from a knowledge of the times required for the reaction to proceed to a given extent in the gas and in solution. In Table 3, the observed rates of the reaction in carbon tetrachloride are compared with corresponding rates for the gaseous reaction, which have been extrapolated from data referring to other temperatures and concentrations. $t_{20\text{-}60 \text{ per cent.}}$ represents the time, in

* *Z. physikal. Chem.*, **B, 12,** 93, (1931).

† Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **A, 131,** 177, (1931).

minutes, required by the reaction to proceed from 20 per cent. to 60 per cent. of completion. Within the limits of experimental uncertainty, the rate of decomposition in

Table 3

$[Cl_2O]$ (gram molecule per litre)	t° C.	$t_{20\text{-}60 \text{ per cent.}}$ (minutes)		$\frac{t_{solution}}{t_{gas}}$
		For solution	For gas	
0·224	70·7	50	47·5	1·05
0·115	71·0	105	90·5	1·16
0·115	59·8	257	225	1·14
0·126	69·8	83	90·5	0·92
0·095	69·7	100	122	0·82
0·120	80·1	55	44	1·25
0·120	75·3	54	61	0·89
0·120	65·2	139	137	1·02
0·120	60·1	200	211	0·95

solution equals that in the gas, the ratio $t_{solution}/t_{gas}$ having an average value of 1·02. The energy of activation for the reaction in solution is 20,300 calories, again corresponding fairly closely to the value for the gaseous reaction (21,000 calories).

The Decomposition of Ozone.

At temperatures of about 100° C., ozone decomposes in the presence of oxygen and other gases, the reaction being predominantly bimolecular and homogeneous, but a small fraction of the ozone molecules decompose unimolecularly, probably on the surface of the vessel.* The velocity of reaction is retarded by an increase in the partial pressure of oxygen, and accelerated by the introduction of nitrogen, carbon dioxide, and inert gases. Griffith and McKeown† explain this on the assumption that an activated complex is produced which can either revert into normal ozone molecules or decompose: the process of reversal is favoured by collision with oxygen molecules and that of decomposition by collision with molecules of other gases. Values for the

* Riesenfeld and Bohnholzter, *Z. physikal. Chem.*, **130**, 241, (1927).

† *Trans. Chem. Soc.*, **127**, 2086, (1925).

energy of activation have been given as 27,800 calories* and 29,000 calories.†

With regard to the molecular statistics of the reaction, it can be shown that if an energy of activation of 28,700 calories per gram molecule be regarded as shared among two square terms only, then for each energetically suitable collision about 13,500 molecules of ozone actually decompose. It is therefore possible that appropriate collisions between two ozone molecules represent the initial stage in a chain reaction, a view which is strengthened by the exothermic nature of the change and by the sensitiveness of the rate to the presence of foreign gases. On the other hand, the activation process may not be simple. If six internal degrees of freedom participate, the theoretical rate at 100° C. would be $1{\cdot}13\times10^{-1}$ litre/gram molecule-second, a value which compares favourably with that of $1{\cdot}59\times10^{-1}$ observed by Griffith and McKeown.

The decomposition of ozone occurs more readily in carbon tetrachloride solution than in the gas.‡ Rather surprisingly, however, the reaction is unimolecular with respect to the ozone. Satisfactory unimolecular constants were obtained with samples of ozone prepared in the silent discharge and electrolytically from aqueous sulphuric acid, and with carbon tetrachloride which had been stringently purified by various methods. The half-life was found not to vary with a five-fold change in the initial concentration of ozone nor to be affected by intensely drying the solvent.

In comparing the velocities of decomposition in the gaseous state and in solution, we must confine ourselves to a single concentration of ozone, since the apparent order of reaction is different in the two systems. Taking $[O_3]_0$ as $1{\cdot}5\times10^{-3}$ gram molecule per litre, it is found that, at 71°

* Belton, Griffith and McKeown, *Trans. Chem. Soc.*, **129**, 3153, (1926).

† Wulf and Tolman, *J. Amer. Chem. Soc.*, **49**, 1650, (1927).

‡ Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc.*, **A, 134**, 211, (1931).

and 55° C., ozone in carbon tetrachloride solution disappears 30 to 40 times as fast as at a corresponding concentration in the gaseous phase.

Examination of the products of reaction showed that ozone had attacked the carbon tetrachloride to some extent. By estimating the concentration of chloride ion in an aqueous extract it appeared that out of about every 17 molecules of ozone which had decomposed, one molecule had reacted with the solvent. This, therefore, does not account for more than a fraction of the total change and is either a relatively unimportant side-reaction or the first stage of a chain reaction in which about 17 molecules of ozone are decomposed for each initial act. The rate being proportional to $[O_3][CCl_4]$, and the subsequent stages being assumed rapid, the reaction would conform to the unimolecular law. If this is the true mechanism, it becomes necessary to correct the observed value of the energy of activation in a manner which will be described in Chapter V. The result is to increase E from 26,160 to 28,750 calories and thus to bring the values for the energies of activation in the two systems into close proximity. It will also be shown later that the observed rate of reaction in solution is from 10 to 22 times as rapid as that calculated on the assumption that the ozone molecules become activated by collision with solvent molecules.

If, on the other hand, the reaction between ozone and the solvent can be regarded simply as a side-reaction we have the very interesting fact that a decomposition, bimolecular in the gaseous state, becomes unimolecular in solution. This would mean that the gaseous reaction was really of the quasi-unimolecular type, the molecules becoming activated by collisions but undergoing subsequent spontaneous change. As we have seen in Chapter I, such reactions appear bimolecular at low pressures and unimolecular at higher pressures or in the presence of an inert gas. In the present example the solvent plays the part of the inert gas,

at great pressures, communicating the energy of activation.

The Decomposition of Ozone Catalysed by Chlorine.

Bodenstein, Padelt, and Schumacher,* studying the gaseous reaction manometrically at 35° and 50° C., where the uncatalysed decomposition of ozone is slow enough to be ignored, found that the rate of disappearance of ozone was given by the relation

$$-\frac{d[O_3]}{dt} = k[Cl_2]^{\frac{1}{2}}[O_3]^{\frac{3}{2}} \quad \text{or} \quad k = \frac{1}{(t_2-t_1)[Cl_2]^{\frac{1}{2}}}\left(\frac{1}{[O_3]_2^{\frac{1}{2}}} - \frac{1}{[O_3]_1^{\frac{1}{2}}}\right).$$

After an initial induction period, k rises to a constant value which is not altered when the initial concentrations of ozone and of chlorine are varied by factors of 4 and 7 respectively. The authors consider the reaction to proceed by a chain mechanism, according to the following scheme:

1. $Cl_2+O_3 \rightarrow ClO+ClO_2$
2. $ClO_2+O_3 \rightarrow ClO_3+O_2$
3. $ClO_3+O_3 \rightarrow ClO_2+2O_2$
4. $ClO_3+ClO_3 \rightarrow Cl_2+3O_2$
5. $ClO+ClO \rightarrow Cl_2+O_2$
6. $ClO+O_3 \rightarrow Cl+2O_2$.

The induction period is regarded as the time required for the shortlived intermediate products ClO_2 and ClO_3 to attain the stationary concentrations governed by the relations

$$+\frac{d[ClO_3]}{dt} = k_2[ClO_2][O_3]-k_3[ClO_3][O_3]-k_4[ClO_3]^2 = 0,$$

$$+\frac{d[ClO_2]}{dt} = -k_2[ClO_2][O_3]+k_3[ClO_3][O_3]+k_1[Cl_2][O_3] = 0.$$

By addition, we have

$$[ClO_3] = \sqrt{\left(\frac{k_1}{k_4}[Cl_2][O_3]\right)}.$$

* *Z. physikal. Chem.*, **B, 5,** 209, (1929).

The term $k_4[ClO_3]^2$, it is assumed, can be omitted in comparison with the term $k_3[ClO_3][O_3]$, although this would be strictly justifiable only with the knowledge that k_4 and k_3 are commensurate. We have thus

$$[ClO_2] = \frac{k_3}{k_2}[ClO_3] = \frac{k_3}{k_2}\sqrt{\left(\frac{k_1}{k_4}[Cl_2][O_3]\right)}.$$

Now the rate at which ozone decomposes is clearly

$$-\frac{d[O_3]}{dt} = k_3[ClO_3][O_3]+k_2[ClO_2][O_3]+k_1[Cl_2][O_3],$$

from which the last quantity, representing the first link in a long chain, can be eliminated, so that

$$-\frac{d[O_3]}{dt} = k_3[O_3]\sqrt{\left(\frac{k_1}{k_4}[Cl_2][O_3]\right)}+k_2[O_3]\frac{k_3}{k_2}\sqrt{\left(\frac{k_1}{k_4}[Cl_2][O_3]\right)}$$

or

$$-\frac{d[O_3]}{dt} = 2k_3\sqrt{\frac{k_1}{k_4}}[Cl_2]^{\frac{1}{2}}[O_3]^{\frac{3}{2}}.$$

This is the desired experimental relation, although derived from somewhat insecure experimental evidence.

Bowen, Moelwyn-Hughes, and Hinshelwood* investigated this reaction in carbon tetrachloride solution at temperatures where the uncatalysed decomposition of ozone can no longer be neglected. If both this and the catalysed reaction proceed simultaneously and independently, we have for the rate of the combined reaction

$$-\frac{d[O_3]}{dt} = k[Cl_2]^{\frac{1}{2}}[O_3]^{\frac{3}{2}}+k'[O_3].$$

This gives on integration:

$$k't = \ln\frac{[O_3]_0}{[O_3]_t} - 2\ln\left(\frac{k[O_3]_0^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}+k'}{k[O_3]_t[Cl_2]^{\frac{1}{2}}+k'}\right).$$

The data found for the reaction in solution conformed moderately well with this equation, the value of k, as with the gaseous reaction, showing a tendency to increase as the reaction proceeded. Only a two-fold change in the initial

* *Loc. cit.*

concentration of ozone was practicable, but $[Cl_2]$ was varied twenty-fold. The average of 7 values for k relating to the reaction in solution at 50° C. is $1{\cdot}45 \times 10^{-2}$ litres/gram molecule-second. Bodenstein, Padelt, and Schumacher find $k = 9{\cdot}50 \times 10^{-3}$ for the gaseous reaction. Hence $k_{solution}/k_{gas}$ is 1·53. The agreement is rather striking considering the unquestionable complexity of the reaction. The critical increment for the gaseous reaction is 20,040 calories, and for the reaction in carbon tetrachloride solution 26,730 calories. The difference may be due to the not inconsiderable experimental error introduced by determining this quantity from velocity measurements carried out at two temperatures only. Alternatively, if we are dealing with a chain reaction, the Arrhenius equation will not be strictly followed, so that the discrepancy can be attributed to the different temperature ranges employed in the two systems.

The Formation of Nitrosyl Chloride.

A termolecular collision is an occurrence of such comparative rarity that unless the critical increment necessary to render such a collision chemically effective is small the rate of reactions depending upon it will be negligible. Trautz and Schueter* find that the combination of nitric oxide with chlorine in the gaseous phase is termolecular ($2NO+Cl_2 \rightarrow 2NOCl$) and possesses the low temperature coefficient which is to be anticipated from the fact that the reaction proceeds with measurable speed. According to the proposed mechanism

$$NO+Cl_2 \rightleftarrows NOCl_2; \qquad K = \frac{[NOCl_2]}{[NO][Cl_2]};$$

$$NOCl_2+NO \rightarrow 2NOCl,$$

the rate of formation is given by the expression

$$+\frac{d[NOCl]}{dt} = k[NOCl_2][NO] = Kk[Cl_2][NO]^2,$$

* *Z. anorg. Chem.*, **136**, 1, (1924).

so that the observed termolecular constant involves an equilibrium constant (K) and a bimolecular constant (k). The reaction has been studied also in the liquid phase by Trautz and Gerwig* who advance cryoscopic evidence for the formation of the intermediate compound. The value of the termolecular constant (Kk) for the reaction in the liquid phase at $-58°$ C. is 10 (gram molecule/litre)$^{-2}$.seconds^{-1}, as compared with the corresponding value of 0·7 found by extrapolation from the data referring to the gaseous reaction. In the condensed state it would appear therefore that the rate is about 14 times as fast as in the gaseous phase. The difference is probably real and indicates a positive solvent effect.

PHOTOCHEMICAL REACTIONS

The general theory of activation demands that only molecules in an exceptional state shall undergo chemical change, but does not specify the manner in which ordinary molecules can enter into that state. In thermal reactions, as we have seen, molecules become activated by the redistribution of energy during impacts. In photochemical reactions, radiation absorbed by the molecules from an external source supplies the necessary energy. The Stark-Einstein law of photochemical equivalence states that, in a photosensitive system illuminated by radiation of frequency ν, one molecule will decompose for each quantum $h\nu$ of energy absorbed. In this simple form the law is true in a few cases only, but there is powerful evidence for regarding it as strictly applicable to the primary process in all photochemical reactions. Generally, therefore, the rate of the primary process, and in certain cases the rate of chemical change also, will be simply the rate at which the molecules absorb radiation. Under the experimental conditions usually employed, this rate is constant, so that many photochemical reactions are of zero order, the number of molecules decomposing per second being independent of

* *Ibid.*, **146**, 1, (1925).

time. The kinetics of reaction, as the term is understood in connexion with thermal processes, do not therefore occupy as prominent a place in the study of photochemical reactions as the determination of the quantum efficiency. This is defined as the ratio of the number of molecules decomposed to the number of light quanta absorbed, or

$$\gamma = \frac{\text{number of molecules decomposed}}{\text{number of molecules activated in the primary process}}.$$

In the majority of cases which have been examined, the activated molecules produced by the absorption of radiation, or the atoms resulting from the dissociation of these activated molecules, are able to bring about the decomposition of fresh molecules of reactant. Frequently also the primary process is but the initiation of a reaction chain wherein several molecules are transformed. For our purpose, however, we are less concerned with the actual quantum yield than with the manner in which it may be influenced by the presence of a solvent. The general problem of photochemical kinetics has been treated in a comprehensive manner by Griffith and McKeown.*

The Decomposition of Hydrogen Iodide.

For each quantum of radiation absorbed by gaseous hydrogen iodide in the spectral region 2,070–2,820 Å, two molecules decompose, this number being independent of temperature.† The following mechanism of the reaction, proposed by Warburg,‡ is now regarded as established:

1. $HI + h\nu \rightarrow H + I$
2. $H + HI \rightarrow H_2 + I$
3. $I + I \rightarrow I_2$.

For each act of initial activation, two molecules decompose. In the liquid state also the quantum efficiency is 2.

The observed quantum sensitivity in hexane solution in-

* *Photoprocesses in Gaseous and Liquid Systems*, Longmans, (1929).

† Bodenstein and Lieneweg, *Z. physikal. Chem.*, **119**, 123, (1926).

‡ *Sitzungsber. Preuss. Akad.*, 314, (1916).

creases from 1·01 in dilute solutions absorbing at $\lambda = 2070$ Å. to 2 for approximately 1-molar solutions absorbing at $\lambda = 2{,}820$ Å. Warburg and Rump* suggest that the concentration effect may be accounted for by the diminished probability of reaction (2) in very dilute solutions, whereas the variation of γ with the wave-length may be associated with the change in absorption coefficient. In aqueous solution, the quantum efficiency, as before, increases with the concentration but is lessened by an increase in the wave-length; it is, furthermore, uniformly lower than in hexane solution.

We therefore see that the relative simplicity of the gaseous reaction is reproduced in the liquid phase. Hexane introduces complications which are probably explicable on physical grounds, but water interferes with the mechanism in a more radical way, possibly by hydrating the hydrogen iodide, as Warburg and Rump suggest.

The Decomposition of Chlorine Monoxide.

The quantum efficiency of 2 found by Bowen† for the gaseous decomposition of chlorine monoxide has been confirmed by Bodenstein and Kistiakowsky‡ who showed the value to be unaffected by chlorine-sensitization. Both investigations yielded evidence of the intermediate formation of a second oxide of chlorine, which is considered by Schumacher and Wagner§ to be ClO, produced by a predissociation mechanism from activated Cl_2O.

The first investigation of the photochemical decomposition in carbon tetrachloride solution gave an apparent quantum efficiency of about 1, a result for which no great accuracy was claimed since the method of analysis was admittedly inadequate to allow for the accompanying formation of chlorine dioxide.|| Correcting quantitatively for the part

* *Z. physikal. Chem.*, **47**, 305, (1928).
† *Trans. Chem. Soc.*, **123**, 2330, (1923).
‡ *Z. physikal. Chem.*, **116**, 371, (1925).
§ *Ibid.*, **B, 5**, 199, (1929). || Bowen, *Trans. Chem. Soc.*, **123**, 1199, (1923).

played by chlorine peroxide, which was estimated photometrically, Dickenson and Jeffreys* found a quantum efficiency of 2, as in the gaseous phase.

The Decomposition of Chlorine Peroxide.

Gaseous chlorine peroxide is transformed, partly into chlorine hexoxide but chiefly into chlorine and oxygen, in blue light, the quantum efficiency being approximately 2;† The primary process again involves the formation of chloric oxide: $ClO_2+h\nu \rightarrow ClO+O$, absorption of radiation with wave-length below 3753 Å. indicating predissociation.‡

The reaction in carbon tetrachloride solution, which seems not to entail the production of chlorine hexoxide and to involve predissociation of chlorine peroxide at an energy level ($\lambda = 4050$ Å.) lower than in the gas, shows a quantum efficiency of about 1 at 4450 Å.§ and 2 at 4150 Å.‖ The limiting value of γ in the inert solvent is thus equal to the value for the gaseous reaction. In aqueous solution the maximum quantum yield is 1. Bowen and Cheung** have shown this to be due to the fact that chloric oxide, a product of the initial activation, which in the gaseous phase or in an inert solvent is available for inducing the decomposition of a second molecule of ClO_2, is deprived of this opportunity in aqueous solution by interaction with the solvent, the net effect being represented by the equation

$$2ClO+H_2O \rightarrow HClO_3+HCl.$$

The Decomposition of Ozone Sensitized by Chlorine.

Bonhoeffer†† found that for each quantum of radiation ($\lambda = 4160$ Å.) absorbed by chlorine, two molecules of ozone

* *J. Amer. Chem. Soc.*, **42**, 4288, (1930).

† Booth and Bowen, *Trans. Chem. Soc.*, **127**, 510, (1925); Bodenstein, Harteck, and Padelt, *Z. anorg. Chem.*, **147**, 233, (1925).

‡ Finkelberg and Schumacher, *Z. physikal. Chem.*, 'Bodenstein Festband', 704, (1931); Urey and Johnston, *Physical Rev.*, **38**, 2131, (1931).

§ Bowen, *Trans. Chem. Soc.*, **123**, 1199, (1923).

‖ Nagai and Goodeve, *Trans. Faraday Soc.*, **27**, 508, (1931).

** *Trans. Chem. Soc.*, 1200, (1932). †† *Z. Physik*, **13**, 94, (1923).

decompose in the gaseous phase, the number being independent of the concentration of the reactants. The photosensitized reaction in carbon tetrachloride solution also exhibited a quantum efficiency of 2.* Weigert's observation† that the temperature coefficient is 1·17 casts some doubt as to whether the reaction is really as simple as the quantum efficiency of 2 would imply. This does not affect, however, the conclusion that the mechanism in the gaseous phase and in carbon tetrachloride solution appears to be essentially the same.

The Decomposition of Nitrogen Trichloride.

Radiation within the spectral region 4360–3650 Å. brings about the decomposition of gaseous nitrogen trichloride: $2NCl_3 \rightarrow N_2+3Cl_2$, in the presence of chlorine as a photosensitizer. The quantum efficiency, which is independent of the wave-length, is about 20 for low concentrations of chlorine but falls to a limiting value in the neighbourhood of 2 as the partial pressure of chlorine is increased. The reaction is initiated by chlorine atoms, and proceeds by way of a reaction chain of short length.‡

The quantum sensitivity in carbon tetrachloride solution is also approximately 2,§ and independent of the wave-length and of whether the reaction is chlorine-photosensitized or directly photolytic. The absence of a high quantum yield probably indicates that the solvent furnishes the maximum deactivation effect which in the gaseous reaction is attributable to added chlorine. As in the thermal decomposition of ozone, the solvent molecules appear to be influencing the reaction by acting as an inert gas at an enormous pressure.

* Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc.*, **A, 134,** 211, (1931).

† *Z. Elektrochem.*, **14,** 591, (1908).

‡ Griffiths and Norrish, *Proc. Roy. Soc.*, **A, 130,** 591, (1931); **135,** 69, (1932).

§ Bowen, *loc. cit.*

Discussion.

Two important consequences emerge from the comparison which has here been drawn between the kinetics of reactions in solution and in the gaseous phase. The first is of considerable value in the information it affords concerning the rates of collisions between dissolved molecules. The second, while being more limited in its applicability, establishes a principle which enables the relative catalytic efficiency of solvents to be estimated.

It is first necessary to reproduce the general equation for the velocity constant of thermal reactions: $k = Z.f(E/T)$, where $f(E/T)$ represents the fractional number of molecules in the critically activated state. The velocity constant for unimolecular reactions, as we have seen, is the ratio of the number of molecules decomposing per second to the total number of molecules, so that Z defines approximately the probability per second that an activated molecule shall decompose. It has the dimensions of a frequency, and for the majority of gaseous reactions its magnitude lies between 10^{11} and 10^{15} seconds^{-1}. The average life of an activated molecule is $1/Z$, and is related to the interval between activation and reaction required for the redistribution of the critical energy within the molecule. The important point is that Z for unimolecular processes is a composite term, involving one quantity which is an inherent property of the reacting molecule and another quantity which depends on the system in which the reaction takes place. The term Z for simple bimolecular reactions is a collision frequency, denoting the number of encounters between the reacting molecules under standard conditions. This is solely a property of the reacting system.

Reference to the experimental data quoted above shows that for two unimolecular reactions and for two other reactions, which although not free from complications are essentially bimolecular in character, the velocity is sensibly the same in the gaseous phase as in solution in inert solvents.

Where such comparison is legitimate, the observed energy of activation also is the same. It follows that the value of Z has not been altered by the solvent. Considering the nature of this term as it relates to reactions of the first order, the result is not startling; it would, in fact, be a matter for surprise if the probability of transformation of an activated molecule were found to be influenced by the presence of a medium the complete inertness of which allows the energy of activation to remain constant. On the other hand, the quantity Z for bimolecular reactions, being a collision term, can on theoretical grounds undergo independent variation while leaving the energetics of the reactions unchanged. Actually, however, its value is virtually identical in the gas and in inert solvents, indicating that the total number of relevant collisions suffered by the reacting molecules is the same in the two systems. Experimental confirmation on this point has hitherto been lacking, although its validity on general grounds has never been seriously contested. The important consequence for our purpose is that the number of collisions between dissolved molecules, in dilute solution in inert solvents, can now be evaluated by means of the expression given by the kinetic theory for the number of collisions between gaseous molecules.

Secondly, the foregoing comparison of data for thermal reactions affords evidence for regarding carbon tetrachloride as a normal solvent in the sense that it allows thermal reactions of varying kinetic type to proceed at the same rate in solution as in the gaseous phase. We have now to examine the behaviour of this solvent towards photochemical reactions.

In an ideal photochemical change the rate of reaction, as previously stated, is simply the rate of absorption of radiation. This the solvent can influence not only by modifying the absorption coefficient but by causing a shift in the position of maximum absorption. Secondary changes, moreover, usually follow the primary stage, and these dark

reactions will be subject to a similar solvent interference as is found in ordinary thermal reactions. It has been shown above that a quantum efficiency of 2 characterizes the photolysis of chlorine monoxide and chlorine peroxide as well as the chlorine-sensitized decomposition of ozone both in the gaseous phase and in carbon tetrachloride solution. Now although this throws no light on the actual rate of reaction in either system, it indicates quite clearly that the number of effective collisions necessary to propagate the dark reactions has not been diminished by the presence of the solvent. Similar remarks apply to the bromine-sensitized oxidation of monobromtrichlormethane,* the chlorination of the same compound,† and the bromine-sensitized conversion of diethyl maleate into diethyl fumarate.‡ The quantum yields found for these three reactions in the liquid phase is not altered by dilution to a considerable extent in carbon tetrachloride. The isomeric change is singularly interesting, for its high quantum efficiency ($\gamma = 295$) and its marked temperature coefficient indicate it to be very complicated. The reaction proceeds by a chain mechanism wherein bromine atoms play a prominent part. The energy possessed by these atoms is therefore not dissipated by repeated collisions with solvent molecules.

That the quantum efficiency of photosensitized reactions in solution is independent of the dilution demonstrates the specific nature of the energy transfer in chain reactions, a conclusion which is fully attested by the action of inhibitors. The same truth has been revealed spectroscopically, and by Hinshelwood's observations on the influence of hydrogen and inert gases on the velocity of unimolecular reactions.

The photochemical evidence, therefore, serves to consolidate the position of carbon tetrachloride as an inert solvent. There is every reason to suppose that other solvents

* Gruss, *Z. Elektrochem.*, **29**, 144, (1923).

† Noddack, *ibid.*, **27**, 359, (1921).

‡ Eggert and Borinski, *Physikal. Z.*, **24**, 504, (1923); **25**, 19, (1924).

—such as silicon tetrachloride, tetramethylmethane, hexane, and cyclohexane, for example—consisting of unassociated, symmetrical (non-polar), and chemically saturated molecules will behave similarly. In the case of reactions which cannot be measured in the gaseous phase, the rates in such solvents may be regarded as standard values with which rates in other solvents may be compared. We may consider as an example the data of Menschutkin* on the velocity of combination of ethyl iodide and triethylamine in a series of twenty solvents (p. 107). The slowest rate was found in hexane solution, k being $4{\cdot}92\times10^{-6}$ litres/gram molecule-second at 100° C.; the fastest rate referred to benzyl alcohol, for which $k = 6{\cdot}93\times10^{-3}$. Benzyl alcohol thus exerts a positive catalytic effect. From the results of von Halban† on the decomposition of triethylsulphonium bromide in tetrachlorethane and in benzyl alcohol, the values of k at 60° C. are found to be $2{\cdot}19\times10^{-4}$ and $5{\cdot}64\times10^{-7}$ seconds^{-1} respectively. Towards this reaction benzyl alcohol acts as a negative catalyst. Finally, we have Plotnikow's observations‡ on the photo-polymerization of vinyl chloride in various solvents; the maximum rate is found in carbon tetrachloride solution and diminishes regularly as alcohols, ethers, and aromatic hydrocarbons are used as solvents. In carbon disulphide solution no reaction was detected.

As a rule, it is clear that carbon tetrachloride behaves precisely in the way which might be expected from its chemical character, and is without influence on the reactivity of molecules dissolved in it.§ By comparisons of the kind

* *Z. physikal. Chem.*, **6**, 41, (1890). † *Ibid.*, **67**, 129, (1909).

‡ *Z. wiss. Phot.*, **21**, 117, (1922).

§ Ozone, however, reacts with this solvent, and, in the presence of minute quantities of water, so does triethylamine. The latter side reaction would not have been detected even in quite accurate work but for the accidentally low solubility of the product, triethylammonium chloride. Thermodynamic evidence will be cited later to show that carbon tetrachloride probably reacts with nitrogen peroxide. Complexes of this substance with ethers and esters have been detected cryoscopically, although their existence is probably confined to fairly low temperature regions. (Wyatt, *Trans. Faraday Soc.*, **25**, 43, (1929).)

which have just been made it becomes possible to distinguish between the positive and the negative catalytic influences of solvents in general, and thus to prepare the way for the further and more difficult task of discovering how these influences are exerted.

IV

BIMOLECULAR REACTIONS

THE vast majority of chemical reactions occur in liquid systems. Most of these are bimolecular.

According to the collision theory in its simplest form, the number of molecules decomposing in a bimolecular reaction is equal to the number of activating collisions. The expression given by the kinetic theory of gases for the total number of collisions occurring per c.c. per second between molecules of types 1 and 2 is

$$ {}_1Z_2 = n_1 n_2 \sigma_{1,2}^2 \left\{ 8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{\frac{1}{2}}. \qquad (1) $$

The Maxwell-Boltzmann term $e^{-E/RT}$ gives the fraction of this number which have critical energies of E or more, hence the rate of chemical change becomes

$$ \frac{dn}{dt} = n_1 n_2 \sigma_{1,2}^2 \left\{ 8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{\frac{1}{2}} e^{-E/RT}. \qquad (2) $$

The bimolecular velocity constant, expressed in litres per gram molecule per second, is defined as

$$ k = \frac{dn}{dt} \frac{1}{n_1 n_2} \frac{N_0}{1{,}000}, \qquad (3) $$

N_0 being the Avagadro constant. Combining, we have

$$ k = \frac{N_0}{1000} \sigma_{1,2}^2 \left\{ 8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{\frac{1}{2}} e^{-E/RT}. \qquad (4) $$

The deduction of this equation and its application to reactions in gases* constitute the first fruitful attempt at studying the velocity of chemical change in the light of the kinetic theory.† This expression gives the theoretical value of the velocity coefficient of uncomplicated bimolecular

* Lewis, *Trans. Chem. Soc.*, **113**, 471, (1918).

† Strutt (*Proc. Roy. Soc.*, **A, 87**, 302, (1912)) had previously compared the number of molecules reacting with the total number of collisions, but not with the number of activating collisions.

reactions, and will frequently be referred to as the equation of Lewis. Differentiating with respect to T,

$$\frac{d\ln k}{dT} = \frac{E+\frac{1}{2}RT}{RT^2}, \qquad (5)^*$$

and comparing with the Arrhenius equation

$$\frac{d\ln k}{dT} = \frac{E_A}{RT^2}, \qquad (6)$$

it is seen that the true critical increment (E) is

$$E = E_A - \tfrac{1}{2}RT. \qquad (7)$$

The correction is not important enough to matter except when the temperature of investigation is high, or when E is small.

Bimolecular Reactions in Gases.

The experimental results found for six bimolecular reactions in gaseous systems are compared in Table 1 with those calculated by the equation of Lewis, taking into account the slight correction in the critical increments. The absolute

Table 1

Reference	Reaction	E (calories)	$T°$ (abs.)	$\sigma \times 10^8$ (cm.)	$k_{observed}$ (litres/gram molecule-second)	$k_{calculated}$ (litres/gram molecule-second)	k_{obs}/k_{calc}
(1)	$2N_2O \rightarrow 2N_2 + O_2$	58,500	1,001	3·3	$3{\cdot}80 \times 10^{-1}$	$3{\cdot}15 \times 10^{-2}$	12
(2)	$CH_3CHO \rightarrow CH_4 + CO$	45,500	800	5·0	$5{\cdot}15 \times 10^{-1}$	$1{\cdot}38 \times 10^{-1}$	3·7
(3)	$2HI \rightarrow H_2 + I_2$	43,800	666	3·5	$2{\cdot}20 \times 10^{-4}$	$4{\cdot}68 \times 10^{-4}$	0·47
(4)	$C_2H_4 + H_2 \rightarrow C_2H_6$	42,400	787	2·0	$1{\cdot}77 \times 10^{-2}$	$3{\cdot}53 \times 10^{-1}$	0·05
(5)	$H_2 + I_2 \rightarrow 2HI$	38,800	660	2·0	$1{\cdot}63 \times 10^{-2}$	$3{\cdot}46 \times 10^{-2}$	0·47
(6)	$2NO_2 \rightarrow 2NO + O_2$	26,500	610	3·3	$2{\cdot}06 \times 10^{0}$	$6{\cdot}93 \times 10^{1}$	0·03

(1) Hinshelwood and Burk, *Proc. Roy. Soc.*, **A, 106,** 284, (1924).
(2) Hinshelwood and Hutchison, *ibid.*, **111,** 380, (1926).
(3)(5) Bodenstein, *Z. physikal. Chem.*, **29,** 295, (1899); Lewis, *loc. cit.*
(4) Pease, *J. Amer. Chem. Soc.*, **54,** 1876, (1932).
(6) Bodenstein and Ramstetter, *Z. physikal. Chem.*, **100,** 68, (1922); Kassel, *The Kinetics of Homogeneous Gas Reactions*, p. 156, (1932).

velocities of the fastest and the slowest of these reactions, at a temperature of 800° absolute, differ by a factor of

* Compare the equation $\frac{d\ln k}{dT} = \frac{A+BT}{T^2}$ proposed by Kooij (*Z. physikal. Chem.*, **12,** 155, (1893).

$1{\cdot}3\times10^6$, compared with which the figures in the last column are of secondary importance. The agreement in cases 2, 3, and 5 is excellent, and the difference in reaction 1 has been fully explained.* On the other hand, the discrepancy in examples 4 and 6 indicates the inadequacy of the simple expression. The desirability for its revision or modification becomes much more urgent when we come to consider further examples of bimolecular reactions in gases.

The decomposition of chlorine monoxide, although not satisfying a simple bimolecular law, depends essentially upon bimolecular processes, each of which has a rate of the order of magnitude given by equation (4). This reaction, therefore, although complicated, has a 'normal' velocity. The decomposition of ozone, however, has a rate about 10^4 times as fast as would be expected on a similar basis, whereas the cis-trans isomerism of dimethylmaleic ester† and the polymerization of 1:3 butadiene‡ appear to be roughly 10^4 times too slow. Furthermore, only a small proportion of the collisions between sodium atoms and cyanogen molecules leads to reaction, although the energy of activation is zero.§

It has been shown in Chapter III that the idea of the activation energy being shared among a number of internal degrees of freedom will explain the fast rate of decomposition of ozone; so will a chain mechanism. As for the slow reactions, it appears that deactivations will not account for the phenomenon, and various other suggestions have been advanced. It is possible that only specially oriented molecules, or molecules in a particular internal phase, can react. With the reasons for the discrepancies we are not at the moment concerned. The important fact is that they do

* Musgrave and Hinshelwood, *Proc. Roy. Soc.*, **A, 135,** 23, (1932).

† Kistiakowsky and Nelles, *Z. physikal. Chem.*, 'Bodenstein Festband', 369, (1931).

‡ Vaughan, *J. Amer. Chem. Soc.*, **54,** 3683, (1932).

§ von Hartel and Polanyi, *ibid.*, **B, 11,** 97, (1930).

exist. The present tendency lies in the direction of attributing these deviations to the chemical nature of the reactions themselves. It will be well to bear this in mind when dealing with anomalous rates of bimolecular reactions in solution, for the slowness of some of these may also be characteristic of the changes themselves and not in any sense due to the presence of the solvent.

Summarizing the results upon these eleven gaseous reactions, we see that about half the number have rates which are in fair agreement with those calculated from equation (4). Upon this evidence the simple collision theory has been accepted and is retained as the correct explanation of the facts.

Methods of Comparing Observed and Theoretical Velocities.

There is no fundamental distinction between the nature of chemical change in gaseous and in liquid systems. It is true that the solvent can, and in many cases is known to, interfere with the mechanism. For the present, however, we shall concern ourselves with reactions of the type reviewed in the previous chapter, for which the mechanism and the actual velocity do not seem to be seriously altered by the presence of the solvent. To discover such instances, we compare the observed rates with those calculated by the equation of Lewis. There is no theoretical reason for changing either the collision formula or the Maxwell-Boltzmann relation. The procedure adopted, therefore, is precisely the same as in the case of gaseous reactions, except that the correction of $\frac{1}{2}RT$ to the critical increment need not be considered at the low temperatures which are usually involved. The comparison between experimental and theoretical rates may be made in various ways.

(1) Using the Arrhenius value of E, we may substitute directly into equation (4), and determine the value of k at any temperature.

The critical increment for the reaction between methyl

iodide and sodium ethylate in ethylalcoholic solution is found to be 19,500 calories.

$$CH_3I+C_2H_5ONa \rightarrow CH_3OC_2H_5+NaI$$

Taking the molecular radii as $2{\cdot}64\times10^{-8}$ and $2{\cdot}74\times10^{-8}$ cm. respectively (Chap. I, equation 4), the calculated value of k at 18° C. becomes $4{\cdot}12\times10^{-4}$ litres/gram molecule-second. The value observed by Hecht and Conrad* is $4{\cdot}96\times10^{-4}$.

(2) The observed energy of activation may be compared with that given by the relation

$$\frac{\text{number of molecules reacting}}{\text{total number of collisions}} = e^{-E/RT}, \qquad (8)$$

which is obtained by combining equations (1) and (2). To evaluate separately the two quantities on the left-hand side of the equation we must choose an arbitrary concentration. One gram molecule per litre is as convenient a unit as any.†

The velocity constant for the combination of ethyl bromide and diethyl sulphide in benzylalcoholic solution at 80° C. is $2{\cdot}44\times10^{-5}$ litres/gram molecule-second (p. 123).

$$C_2H_5Br+(C_2H_5)_2S \rightarrow (C_2H_5)_3SBr$$

The number of molecules combining per c.c. per second, is, by equation (3), $2{\cdot}44\times10^{-5}\times6{\cdot}06\times10^{20} = 1{\cdot}48\times10^{16}$. Equation (1) gives the total number of collisions as $1{\cdot}59\times10^{32}$, hence $E = 25{,}800$ calories. The experimental value is 24,470 calories, and is liable to an error of $\pm1{,}000$.

(3) The constant Z of the Arrhenius equation may be compared with the theoretical value, which is

$$Z = \frac{N_0}{1000}\sigma_{1,2}^2\left\{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}^{\frac{1}{2}}. \qquad (9)$$

* *Z. physikal. Chem.*, **3**, 450, (1889).

† The consistent use of the molar unit avoids the confusion which may arise from the adoption of the terms 'normal' or 'equivalent'.

The velocity of the following reaction has been measured very carefully at intervals of 10° between 70° and 130° C.:*

$$CH_2Cl.COO^- + OH^- \rightarrow CH_2OH.COO^- + Cl^-.$$

By plotting $\ln k$ against $1/T$ in the usual way, it is found that Z is $4{\cdot}55 \times 10^{11}$. The theoretical value is $2{\cdot}86 \times 10^{11}$. The justification of including ionic reactions among those which can be analysed in this way must be postponed until Chapter VII.

This is the method of comparison most commonly used in the present book.

Further examples are given in Table 2. In many of these, theory and observation are in excellent harmony, and in all of them the difference is no greater than can be allowed for by a reasonable error in calculation or in experiment. The absolute velocities, compared at a temperature of 40° C., differ by a factor of $1{\cdot}1 \times 10^9$, which is somewhat greater than the range covered by the gaseous reactions cited in Table 1.

It is evident that the theoretical collision frequency varies but slightly from reaction to reaction, the average value being about $2{\cdot}77 \times 10^{11}$. A figure not very different from this is found for all systems of molecules over a very wide range of temperature. For rough calculations, therefore, this is a useful quantity to remember. Its approximate constancy is due to the compensating influence of two rival factors. The effect on the collision frequency caused by the rapidity of light molecules is cancelled by their small cross-sectional area; on the other hand, the effect due to the slower velocity of heavy molecules is almost exactly balanced by their greater collisional diameter. In a pair of ideal bimolecular reactions, therefore, the difference in velocity will be given by the term $e^{\frac{E_1 - E_2}{RT}}$ or $e^{\frac{\Delta E}{RT}}$. We have seen that the range of velocity in the case of the gaseous reactions given

* Schwab, quoted by van 't Hoff, *Studies in Chemical Dynamics*, pp. 15, 129 (1896).

Table 2

Reference	Reaction	Solvent	E (calories)	$Z \times 10^{-11}$ Observed	$Z \times 10^{-11}$ Calculated	k_{calc}/k_{obs}
(1)	$CH_3ONa + 1{:}2{:}4\text{-}ClC_6H_3(NO_2)_2$	CH_3OH	17,450	1·91	2·42	1·3
(1)	$C_2H_5ONa + 1{:}2{:}4\text{-}ClC_6H_3(NO_2)_2$	C_2H_5OH	16,760	1·80	2·39	1·3
(2)	$C_2H_5ONa + CH_3I$	C_2H_5OH	19,490	2·42	1·93	0·8
(3)	$C_2H_5ONa + C_2H_5I$	C_2H_5OH	20,650	1·49	2·23	1·5
(3)	$C_2H_5ONa + C_6H_5CH_2I$	C_2H_5OH	19,900	0·15	2·17	14·5
(4)	$C_6H_5ONa + C_3H_7I$	C_2H_5OH	22,450	3·53	2·31	0·7
(4)	$C_6H_5ONa + iso\text{-}C_3H_7I$	C_2H_5OH	22,100	1·74	2·31	1·3
(4)	$C_6H_5ONa + C_{16}H_{33}I$	C_2H_5OH	22,430	2·78	2·92	1·0
(5)	$C_6H_5CH_2ONa + C_4H_9I$	C_2H_5OH	21,560	2·92	2·43	0·8
(5)	$C_6H_5CH_2ONa + iso\text{-}C_4H_9I$	C_2H_5OH	21,350	2·45	2·43	1·0
(5)	$C_6H_5CH_2ONa + C_{16}H_{33}I$	C_2H_5OH	21,090	1·26	3·12	2·5
(6)	$o\text{-}CH_3C_6H_4ONa + CH_3I$	C_2H_5OH	21,180	1·30	1·99	1·5
(6)	$m\text{-}CH_3C_6H_4ONa + CH_3I$	C_2H_5OH	19,490	2·27	1·99	0·9
(6)	$p\text{-}CH_3C_6H_4ONa + CH_3I$	C_2H_5OH	20,900	8·49	1·99	0·2
(7)	$\beta\text{-}C_{10}H_7ONa + C_2H_5I$	CH_3OH	21,010	0·10	2·21	22·1
(7)	$\beta\text{-}C_{10}H_7ONa + C_2H_5I$	C_2H_5OH	19,840	0·11	2·21	20·1
(7)	$\beta\text{-}C_{10}H_7ONa + C_3H_5I$	C_2H_5OH	21,300	0·40	2·21	5·5
(8)	$CH_3ONa + o\text{-}C_6H_4(NO_2)_2$	CH_3OH	20,590	6·11	2·48	0·4
(8)	$C_2H_5ONa + o\text{-}C_6H_4(NO_2)_2$	C_2H_5OH	20,480	3·03	2·45	0·8
(9)	$(CH_3)_2SO_4 + NaCNS$	CH_3OH	17,360	0·19	1·91	10·0
(9)	$(CH_3)_2SO_4 + KCNS$	CH_3OH	17,880	0·57	1·91	3·4
(10)	$(C_2H_5)_2S + C_2H_5Br$	$C_6H_5CH_2OH$	24,470	0·31	2·62	8·5
(11)	$C_2H_5ONa + C_2H_5OOC.CH_2.COOC_2H_5$	C_2H_5OH	16,760	0·17	1·80	10·6
(12)	$NH_4CNO \rightarrow (NH_2)_2CO$	H_2O	23,170	42·7	4·05	0·1
(13)	$CH_2Cl.COOH + OH^-$	H_2O	25,850	4·55	2·86	0·6
(14)	$C_6H_4\langle^{CH_2}_{CO}\rangle O + OH^-$	H_2O	12,500	41·7	2·93	0·07
(15)	$CH_2I.COO^- + OH^-$	H_2O	22,370	6·3	2·98	0·5
(15)	$CH_2I.COO^- + C_6H_5O^-$	H_2O	21,010	0·4	1·85	4·6
(15)	$CH_2I.COOH + Cl^-$	H_2O	22,850	7·9	2·66	0·3
(15)	$CH_2Cl.COOH + I^-$	H_2O	19,770	0·13	1·47	11·3
(15)	$CH_2I.COOH + SCN^-$	H_2O	18,190	0·40	2·17	5·4
(16)	$CH_2OH.CH_2Cl + OH^-$	H_2O	19,870	25·5	2·78	0·1
(17)	$CH_3[CH_2]_3Cl + I^-$	$(CH_3)_2CO$	23,500	2·24	1·64	0·7
(17)	$C_6H_5CO[CH_2]_3Cl + I^-$	$(CH_3)_2CO$	22,160	10·5	1·88	0·2
(18)	$CH_3S[CH_2]_2Cl + I^-$	$(CH_3)_2CO$	20,740	0·085	1·57	18·5
(18)	$^{\alpha}_{\beta}\}C_{10}H_7O[CH_2]_2Cl + I^-$	$(CH_3)_2CO$	22,420	0·15	1·73	11·5
(19)	$C_2H_5Br + OH^-$	C_2H_5OH	21,400	4·30	3·86	0·9
(20)	$C_3H_6Br_2 + I^-$	CH_3OH	25,100	1·07	1·39	1·3

(1) Talen, *Thesis*, Leiden (1927); *Tables Annuelles*, (1931).
(2) Conrad, *Z. physikal. Chem.* **3**, 450, (1889).
(3) Hecht, Conrad, and Brückner, *ibid.*, **4**, 273, (1889).
(4) Segaller, *Trans. Chem. Soc.*, **105**, 106, (1914).
(5) Haywood, *ibid.*, **121**, 1904, (1922).
(6) Conrad and Brückner, *Z. physikal. Chem.* **7**, 274, (1891).
(7) Cox, *Trans. Chem. Soc.* **119**, 142, (1921).
(8) Steger, *Z. physikal. Chem.*, **49**, 329, (1904).
(9) Walden and Centnerszwer, *Z. Elektrochem.*, **15**, 310, (1909).
(10) Corran, *Trans. Faraday Soc.*, **23**, 605, (1927).
(11) Conrad and Brückner, *Z. physikal. Chem.*, **7**, 274, (1891).
(12) Walker and Hambly, *Trans. Chem. Soc.*, **67**, 746, (1895).
(13) Schwab, *loc. cit.*
(14) Tasman, *Thesis*, Leiden (1927); *Tables Annuelles*, (1931).
(15) Wagner, *Z. physikal. Chem.*, **115**, 121, (1925).
(16) Evans, *ibid.*, **7**, 337, (1891).
(17) Conant and Kirner, *J. Amer. Chem. Soc.*, **46**, 232, (1924).
(18) Kirner and Richter, *ibid.*, **51**, 3409, (1929).
(19) Grant and Hinshelwood, *Trans. Chem. Soc.*, 258, (1933).
(20) Dillon, *J. Amer. Chem. Soc.*, **54**, 952, (1932).

in Table 1 is $1{\cdot}3\times10^6$; in the case of the reactions in solution given in Table 2, the range is $e^{13,250/323R} = 1{\cdot}1\times10^9$.

Compared at 0° C., the velocities of the fastest and slowest bimolecular reactions known in both gaseous and liquid systems bear a ratio of 10^{47}. This is the right way to regard the problem. Two chemical changes with rates differing by this stupendous amount, as well as a large and varied number of reactions with intermediate rates, can be satisfactorily interpreted in terms of the simple collision theory. The experimental results for bimolecular reactions in gases and in solution supplement each other in demonstrating both the applicability of the theory in some cases and its inadequacy in others.

A General Survey of Bimolecular Reactions in Solution.

There is an abundance of uncoordinated information upon the kinetics of bimolecular reactions in solution, but it is not uniformly valuable, and a certain amount of winnowing has been rendered necessary. For reasons which have been already advanced, no reference need be made to the vast volume of work which has been carried out at single temperatures. As a general rule, examples which appear to contradict Arrhenius's law may also be omitted, for experience has shown that such seeming deviations can usually be attributed to the presence of impurities or to inadequate control of temperature. The number thus lost is very small. Leaving out of the count examples which for these and other reasons are of dubious value, it is found that the critical increments for 181 bimolecular reactions have been measured in solution with a precision which makes them suitable for discussion. More than 40 per cent. of these have normal velocities in the sense that they have rates very nearly equal to those predicted by the equation of Lewis.

Hitherto we have dealt exclusively with reactions belonging to this category, purposely suppressing any reference to those which do not agree with the simple theory. This has

been made necessary in order to present the matter in its true perspective, and to dispel the illusion that a degree of harmony which has been accepted as genuine in the case of gaseous reactions must be accidental when relating to reactions in solution. While it is true to say that calculations referring to solutions are not entirely free from objection, the error is clearly negligible compared with the range of absolute magnitudes involved.

Christiansen,* in an important paper discussing the general theory of bimolecular reactions in solution, was the first to make comparisons of the type which have been drawn here. Accepting equation (1) as giving the collision frequency correctly as regards order of magnitude, Christiansen showed that the hydrolysis of amides and of esters in aqueous solutions as well as four reactions in alcoholic solution have velocities which are from 10 to 100,000 times as slow as those given by equation (4). The conclusion was not unnaturally drawn that the effect may be a general one. The most probable explanation which presented itself was that the activated complex molecules were subject to many deactivating collisions with molecules of the solvent. It is an unfortunate occurrence that these results, important enough in themselves, have been viewed in an exaggerated light and have subsequently been made the basis of unwarranted generalizations. It is now known that low efficiency of activating collisions is by no means confined to reactions in solution and, furthermore, that deactivations by solvent molecules are definitely not the cause of the slowness with which these reactions proceed in the liquid systems. The discovery of bimolecular reactions proceeding in solution with normal velocities has been made quite recently.† Emphasis on these gives us a much less distorted vision of the whole field of inquiry.

* *Z. physikal. Chem.*, **113**, 35, (1924).

† Chapter III; also *Chemical Reviews*, **10**, 241, (1932) *Phil. Mag.*, vii, **14**, 112, (1932).

In the systematic study of bimolecular reactions in solution it will therefore be convenient to imagine them as belonging to three groups, according to whether their velocities are normal, fast, or slow. A bimolecular reaction may be said to have a normal velocity when its constant is

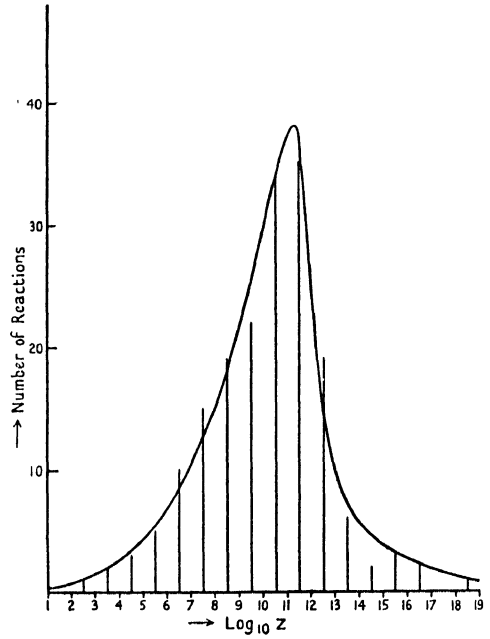


FIG. 1.

given, within a reasonable factor of 10 or so, by the expression $k = 2{\cdot}8 \times 10^{11} e^{-E/RT}$. The apparent arbitrariness of this three-fold classification is removed when it is found that the experimental results, considered quite empirically, distribute themselves automatically into the same three groups. In Figure 1, the abscissae are values of $\log_{10} Z$, determined experimentally from the Arrhenius curves, and the ordinates give the number of reactions with the assigned value of Z. It is seen, for example, that 35 reactions have values of Z lying between 10^{11} and 10^{12}, but only 6 have

values 100 times greater. The maximum probability refers to $\log_{10} Z = 11{\cdot}3$, which is in very striking proximity to the theoretical collision frequency for all the systems involved.* In other words, more bimolecular reactions belong to the normal group than to any other. Since the slope of the curve is steeper on the high side of Z, it is evident that fast reactions are of less frequent occurrence than slow ones.

The inquiry from now on must be directed to a search for the various factors which may account for the deviations from the behaviour which we are regarding as standard. Some of the possibilities have already been mentioned, and others will be discussed in appropriate places. For the present we may summarize by stating that chief among the causes responsible for reducing below its normal value the rate of a second-order reaction in a homogeneous system are: (1) endothermic formation of a complex prior to the reaction proper; (2) the necessity for the ionization of either or both of the reactants; (3) deactivation by solvent molecules; and (4) stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact. On the other hand, some of the factors which will allow a faster reaction velocity than that permitted by the simple collision theory are: (*a*) exothermic formation of a complex prior to the reaction proper; (*b*) the distribution of the energy of activation among a number of internal degrees of freedom of the reacting molecules; (*c*) the propagation of reaction chains; and (*d*) activation by some means other than by collision, e.g. by radiation. Evidence from individual reactions may be quoted in support of each of these.

The following will serve as provisional clues in detecting which of these factors is more likely to be at work. Activation due to radiation is most readily demonstrated by

* A similar analysis of unimolecular reactions shows that a value of 10^{13}–10^{14} occurs more frequently than any other (Polanyi and Wigner, *Z. physikal. Chem.*, 'Haber-Band', 439, (1928)).

investigating the reaction in the dark* and in the presence of suitable illumination. The presence of reaction chains is to be suspected in all cases where the instantaneous velocity (dc/dt) is a function of the initial concentration raised to a high power, and is sensitive to the presence of added substances. Ionization may be expected to enter into the problem whenever the rate of chemical change varies markedly with the dilution, with the addition of electrolytes, and with the nature of the solvent. When the apparent energy of activation undergoes a profound change from solvent to solvent, the formation of a complex is indicated.

Complications due to photo-activation and to the propagation of reaction chains usually go hand in hand, but are not of frequent occurrence. There thus remain two possible methods of explaining the velocity of fast reactions. Activation among a number of degrees of freedom is always possible theoretically when the reacting molecules are complex. If the maximum value of F allowable does not account for the rate, we must have recourse to the alternative idea of an exothermic intermediate complex.

In view of the experimental evidence that deactivations do not occur in those reactions where the hypothesis has been put to the test, this explanation must be regarded, temporarily at least, as being less probable than the ionization view, or the endothermic complex theory.

Homologous Bimolecular Reactions.

Esters of most fatty acids are hydrolysed at much the same rate.† The velocity of transformation of oximes into nitriles is also sensibly independent of their complexity.‡

* When a reaction is suspected to be catalysed by visible light, the dark reaction may be studied in a thermostat containing a liquid which is deeply coloured. Nigrosin is a useful dye for water-thermostats. Alternatively, the reaction vessel may be painted black, or kept in a metal container. Solutions may be prepared in a room flooded with light of least injurious colour.

† Hemptinne, *Z. physikal. Chem.*, **13**, 561, (1894).

‡ Hantzsch, *ibid.*, **13**, 509, (1894).

So also is the rate of benzylation of amines,* and of the hydrolysis of acetals† and formals.‡ Examples of the same type of behaviour are so numerous that one may consider it to be almost universal. When a series of homologous molecules undergo a similar chemical change, the velocity is altered but little. This is to be anticipated on theoretical grounds provided the critical increment is the same for the various homologous reactions, for it is known that the collision frequency is virtually constant.

The provision is amply fulfilled in the majority of the reactions which have been studied. Some of the experimental results found by Segaller§ for the reaction between alkyl iodides and sodium benzylates and by Haywood|| for the corresponding reactions with sodium phenolate are reproduced in Table 3. The average value of E for the

Table 3

	RI + C_6H_5ONa			RI + $C_6H_5CH_2ONa$		
R	$k_{42.5°C} \times 10^5$	E	$Z \times 10^{10}$	$k_{50°C} \times 10^5$	E	$Z \times 10^{11}$
CH_3	101	22,120	36·3	266	20,570	20·65
C_2H_5	22·5	22,000	8·91	23·7	21,860	15·67
C_3H_7	8·67	22,450	7·41	9·24	21,730	4·86
C_4H_9	8·08	22,090	1·45	6·69	21,560	2·92
C_7H_{15}	7·52	22,230	2·24	6·68	21,510	2·48
C_8H_{17}	7·23	22,500	3·39	6·68	21,450	2·21
$C_{16}H_{33}$	7·15	22,430	4·47	6·90	21,090	1·26
iso C_3H_7	7·58	22,100	1·15	5·52	21,410	1·75
iso C_4H_9	3·22	21,790	0·39	8·68	21,350	2·45
iso C_5H_{11}	4·75	22,250	1·59	3·39	21,410	1·07
sec. C_6H_{13}	7·22	22,190	1·48	9·61	21,580	4·01
sec. C_8H_{17}	6·85	22,110	1·41	7·25	21,450	2·40

analogous formation of ethyl-alkyl ethers is 19,710 calories.** All three sets of experiments were carried out in ethyl-alcoholic solution, and can lay claim to considerable accuracy.

* Thomas, *Trans. Chem. Soc.*, **104**, 594, (1913).
† Skrabal and Belaric, *Z. physikal. Chem.*, **103**, 451, (1922).
‡ Skrabal and Eger, *ibid.*, **122**, 349, (1926).
§ *Trans. Chem. Soc.*, **103**, 1421, (1913); *ibid.*, **105**, 106, (1914).
|| *Ibid.*, **121**, 1904, (1922).
** Hecht and Conrad, *Z. physikal. Chem.*, **3**, 450, (1889).

One of the most thoroughly investigated reactions known is the hydrolysis of ethyl acetate by aqueous alkalis. Reicher* showed the bimolecular velocity constant to be unaffected by the concentration of ester or alkali, and to have the same value whether caustic soda or baryta was employed. This proved the reaction to be ionic:

$$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH.$$

At five temperatures ranging from 9·4 to 44·9° C., Reicher's constants are given by the equation $\log k = \frac{1780}{T} + 0{\cdot}00754T + 4{\cdot}53$, but they are summarized equally well by the simpler relation $\ln k$ (seconds^{-1}: gram molecules per litre) $= 16{\cdot}79 - \frac{11{,}210}{RT}$. The effect of temperature was studied even more accurately by Warder,† whose data, relating to 15 temperatures, are in excellent agreement with the Arrhenius equation $\ln k = 16{\cdot}47 - \frac{11{,}200}{RT}$. These values, measured by the titration method, have been confirmed by the electrical conductivity measurements of Walker,‡ who further showed that k is increased by 26 per cent. when the solution is subjected to an external pressure of 1,000 atmospheres. The influence of dilution upon the velocity of saponification was examined by Arrhenius,§ and more fully by Burgarsky,‖ whose results are given in Table 4.

Table 4

Base	$k_{19{\cdot}4°C} \times 10^2$ (litres/gram molecule-second)			
	V = 20 litres	V = 40 litres	V = 80 litres	V = 160 litres
LiOH	6·39	..	..	..
NaOH	6·36	6·32	6·21	..
KOH	6·65	6·46	..	..
$Ca(OH)_2$	..	6·06	6·31	6·32
$Sr(OH)_2$	..	6·08	..	..
$Ba(OH)_2$	6·23	6·29	6·35	..

* *Annalen*, **228**, 257, (1885); **232**, 103, (1885); **238**, 276, (1887).
† *Berichte*, **14**, 1361, (1881); *J. Amer. Chem. Soc.*, **3**, 203, (1881).
‡ *Proc. Roy. Soc.*, **A**, **78**, 157, (1906).
§ *Z. physikal. Chem.*, **1**, 110, (1887). ‖ *Ibid.*, **8**, 398, (1891).

The saponification of other esters has been investigated more recently by Smith and Olsson;* their data, along with those of Reicher and Warder, are given in Table 5. With one exception the critical increments have an average value of 11,290 calories±330 (see Fig. 2). The critical increment

Table 5

$CH_3.COOR + OH^- \rightarrow CH_3.COO^- + ROH$ *in aqueous solution*

R	$k_{20°C} \times 10^2$	E	$Z \times 10^7$
C_2H_5	6·78	11,210	1·66
C_3H_7	7·05	11,320	2·09
iso C_3H_7	2·10	11,440	0·64
C_4H_9	6·55	11,370	2·13
iso C_4H_9	6·90	11,620	3·00
sec. C_4H_9	1·36	11,020	0·24
tert. C_4H_9	0·135	13,040	0·78
iso C_5H_{11}	6·02	11,040	1·07

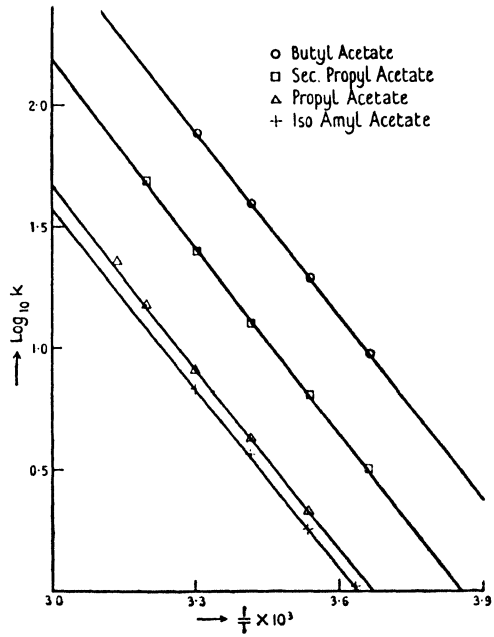


FIG. 2.—Hydrolysis of esters by aqueous alkali.

* *Z. physikal. Chem.*, **118**, 99, (1925).

for the hydrolysis by acids of a series of dihydroxypropyl esters has a constant value.* The indifference of E towards the alkyl group present is thus maintained in a series of homologous reactions even when these have rates far below the standard values, for, adopting the same basis of calculation as before, it is apparent that the chemical efficiency of activating collisions is here about 1 in 10,000. The same regularity is observed when the reactions are catalytic or when they proceed in non-aqueous solvents, as the data in Table 6 reveal.

Table 6

Hydrolysis of amides catalysed by hydrogen ion in aqueous solution		Examples of the Finkelstein reaction in acetone solution	
$R.CONH_2+H_3O^+ \rightarrow R.COOH+NH_4^+$		$RCl+I^- \rightarrow RI+Cl^-$	
R	E	R	E
H	19,070	C_3H_7	18,610
CH_3	20,460	C_4H_9	19,610
C_2H_5	19,770	C_5H_{11}	18,370
C_3H_7	20,090	C_6H_{13}	18,620
iso C_3H_7	19,430	C_7H_{15}	18,990
C_4H_9	20,040	C_8H_{17}	18,850
		$C_{14}H_{29}$	19,060
		$C_{16}H_{33}$	19,040

Within the fairly wide margin of error which must be allowed in the experiments upon which these figures are based,† the critical increments must be regarded as constant for each series.

Constancy of critical increments for a series of similar chemical changes is the most notable feature of bimolecular reactions in solution. The truth underlying this observation is simply that in a reaction of the type $A+B \rightarrow C+D$, the energy of activation is insensitive to the length of the chain of carbon atoms in the molecule A. It has already been shown that E is unaffected by the radical R_1 in the reaction

$$R_1I+R_2ONa \rightarrow R_1OR_2+NaI.$$

* Ingold, Jackson, and Kelly, *Trans. Chem. Soc.*, 2035, (1931).

† Crocker, *Trans. Chem. Soc.*, **91**, 593, (1907); Conant and Hussey, *J. Amer. Chem. Soc.*, **47**, 476, (1925).

The following results (Table 7) show that when R_2 is varied, there is a small but real change in E.

Table 7

$CH_3I + R_2ONa \rightarrow CH_3OR_2 + NaI$

R_2	E
CH_3	21,180
C_2H_5	19,490
C_6H_5	22,120
$C_6H_5CH_2$	20,510
o-$CH_3C_6H_4$	20,240
m-$CH_3C_6H_4$	20,510
p-$CH_3C_6H_4$	21,220

The Energy of Activation.

These empirical rules give a clue to the nature of the activation process. Concerning the critical increment for gaseous bimolecular reactions, Hinshelwood* points out that it may be constituted in two ways, between which experiment will not allow us to choose. The activation energy may be regarded as the sum of the components, measured along the line of centres, of the kinetic energy of translation possessed by the two molecules at the moment of impact, there being no restriction concerning the relative contribution made by either molecule; that is, E may vary independently in two square terms. On the other hand, it may be considered as the sum of two independent critical increments, E_1 and E_2, each associated with one vibrational degree of freedom in the two reacting molecules. According to the first mechanism, the condition for chemical change is that two molecules shall possess in a head-on collision combined kinetic energy equal to or greater than the energy of activation. The geometric conditions governing the efficiency of such encounters must be fairly stringent. Since the critical increment is entirely kinetic, activated molecules will move faster than the normal molecules in the approximate

* *Kinetics*, p. 123.

ratio of $\sqrt{\left(\frac{E+RT}{RT}\right)}$. For most of the reactions with which we have to deal ($E \simeq 30{,}000$; $T \simeq 300$), this correction leads to a calculated rate about 7 times as great as that given by the simpler expression. It may be pointed out, however, that the true factor is actually somewhat greater than this, for the collision frequency according to this mechanism is virtually independent of temperature, and the term $\frac{1}{2}RT$ need not be added to the Arrhenius critical increment. According to the second mechanism, the two reacting molecules may become individually activated, by collisions as before, to the extent of E_1 and E_2 calories respectively, where $E_1+E_2 = E$. These energies may be regarded as being accommodated within each molecule in the form of vibrations between two constituent atoms or groups. Four square terms are thus involved, but E cannot vary independently among these. The remaining condition for reaction is simply that two such activated molecules shall meet before losing their critical energies. The average velocity of these activated molecules does not differ from that of normal molecules; and there is no reason for imposing any special steric restrictions upon the chemical effectiveness of encounters between them. This idea of the separate activation of the two reacting species has more in common with our notions concerning activation in complicated molecules than has the idea of violent collisions. Furthermore, the energy of activation is known to increase the nuclear separation of the atoms; this it can do readily by absorption of energy in the form of vibration. Since the distinction drawn on purely kinetic grounds between reactions of the first and second orders is now known to be one of degree only, this view of independent activation is to be preferred on general grounds.

Experiment should allow us to decide between the two possibilities. Consider two homologous reactions possessing the same critical increment. The collision frequencies for

both will be equal, within about 5 per cent. Provided no special steric influence comes into play, the rate of chemical change should therefore be nearly equal for the two reactions. If collisions of critical violence are necessary, the chance of these occurring with the right orientation will diminish as the size of the molecules increases, and k should be lower for the higher homologue. In most examples there is no evidence of this (Table 8); propyl and cetyl halides react at about the same rate.

Table 8

Reaction	Solvent	$t°$ C.	$k_{observed} \times 10^5$ (litres/gram mol.-sec.)		$\frac{k_3}{k_{16}}$
			R = C_3H_7	R = $C_{16}H_{33}$	
$RI + C_6H_5ONa$	C_2H_5OH	42·5	8·67	7·15	1·2
$RCl + KI$	$(CH_3)_2CO$	50	2·95	2·95	1·0
$RI + C_6H_5CH_2ONa$	C_2H_5OH	30	9·24	6·90	1·3

We therefore conclude that the molecules are not activated solely by those collisions which lead to chemical reaction. They may well receive their energy of activation by previous collisions.

The Orientation Factor in Collisions.

Although it is impossible at present to pronounce with certainty, it does not appear that the orientation of gaseous molecules during collision plays a prominent role in the velocity of reaction, but the absence of such an effect may well be due to the fact that most of the bimolecular reactions known in the gas phase are those of symmetrical, or in any case very small, molecules. With complicated organic molecules, exacting steric conditions may sometimes prevail, causing a diminution in the efficiency of collisions.

The introduction of a $-CH_2-$ group into an aliphatic molecule does not, as a rule, cause a great change in the rate at which the molecule reacts. The first transition from the methyl to the ethyl derivative shows the greatest

effect; beyond the third or fourth addition of CH_2 groups, the effect is unimportant. Weighting the molecule in one position, however, may have an effect which is not found in another. The rate of hydrolysis of esters by acids,* for example,

$$R_1.COOR_2+H_2O \rightarrow R_1.COOH+R_2OH$$

is sensitive to substitution of a CH_2 group into R_1 but not into R_2, as shown in Table 9.†

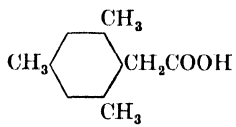
Table 9

	$k_{25°\,C.} \times 10^3$		
	Acetate	Propionate	Butyrate
Methyl	6·6	7·1	3·9
Ethyl	6·8	7·3	4·2
Propyl	6·7	7·2	4·1

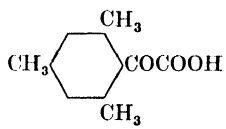
When the same esters are hydrolysed by alkalis, neither R_1 nor R_2 can be modified without causing a noticeable change in k.

Aromatic compounds are usually much more sensitive to molecular rearrangements. Mesityl-acetic acid (I) and mesityl-glyoxylic acid (II) readily form esters, but mesityl-formic acid (III) is said to be uninfluenced under the same conditions. Identical behaviour is found with the tribrom-compounds.‡

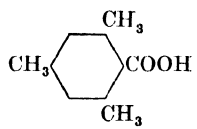
I



II



III



Menschutkin§ gives the following relative rates of esterifica-

* Reference will be made in Chapter VII to Ingold's work on the effect of polar groups on the rate of hydrolysis of esters.

† van 't Hoff, *Studies in Chemical Dynamics*, p. 119, (1896).

‡ Meyer, *Berichte*, **28**, 1294, (1895).

§ *Z. physikal. Chem.*, **1**, 611, (1887).

tion of acetic anhydride with various alcohols in benzene solution:

Alcohol . .	CH_3OH	CH_2ROH	CHR_2OH	CR_3OH
Relative rate of esterification.	100	48	13	0·8

An enormous amount of attention has been given to the measurement of the comparative velocities with which ortho, meta, and para di-substituted benzene derivatives undergo reactions of various kinds. We must content ourselves with a few typical instances only* (Table 10).

Table 10

$R.C_6H_4.COOH + C_2H_5OH \rightarrow R.C_6H_4COOC_2H_5 + H_2O$

R	*o.*	*m.*	*p.*
CH_3	0·011	0·047	0·024
Br	0·020	0·055	0·045
NO_2	0·0028	0·030	0·026

$R.C_6H_4NH_2 + H.COOH \rightarrow R.C_6H_4NH.CHO + H_2O$

R	*o.*	*m.*	*p.*
CH_3	0·11	0·53	0·67
Cl	0·013	0·15	0·25
Br	0·0028	0·14	0·21

$R.C_6H_4CONH_2 + H_2O \rightarrow R.C_6H_4.COOH + NH_3$

R	*o.*	*m.*	*p.*
CH_3	0·22	1·93	1·75
NH_2	0·18	0·18	1·98
NO_2	0·054	1·96	2·36

Comparisons of velocity constants alone cannot take us very far because the rearrangement of atoms within the reacting molecule usually affects the energy of activation as well as the spatial factors governing the fruitfulness of collision. The relative importance of the two contributions can be gauged only when the temperature coefficients of the reactions are known with considerable precision. Since

* Numerous examples are given by Wittig, *Stereochemie*, p. 333, Leipzig, (1930).

$k = Ze^{-E/RT}$ in general, we have for any pair of bimolecular reactions

$$RT \ln \frac{k_1}{k_2} = RT \ln \frac{Z_1}{Z_2} - E_1 + E_2.$$

If experiment shows that $RT \ln \frac{k_1}{k_2} = E_2 - E_1$, then Z_1 must equal Z_2 and there is no indication of any steric effect entering. When the two critical increments are found to be equal, any change in k is clearly due to a change in Z. These simple considerations have been advanced by W. Hückel,* who quotes examples from the work of Vavon† where both conditions appear to be fulfilled. The hydrolysis of the cis and trans forms of the succinic ester of isopropylcyclohexanol have the following velocity constants (the time unit being the hour):

$t°$ C.	cis form	trans form	$RT \ln \frac{k_{trans}}{k_{cis}}$
0	0·0068	0·46	2,280
39	0·15	6·0	2,280
68	1·02	28·0	2,260

The difference in k is almost exactly that caused by the change in the critical increment: there appears to be no steric effect. For the hydrolysis of phthalyl esters of borneol and isoborneol we have

$$k_{\text{born.}} = 1{\cdot}41 \times 10^9 e^{-13,370/RT}$$
$$k_{\text{isoborn.}} = 7{\cdot}98 \times 10^7 e^{-13,560/RT}.$$

In this case there seems to be a definite influence which is independent of temperature and may or may not be steric. Unfortunately the data refer to two temperatures only. Another pair of reactions is quoted which is intermediate in character, but the Arrhenius equation is not obeyed. It is difficult to decide how far the examples selected by

* *Berichte*, **61**, 1517, (1928).

† *Bull. Soc. Chim.*, **39**, 666, (1926); **41**, 357, (1927); **43**, 667, (1928).

Hückel are really suitable for the present purpose, but the method of analysing experimental data is clearly the correct one, and has been independently adopted by others.*

After correcting the critical increments (equation (7)) for the reaction between ethyl halides and hydroxyl ions in ethylalcoholic solution, Grant and Hinshelwood† give the following experimental values:

(1) Iodide $k = 2{\cdot}70 \times 10^{10} \sqrt{T} \times e^{-21,000/RT}$.

(2) Bromide $k = 1{\cdot}28 \times 10^{10} \sqrt{T} \times e^{-21,000/RT}$.

(3) Chloride $k = 0{\cdot}793 \times 10^{10} \sqrt{T} \times e^{-23,000/RT}$.

The calculated values of the non-exponential term are nearly identical in the three cases, hence the difference between the velocities of reactions (1) and (3) is connected with the change in E.

Reference to Table 10 indicates that the reactivity of meta and para compounds, as reflected by the bimolecular constants, is greater than that of ortho compounds. This is by far the most frequent sequence obtaining, although there are numerous exceptions. It is, however, quite reasonable to suppose that the presence of a radical in the ortho position exerts greater hindrance upon the approach of a second molecule than does a group in either the meta or the para position. If this is true, the constants Z should be in the order $Z_p > Z_m > Z_o$. In the reaction between methyl iodide and the sodium cresolates (Table 2), this is the case—a result which has some weight because the three critical increments have different values.

One other class of reactions must be cited in this connexion. The hydrolysis of sugars by dilute acids has been studied with almost unparalleled accuracy. The results given in Table 11 refer to 25° C., and a concentration of hydrochloric acid of 0·1N. The critical increments are close averages of 36 values. Here it is evident that E is constant,

* Semenaro, *Gazzetta*, **61**, 921, (1931); Peacock, *Nature*, **129**, 57, (1932).

† *Trans. Chem. Soc.*, 258, (1933).

Table 11

Sugar	$k_{25°C} \times 10^5$	E	$Z \times 10^{-13}$
Sucrose	1·30	25,580	8·59
Raffinose	1·08	25,430	5·53
Melezitose	0·47	25,640	3·48

and the changes in Z and k are roughly parallel. The calculated collision frequency between hydrogen ion and the trisaccharides (which are derivable from sucrose by condensation with a galactose or a glucose molecule at suitable junctures) is actually somewhat greater than that for H_3O^+ and sucrose.

The influence of structure upon the velocity of chemical change has recently been re-examined in a novel and comprehensive manner by Polanyi and his collaborators.* The gaseous reactions which have been studied are those occurring between sodium atoms and halogen compounds, of the type

$$Na + CH_3Cl \rightarrow CH_3 + NaCl.$$

The velocity is measured by estimating the breadth of the reaction zone when the two vapours interdiffuse at very low pressures. With alkyl iodides, no critical energy is required, every collision between sodium atoms and the organic molecules being effective. E is small but measurable for the other halides, as the following results show.† The figures express the total number of collisions needed to bring about

Table 12

10^6	10^4	50	1
CH_3F	CH_3Cl	CH_3Br	CH_3I
	C_2H_5Cl	C_2H_5Br	C_2H_5I
	C_6H_5Cl	C_6H_5Br	C_6H_5I

the decomposition of one organic molecule. Gaseous reactions compared with ionic reactions in solution reveal a striking similarity in the influence of substituents and general

* von Hartel, Meer, and Polanyi, *Z. physikal. Chem.*, **B, 19,** 139, (1932); Meer and Polanyi, *ibid.*, p. 164.

† Polanyi, *Atomic Reactions*, p. 54, (1932).

configuration upon the velocity of chemical change.* The terms positive and negative mechanisms require explanation. When primary, secondary, and tertiary compounds react in

Table 13

	Reaction with sodium vapour	Ionic reaction	
		Negative mechanism	Positive mechanism
Series F, Cl, Br, I	Increase	Increase	
C=C in neighbouring position	Increase	Increase	
C=O	Increase	Increase	
Multiple substitution	Increase	Increase	
C=CCl in place of C−CCl	Decrease	Decrease	
Lengthening of chain	Decrease	Decrease	
Branching of chain	No effect	Decrease	
Primary, secondary, tertiary	Increase	Decrease	Increase

solution with positive ions (e.g. amines with acids) the velocity increases in this order, but when they react with negative ions (e.g. the saponification of esters) the order is reversed. This Polanyi explains by considering steric influences in the two cases. As shown in Fig. 3,* steric hindrance is small or zero with the positive mechanism, but considerable with the negative mechanism. The same geometric considerations account also for the absence or presence of optical inversion.

The whole question of orientation in collisions is extremely difficult. Even with the most accurate data it is impossible to decide, because though Z should be definitely parallel with k, it is clearly not logical to interpret this as evidence for the orientation effect.

In the development of the collision theory of chemical reaction rates there is always the danger that its exposition may tend to interpret all the phenomena on a purely mechanical basis, which cannot by its nature account for the specific chemical effects which are known to enter.

* Polanyi, *ibid.*, p. 61.

Activating collisions are always necessary, but they are not always sufficient to ensure chemical change. The study of ionic reactions shows that the replacement of a chlorine atom by a bromine atom may increase the observed 'collision' frequency about 100 times. This is out of all proportion to any change that the new atom may bring about

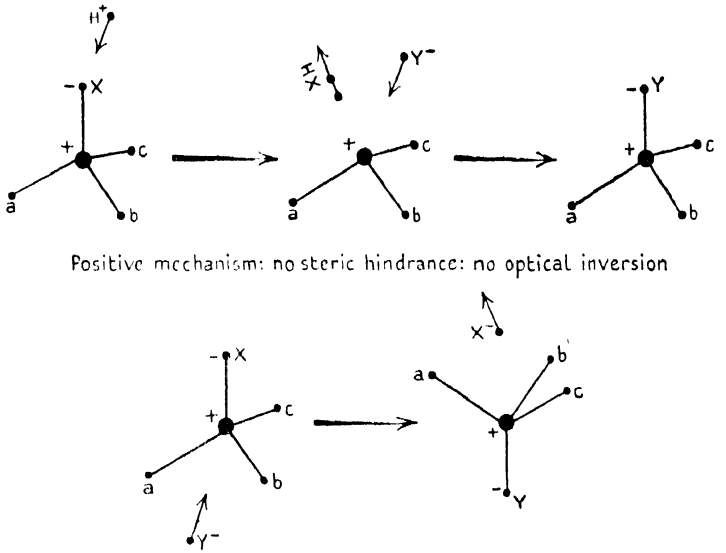


FIG. 3.

in the configuration and diameter of the reacting molecule. Its presence does not alter the apparent energy of activation, but it is quite possible that it may alter the frequency of internal vibrations, upon which energy fluctuations within the activated molecule depend. This interpretation, of course, is still mechanical, but it brings into prominence the part which is played by the internal dynamics of activated molecules—a subject which has up to the present been little explored, but which has the advantage of being able to account for those specific chemical effects which the cruder kinetics of collisions ignores.

The Influence of Dilution upon the Bimolecular Velocity Constants.

Occasionally, as with the saponification of esters, the bimolecular constant is found to be quite independent of the initial concentration of either reactant. Steger* found the following constants for the reactions between *o*- and *p*-dinitrobenzene with sodium ethoxide and with sodium methoxide in the corresponding alcohols:

Table 14

Dilution V (litres/gram molecule)	$k_{45°\,C} \times 10^3$ (litres/gram molecule-sec.)	
	With $NaOC_2H_5$ in HOC_2H_5	With $NaOCH_3$ in $HOCH_3$
20	3·83	2·32
40	3·82	2·33
60	3·82	..
80	3·83	2·35
100	3·82	..

This behaviour is rather exceptional. In the majority of cases, k increases with the dilution, often reaching a limiting value at a concentration of about 1/100 molar. Hecht, Conrad, and Brückner† found that the constants for the reaction between methyl iodide and sodium ethoxide varied with the dilution in the following manner:

$$k_v = k_1 + \omega \log_{10} v.$$

k_1 is the velocity when both reactants are at a concentration of 1 gram molecule per litre; the constant ω is specific for the reaction but independent of temperature. Table 15 shows that an equation of this form summarizes the dilution effect quite well. The calculated values have been obtained from the equation

$$k = 0{\cdot}001497(1 + 0{\cdot}4546 \log v) . 10^{0{\cdot}0520t},$$

where t is the temperature in degrees centigrade. The effect of changing the initial concentration upon the same reaction at 36° C. is shown graphically in Fig. 4. These equations are

* *Z. physikal. Chem.*, **49**, 329, (1904). † *Ibid.*, **5**, 289, (1890).

quite empirical, for there can be no special significance attaching to the value of the velocity constant relating to

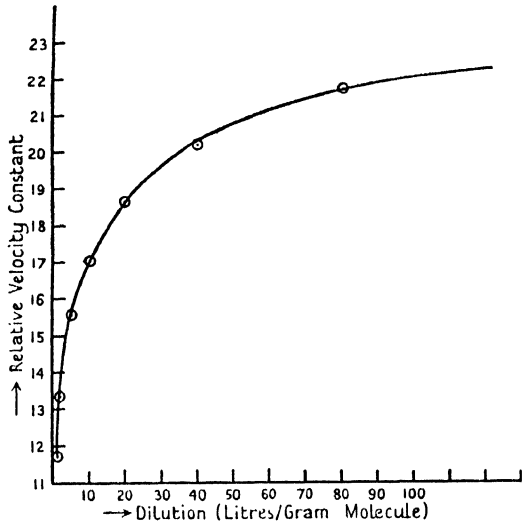


FIG. 4.—Reaction between methyl iodide and sodium ethoxide in ethyl-alcoholic solution at 36° C.

Table 15

$CH_3I + C_2H_5ONa$ *in* C_2H_5OH *at* 24° C.

Dilution (litres/gram mol.)	*k* (arbitrary units)	
	Observed	By equation
1	27·6	27·4
2	31·4	31·1
5	35·9	36·1
10	39·8	39·8
20	43·5	43·6
40	47·2	47·3
80	51·1	51·1

a solution of unit molar concentration. Hecht's equation has been found by Cox* to apply to a similar series of reactions (Table 16). The immediate value of these results is that they demonstrate conveniently the magnitude and direction of the dilution effect. In order to double the

* *Trans. Chem. Soc.*, **113**, 666, (1918); **119**, 143, (1921); **121**, 1904, (1922).

velocity of reaction, the dilution usually has to be increased from 10 to 1,000 times.

Table 16.

Reaction	k_1 (arbitrary units)	ω (arbitrary units)
α-$C_{10}H_7ONa+CH_3I$	41·1	17·1
„ $+C_2H_5I$	9·19	7·20
„ $+C_3H_7I$	4·30	4·37
β-$C_{10}H_7ONa+CH_3I$	35·6	16·7
„ $+C_2H_5I$	7·90	5·80
„ $+C_3H_7I$	3·16	3·25

The velocity of reaction at great dilutions is thus about 4–2 times the velocity in 1 molar solution: this always brings the observed rates and those calculated by the equation of Lewis (Table 2) into closer agreement. The implication in Hecht's equation that k should increase indefinitely with the dilution is not borne out by experiment. His own work as well as that done upon two slow reactions in carbon tetrachloride solution* indicates the tendency to reach a definite limit.

Further investigations upon the kinetics of reactions in highly dilute solution are much to be desired.

The results of Hecht and many others have been interpreted by Acree and his collaborators in terms of the dual hypothesis.† On the assumption that both ions and neutral molecules react, we have

$$k_{\text{obs}} = k_i\alpha + k_m(1-\alpha),$$

where k_i and k_m are the reactivities of the ion and undissociated molecule respectively and α is the 'degree of ionization'. We are here ignoring the salt effect, which is known to be only about 7 per cent. Hecht, Conrad, and Brückner found that the presence of 0·07 molar potassium iodide did not alter the velocity of reaction: neither did

* *Ibid*, 230, (1932).

† See, for example, Robertson and Acree (*J. Amer. Chem. Soc.*, **37**, 1902, (1915)), where reference to twenty preceding papers of the same series will be found.

the presence of the other product (diethyl ether) when present at the high concentration of 4·5 gram molecules per litre. The freedom from salt effects, autocatalysis, and reverse reaction makes these etherifications admirable cases for testing the hypothesis. Writing the equation in the form

$$k_{obs} = k_m + \alpha(k_i - k_m),$$

it is seen that k_i and k_m can be found by plotting the observed velocity against the degree of dissociation. The curve should be linear, with a slope equal to $(k_i - k_m)$ and an intercept of k_m.

An equation of this kind accounts satisfactorily for the velocity of reaction between 1-phenyl-thiourazol and ethyl iodide at various dilutions in ethylalcoholic solution at 25° C.,* k_m being 0·1579 and k_i being 0·4625 (Table 17). Tables 18

Table 17

Dilution	α	k_{obs}	k by equation
4	0·248	0·227	0·233
8	0·334	0·258	0·260
16	0·421	0·290	0·286
32	0·514	0·312	0·314
84	0·607	0·335	0·343

and 19, which refer to Hecht's reaction at 25° C., show that k_i calculated in this manner is sensibly independent of the dilution and of the metallic cation. As required by the theory, k_m is specific for each base. Not always, however, do such regularities occur.

Table 18

Dilution	$k \times 10^2$	α	k_i	k_m
2	7·50	0·234	0·129	..
4	8·08	0·312	0·125	0·0577
8	8·57	0·393	0·128	0·0603
16	9·23	0·481	0·124	0·0583
40	9·98	0·605	..	0·0607

As to the general validity of the idea underlying the theory of dual catalysis there can be no doubt, but it is by

* Chandler and Acree, *Z. physikal. Chem.*, **91**, 607, (1916).

Table 19

Reaction	k_i	k_m
$CH_3I+C_2H_5OLi$	0·137	0·039
$CH_3I+C_2H_5ONa$	0·128	0·059
$CH_3I+C_2H_5OK$	0·126	0·069

no means clear whether the results quoted here can be regarded as real evidence in its favour. All the calculations referred to are based on the assumption that the degree of ionization can be evaluated from the equivalent conductivities by means of the simple equation $\alpha = \Lambda_v/\Lambda_0$. This relation, as is now well known, is true only in rare cases—a fact which is in no way altered by the circumstance that the Ostwald dilution law appears to hold for the dissociation of sodium alkylates. Metallic derivatives of the alcohols are strong electrolytes, for which the expression

$$\frac{\Lambda_0-\Lambda_v}{\Lambda_0} = A\sqrt{C}$$

holds good.* C is the concentration of electrolyte, and A is a constant dependent upon the electrical properties of the ions and the medium. Hence, what has really been demonstrated from the kinetic measurements described is that

$$k_{\text{obs}} = k_m+\frac{\Lambda_v}{\Lambda_0}(k_i-k_m)$$

or

$$\frac{\Lambda_0-\Lambda_v}{\Lambda_0} = \frac{k_i-k_{\text{obs}}}{k_i-k_m}.$$

The alkylates behaving as strong electrolytes, we may write

$$A\sqrt{C} = \frac{k_i-k_{\text{obs}}}{k_i-k_m}$$

or

$$k_{\text{obs}} = k_i+k'\sqrt{C}$$

in which $k' = (k_m-k_i)A$. Since the Onsager expression is valid at high dilution only, it is only in this region that proportionality should be observable between k_{obs} and $\sqrt{C}$.

* Unpublished work carried out by Mr. O. L. Hughes.

There are not sufficient data to test this adequately, but there are distinct tendencies towards linearity in the curves found by plotting the data of Hecht and Acree in this way. Superficially, therefore, it would appear that the dilution effect in these cases might be attributed entirely to changes in the ionic environment, but the fact that k' is negative rules out this possibility. The dual theory still holds the field, therefore, as the most reasonable explanation of the dilution effect in these reactions, but recalculations based upon more reliable values of α are needed to consolidate its position.

Composite Velocity Coefficients.

The rates of many reactions in aqueous solution are sensitive to hydrogen ions and to hydroxyl ions and the observed velocity at any given temperature can be represented by an equation of the type

$$k_{obs} = k_0 + k_1 f_1[H^+] + k_2 f_2[OH^-].$$

This is best understood by regarding the change as the sum of three simultaneous reactions, viz. a spontaneous change, or a change depending upon undissociated molecules of the solvent, and two ionic catalyses. The Arrhenius critical increment determined by the relation $E_A = RT^2 \frac{d \ln k_{obs}}{dT}$ in such a case is meaningless. The peculiarities of these reactions are not known until the nature of f_1 and f_2 has been established, and k_0, k_1, and k_2 have been evaluated separately at various temperatures. A simple instance of multiple catalysis may conveniently be dealt with at this stage but the general treatment is given in Chapter VIII.

The hydration of acetic anhydride in aqueous solution is kinetically unimolecular, and has been examined by various investigators.* The unimolecular constant has been found

* Rivett and Sidgwick, *Trans. Chem. Soc.*, **97**, 732, 1677, (1910); Orton and Jones, *ibid.*, **101**, 1708, (1912); Verkade, *Rec. trav. chim. Pays-bas*, **35**, 79, 299, (1915); Jowett, *Thesis*, Liverpool, (1923).

by Jowett to increase with the dilution. If c is the concentration of anhydride,

$$k_{obs}(\text{at } 25^\circ \text{ C.}) = 0{\cdot}002584\ (1-0{\cdot}02857c)$$
$$k_{obs}\ (\text{at } 0{\cdot}5^\circ \text{ C.}) = 0{\cdot}0004804\ (1-0{\cdot}2935c).$$

Combining these results the kinetics of the net reaction corresponding to infinite dilution are

$$k_{obs} = 2{\cdot}5\times10^5 e^{-10{,}840/RT}.$$

Values of E found from the data of the other workers are 11,600 (R. and S.), 10,100 (O. and J.) and 10,600 (V.). The observed critical increments for the hydration of the anhydrides of propionic acid, butyric acid, and iso-butyric acid are 10,800, 10,600, and 10,400 calories respectively (Verkade). The average value of 10,650 holds for the homologous series, a fact which suggests that the changes are bimolecular, the approximately constant concentration of water furnishing pseudo-unimolecular conditions. Direct proof has been afforded by the work of Philip* upon the velocity of reaction in acetone solution. Reproduction of results is naturally difficult, but with equal concentrations of water and acetic anhydride, the following very approximate relation holds: $k_{bi} = 10^5 e^{-16{,}000/RT}$. Jowett finds that when the anhydride is hydrated in aqueous solution the displacement of water by sucrose causes k_{obs} to fall, the ratio $k_{obs}/[H_2O]$ remaining constant. This again points to a reaction of the second order. We are thus fully justified upon experimental grounds in expressing the velocity of the reaction in aqueous solution as

$$\frac{-d[(CH_3CO)_2O]}{dt} = \{k_w[H_2O]+k_H[H_3O^+]+K_{OH}[OH^-]\}[(CH_3CO)_2O].$$

In the presence of acids $[H_2O]$ is constant and $[OH^-]$ is

* *Trans. Chem. Soc.*, **28**, 259, (1912).

negligibly small, hence

$$k_{obs} = -\frac{d[(CH_3CO)_2O]}{dt}\frac{1}{[(CH_3CO)_2O]} = k'_w + k_H[H_3O^+].$$

This equation has been verified by Jowett, who finds

$$k_{obs} \text{ (at } 0{\cdot}5^\circ \text{ C.)} = 0{\cdot}000425 + 0{\cdot}000505[HCl]$$
$$k_{obs} \text{ (at } 25{\cdot}0^\circ \text{ C.)} = 0{\cdot}00215 + 0{\cdot}00695[HCl].$$

By calculating the critical increments separately for k'_w and k_H we find $k_H = 3{\cdot}61 \times 10^{10} e^{-17,280/RT}$,

i.e. within a factor of 8 the velocity agrees with the theoretical value calculated on the simple collision theory. The true critical increment for the reaction between acetic anhydride and undissociated water molecules, obtained by a method which will be explained later, becomes 15,100 calories which is equal within the limit of error to E for the bimolecular reaction in acetone solution.

As far as this reaction goes, the analysis of the experimental results has revealed a catalytic reaction with normal velocity, as well as a bimolecular reaction between acetic anhydride and water molecules which in two solvents proceeds at a rate lower than the calculated value by several powers of ten. The discrepancy factor is similar to that found in non-aqueous solvents for other reactions shortly to be discussed.

The hydration of acetic anhydride has been dealt with rather fully in order to illustrate the method of analysing results. Among other examples which lend themselves to the same treatment are the mutarotation of glucose (p. 232) and the decomposition of carboxylic acids (p. 224).

Slow Reactions.

The study of the combination of amines and alkyl halides has played a prominent part in the development of our views upon the subject of reaction kinetics in general.

$$(C_2H_5)_3N + C_2H_5I \rightarrow (C_2H_5)_4NI.$$

Menschutkin* measured the velocity of the formation of tetraethyl-ammonium iodide in a number of solvents at 100° C. and found the medium to have a profound influence upon it. The relative values of the constants obtained (Table 20) show that the reaction is always faster in an aromatic solvent than in the corresponding aliphatic solvent.

Table 20

Solvent		Relative k
Hydrocarbons	Hexane	0·13
	Heptane	0·17
	Xylene	2·2
	Benzene	2·4
Halogen Derivatives	Propyl chloride	4·0
	Chlorobenzene	17·4
	Bromobenzene	20·3
	α-Bromonaphthalene	84·9
Ethers	Ethyl-*iso*-amyl ether	0·47
	Diethyl ether	0·57
	Phenetole	16·0
	Anisole	30·3
Esters	*Iso*-butyl acetate	4·3
	Ethyl acetate	16·7
	Ethyl benzoate	19·4
Alcohols	*Iso*-butyl alcohol	19·4
	Ethyl alcohol	27·4
	Allyl alcohol	32·5
	Methyl alcohol	38·0
	Benzyl alcohol	100·0
Ketones	Acetone	45·7
	Acetophenone	97·3

The 'slow' solvents are the hydrocarbons and ethers; the 'fast' solvents are the alcohols and ketones. The positive catalytic influence of the solvent thus runs roughly parallel with its general chemical reactivity—a result which Menschutkin interprets by classifying the solvent influence among specific chemical effects. Apparently, therefore, one or both of the reactant molecules can combine in one way or another with the solvents in varying degrees: the union between solute and solvent is least in the case of aliphatic

* *Z. physikal. Chem.*, **6**, 41, (1890).

hydrocarbons and greatest in the case of aromatic alcohols. It may be mentioned that the same order of solvent activity has been found for some unimolecular reactions, e.g. the isomerization of camphene hydrochloride,* the decomposition of xanthogenic acid,† and the decomposition of trinitrobenzoic acid.‡

The temperature coefficients of Menschutkin's reaction have only recently been determined, but values of E for kindred changes have long been known and were used by Christiansen§ in the calculations to which reference has already been made. To explain the great disparity between the observed constants and those given by the equation of Lewis, Christiansen suggested that solvent molecules rob the reactants of their critical energy in de-activating collisions. Norrish and Smith|| endorsed this view, after an investigation of the reactions between trimethylamine and *o*- and *p*-nitrobenzyl-chloride in benzene solution, and a review of the results of Cox**

$$NO_2.C_6H_4.CH_2Cl+(CH_3)_3N \rightarrow NO_2.C_6H_4.CH_2N(CH_3)_3Cl$$

and of Hawkins†† upon the kinetics of two similar reactions in various solvents:

$$C_6H_5NH_2+p\text{-}Br.C_6H_4.CO.CH_3 \rightarrow C_6H_5.NH.C_6H_4.CO.CH_3, HBr.$$

$$C_5H_5N+C_3H_5Br \rightarrow C_5H_5N(C_3H_5)Br.$$

The ratio (observed velocity: calculated velocity) was found to be greater with polar solvents than with non-polar solvents.

From the results of the experiments which have been described in Chapter III it is known that carbon tetrachloride usually behaves as an ideal, inert solvent. It is therefore a matter of interest to know the velocity of Menschutkin's

* Meerwein and Montfort, *Annalen*, **435**, 207, (1925).
† von Halban and Kirsch, *Z. physikal. Chem.*, **82**, 325, (1913).
‡ Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **A**, **113**, 186, (1931).
§ *Z. physikal. Chem.*, **113**, 35, (1924). || *Trans. Chem. Soc.*, 129, (1928).
** *Ibid.*, **119**, 142, (1921). †† *Ibid.*, **121**, 1170, (1922).

reaction in this solvent. Experiments showed that the reaction proceeds in carbon tetrachloride at a rate which is not very different from that in the aliphatic hydrocarbons. In Table 20, CCl_4 takes its place between heptane and xylene among the slow solvents. This suggests that the slow rates are the normal ones, and that the solvents in which the reaction is fast exert a positively catalytic influence.* From the temperature coefficient of the velocity constant in hexane, which is an even better solvent for this reaction than carbon tetrachloride, it was shown that there is still a disparity of 10^8 between the observed rate and the calculated rate for the hypothetical gaseous reaction. In order to determine whether this is in reality due to deactivation by solvent molecules, the velocity of reaction was measured in the gaseous phase, where, even in spite of catalysis by the wall of the vessel, k is only about 5 times as great as in hexane, and is actually less than the value found in carbon tetrachloride.

It is therefore clear that whatever the cause of the slowness of the reaction may be it is not due to deactivation by solvent molecules since the observed rate in the vapour phase and in two inert solvents are of the same order of magnitude. Now the type of reaction under discussion ($A+B \rightarrow AB$) involves the formation of one molecule of resultant from two molecules of reactant and is of a kind that may require a triple collision before activation becomes effective (cf. combination of hydrogen atoms, Chap. V). Lest the great divergence between the observed rate and that calculated from the simple theory should be due to a special collisional restriction of this kind, the kinetics of a bimolecular reaction of the type $A+B \rightarrow C+D$ were examined.

Velocity constants for the following reaction in various solvents at single temperatures have long been known,†

* Moelwyn-Hughes and Hinshelwood, *ibid.*, 230, (1932).

† Menschutkin, *Z. physikal. Chem.*, **1**, 611, (1887); Soper and Williams, *Trans. Chem. Soc.*, 2297, (1931).

but the temperature effect has only recently been studied:

$$(CH_3CO)_2O+C_2H_5OH \rightarrow CH_3COOC_2H_5+CH_3COOH.$$

With two inert solvents, the following results hold:

In hexane, $k = 9{\cdot}16\times10^4e^{-12,400/RT}$

In carbon tetrachloride, $k = 4{\cdot}14\times10^5e^{-13,400/RT}$.

The reaction, therefore, like the previous one is abnormally slow, but the slowness cannot be due to deactivation by solvent molecules for the velocity of this reaction also in the gaseous phase is of the same order of magnitude as that in the two inert solvents.*

To attempt to discover the cause of the tardiness of these reactions is a difficult matter, and at the present stage must be rather speculative. Nevertheless, some of the possibilities may be briefly discussed.

If, as it appears possible in the reactions studied by von Hartel and Polanyi, by Kistiakowsky and Nelles, and by Vaughan, the activated molecules can react only when they are in a suitable internal phase at the moment of collision, the discrepancy can be readily explained. Suppose reaction can set in only when one of the vibrating atoms is at the extremity of its swing, the calculated velocity of reaction as given by the equation of Lewis must be reduced by a factor which is proportional to the frequency of the internal vibration. This view has much to commend it. The main objection to it is that since the phase factor is an inherent function of the reacting molecule, it might be expected to change but little due to the presence of inert solvent molecules. Actually, however, the kinetics of these reactions show considerable variation in the different solvents, especially in the values of the apparent energy of activation.

The word apparent recalls the assumption underlying all the previous calculations that the Arrhenius critical incre-

* Moelwyn-Hughes and Hinshelwood, *loc. cit.*

ment is the true energy of activation. The results in Table 21 cast some doubt upon the truth of this. The data have been

Table 21

Reactions showing Disparity between Observed and Calculated Rates

Reaction	Solvent	E	$k_{60°\,C.}$ Observed $\times 10^5$	$k_{60°\,C.}$ Calculated $\times 10^{-2}$	$\frac{k_{calculated}}{k_{observed}}$
$(C_2H_5)_3N+C_2H_5Br$	C_6H_6	11,190	1·28	239	$1·9\times10^9$
$C_6H_5N(CH_3)_2+CH_3I$	$C_2H_2Cl_4$	11,680	45·4	93·1	$2·1\times10^7$
$(C_2H_5)_3N+C_2H_5Br$	$(CH_3)_2CO$	11,710	17·5	108	$6·2\times10^7$
p-$H\phi NH_2+H\phi Cl$[1]	99·6% C_2H_5OH	11,860	9·80	36·1	$3·7\times10^7$
$(C_2H_5)_3N+C_2H_5Br$	50% $(CH_3)_2CO$, 50% C_6H_6	12,040	8·97	65·5	$7·3\times10^7$
$(C_2H_5)_3N+C_2H_5Br$	80% $(CH_3)_2CO$, 20% C_6H_6	12,100	16·0	59·7	$3·7\times10^7$
$(C_2H_5)_3N+C_2H_5Br$	20% $(CH_3)_2CO$, 80% C_6H_6	12,180	4·92	53·0	$1·1\times10^8$
$C_6H_5N(CH_3)_2+CH_3I$	$C_6H_5NO_2$	13,020	6·65	12·4	$1·9\times10^7$
$C_5H_5N+CH_3I$	$C_2H_2Cl_4$	13,220	182	9·04	$5·0\times10^5$
$C_6H_5NH_2+H\phi Cl$	99·6% C_2H_5OH	13,450	13·8	3·25	$2·4\times10^6$
$CS(NH_2)_2+CH_3I$	$(CH_3)_2CO$	13,620	383	4·45	$1·2\times10^5$
$C_6H_5N(CH_3)_2+C_2H_5I$	$(CH_3)_2CO$	13,680	3·11	4·81	$1·6\times10^7$
$C_6H_5N(CH_3)_2+CH_3I$	$C_6H_5CH_2OH$	14,400	250	1·50	$6·0\times10^4$
$CS(NH_2)_2+C_2H_5I$	C_2H_5OH	14,620	143	0·973	$6·8\times10^4$
$C_6H_5NH_2+p$-$NO_2\phi Cl$	99·6% C_2H_5OH	14,680	5·77	0·548	$9·5\times10^5$
$(CH_3)_2NH+C_2H_5I$	C_2H_5OH	14,740	275	1·10	$4·0\times10^4$
(*iso* $C_5H_{11})_3N+C_2H_5I$	C_2H_5OH	15,190	180	0·577	$3·2\times10^4$
p-$H\phi NH_2+H\phi Cl$	99·6% C_2H_5OH	16,050	25·2	0·063	$2·5\times10^4$

[1] ϕ = $-C_6H_4CH_2-$ or $-CH_2C_6H_4-$.

gathered from the work of Hawkins,* Hemptinne and Bekaert,† Essex and Gelormini,‡ Byrne,§ and Preston and Jones.|| A slightly inaccurate collision formula has been used in calculating the theoretical rates,** but this is of no importance. Considering these results broadly, it is seen that rates which for normal reactions would be associated with an energy of activation of about 22,000 calories are here related to reactions which in all cases have values well

* *Loc. cit.*

† *Z. physikal. Chem.*, **28**, 225, (1899).

‡ *J. Amer. Chem., Soc.*, **48**, 882, (1926).

§ *Thesis*, Liverpool, (1924).

|| *Trans. Chem. Soc.*, **101**, 1930, (1912).

** Moelwyn-Hughes, *Chemical Reviews*, **10**, 241, (1932).

below that figure. Furthermore, divergence between the experimental and theoretical k's diminishes steadily as the observed value of E increases, finally disappearing as E approaches that quantity (22,000 calories) which characterizes normal reactions proceeding with this rate. The observed critical increments thus appear to be false, in the sense that—by some unknown mechanism—they have been depressed from the normal values.

The problem now resolves itself into tracing a cause which will explain the low value of both the E and Z terms of the Arrhenius equation.

Suppose one of the reactants combines with the solvent, and that chemical change takes place due to collisions of the complex AS with the solvent.

$$A+S \rightleftarrows AS; \qquad K=\frac{[AS]}{[A][S]};$$

$$AS+B \rightarrow \text{Products.}$$

The theoretical rate should thus be

$$k[AS][B] = kK[S][A][B] = kK'[A][B].$$

The experimental rate is simply $k_{\text{obs}}[A][B]$ hence

$$k_{\text{obs}} = kK' = Z_c e^{-E_c/RT} W e^{-Q/RT},$$

where E_c is the critical increment of the bimolecular process, and Q is the heat absorbed during the formation of the complex. Since $k_{\text{obs}} = Z_{\text{obs}} e^{-E_{\text{obs}}/RT}$ it follows that

$$Z_{\text{obs}} e^{-E_{\text{obs}}/RT} = Z_c W e^{-\left(\frac{E_c+Q}{RT}\right)}.$$

If E_c is greater than E_{obs}, Q must be negative, i.e. the complex would have to be formed exothermically. The objection to interpretations of this kind in general is that they elude the practical test. In this particular case, there is also the drawback that the chemically inert solvent should produce more stable complexes than the active solvents.

There is another interpretation of the phenomena under

discussion which is also able to explain the simultaneous lowering of both Z and E, and has the advantage of being verifiable experimentally. Consider the reaction

$$(CH_3CO)_2O+C_2H_5OH \rightarrow CH_3COOC_2H_5+CH_3COOH.$$

We have seen that in carbon tetrachloride solution and in hexane solution, only about 1 in 10^6 of the activating collisions is fruitful. Suppose the reaction can only take place when one of the molecules is ionized, e.g.

$$(CH_3CO)_2O+C_2H_5O^- \rightarrow CH_3COOC_2H_5+CH_3COO^-.$$

The observed velocity would then be low because the number of ions in solution is small. The examples quoted in Table 2 are largely ionic: it is known, for example, that sodium derivatives of the alcohols are all highly dissociated in alcoholic solution. This interpretation is consistent with the general trend of recent work, and promises to justify further investigation. The idea, of course, is not novel.* The first requirement is a knowledge of the very small dissociation constants of substances such as ethyl alcohol in inert solvents. This is seldom available. An attempt at explaining quantitatively the disparity with which we are dealing may be described here.

The above esterification reaction in ethyl alcohol as solvent is unimolecular with respect to the anhydride, the velocity constant at nine temperatures leading to the equation $k_{uni} = 4{\cdot}4\times10^8 e^{-18,710/RT}$.† If reaction occurs between neutral molecules of solute and solvent, we must introduce a correction (p. 159) which makes E equal to 21,210 calories. The number of alcohol molecules encountered per second by each molecule of anhydride is $\frac{3\pi\eta\sigma}{2m}$ (Chap. I, equation 7), which is $1{\cdot}2\times10^{13}$ at 50·5° C. The fraction of this number which is effective is $e^{-E/RT} = 4{\cdot}3\times10^{-15}$, hence the calculated

* Brühl, *Berichte*, **32**, 2326, (1899); Euler, *Z. physikal Chem.*, **32**, 348, (1900).

† Moelwyn-Hughes and Rolfe, *Trans. Chem. Soc.*, 241, (1932).

unimolecular constant is $5{\cdot}1\times10^{-2}$, which is 630 times lower than the observed value. Now if reaction occurs between acetic anhydride molecules and ethoxide ions, we have

$$k_{bi} = -\frac{d[(CH_3CO)_2O]}{dt}\frac{1}{[(CH_3CO)_2O][C_2H_5O^-]}$$
$$= \frac{k_{uni}}{[C_2H_5O^-]}.$$

Macfarlane and Hartley,* from measurements of the potential of the hydrogen electrode in ethyl alcohol, give the dissociation constant at 25° C. as $K = [C_2H_5O^-][H^+] = 1{\cdot}9\times10^{-19}$. It has not been possible to find how this varies with temperature, but we can take the heat of dissociation to be approximately equal to the heat of neutralization of strong acids with sodium methoxide, which is 11,200 calories.† From these two data, we can estimate the concentration of ethoxide ion in ethyl alcohol at any temperature; $[C_2H_5O^-] = K^{\frac{1}{2}} = 5{\cdot}75\times10^{-6}e^{-5,600/RT}$. At 50·5° C., $k_{uni} = 8{\cdot}1\times10^{-5}$ secs.$^{-1}$, and $[C_2H_5O^-] = 7{\cdot}3\times10^{-10}$ gram ion per litre, hence $k_{bi} = 1{\cdot}1\times10^{+5}$. In order to calculate the theoretical rate for the bimolecular process, we use the equation of Lewis, as before, inserting the value of E found in the following way:

$$k_{bi} = k_{uni}/[C_2H_5O^-] = k_{uni}\times K^{-\frac{1}{2}}$$
$$\ln k_{bi} = \ln k_{uni} - \tfrac{1}{2}\ln K.$$

Differentiating with respect to temperatures, and multiplying each term by RT^2, we have

$$E_{bi} = E_{uni} - \tfrac{1}{2}Q$$
$$= 18{,}800 - 5{,}600 = 13{,}200 \text{ calories.}$$

Upon this basis, the calculated rate at 50·5° C. becomes $2{\cdot}15\times10^{2}$, i.e. 520 times less than the observed value. The result, although approximate, is qualitatively correct. The

* *Phil. Mag.*, **13**, 425, (1932).

† Wolfenden, Jackson, and Hartley, *J. Physical Chem.*, **31**, 850, (1927).

observed rate therefore lies between the theoretical values calculated upon the assumption that the reaction is either

(1) $(CH_3CO)_2O+C_2H_5OH \rightarrow CH_3.COOC_2H_5+CH_3.COOH$

or

(2) $(CH_3CO)_2O+C_2H_5O^- \rightarrow CH_3.COOC_2H_5+CH_3.COO^-$.

The importance of this is that it proves the correction which is possible upon the ionization theory to be of the right order of magnitude to account for the very large discrepancy. Since the heats of dissociation are functions of the solvent, we have also a ready explanation of the variation in the Arrhenius critical increment for a given reaction in various media.

It may be significant that the two outstanding instances of slow reactions are highly exothermic, the heat evolved being not very different from the energy of activation:

Reaction	Solvent	E	Q
$(CH_3)_2NC_3H_5+CH_3I$	$C_6H_5NO_2$	13,020	15,000*
$(CH_3CO)_2O+H_2O$	H_2O	10,600†	9,400‡

The transition of activated molecules into normal ones in such cases may conceivably be linked with quantum-mechanical restrictions.

Discussion.

The existence of a large number of bimolecular reactions proceeding in solution with normal velocities has now been placed beyond doubt. Special value attaches to the conversion of ammonium cyanate into urea and to the hydrolysis of phthalide, for these examples show the agreement to be not confined to the etherification reaction. The development of the subject at this stage calls for the examination of a large variety of chemical changes. From the results at present available the following observations emerge.

Most of the reactions with normal velocities (Table 2)

* Essex and Gelormini, *J. Amer. Chem. Soc.*, **48**, 882, (1926).

† Verkade, *Rec. trav. chim. Pays-bas*, **33**, 299, (1915).

‡ Thomsen, *Thermochemistry*, p. 373, (1908).

seem to occur between ions and neutral molecules. The simple reactions of inorganic chemistry, which take place between oppositely charged ions,* are extremely rapid or even instantaneous, whereas many of the reactions undergone by complex organic molecules are extremely slow. Regarded from the kinetic standpoint, there appear to be three classes of bimolecular reactions, typified by the following examples:

(1) $NaOH+HI \rightarrow H_2O+NaI$, in aqueous solution; rate is instantaneous ($E = 0$).

(2) $NaOC_2H_5+C_2H_5I \rightarrow (C_2H_5)_2O+NaI$, in alcoholic solution; rate equals that predicted by theory.

(3) $(C_2H_5)_3N+C_2H_5I \rightarrow (C_2H_5)_4NI$, in most solvents; rate is much lower than that given by theory.

Reaction (1) is simple, in that the ions OH^- and H_3O^+ have simply to find each other out, when their electrical charges are sufficient to ensure permanency of combination. The rate of reaction (2) depends upon encounters between ethoxide ion $C_2H_5O^-$ and ethyl iodide, but a covalent bond in the molecule must be loosened or broken by the acquisition of energy before chemical change can take place. It is therefore possible that the slowness of reaction (3) may be due to the fact that neither reactant is appreciably ionized. The difference in the velocities cannot be attributed to the solvent, and must be a function of the reacting molecules. Denoting a charged molecule by A^z or B^z, and an uncharged molecule by A^0 or B^0, we may write:

(1) $A^z+B^{-z} \rightarrow$ instantaneous reaction, provided the compound formed is electrovalent.

(2) $A^0+B^{\pm z} \rightarrow$ normal velocity.

(3) $A^0+B^0 \rightarrow$ abnormally slow velocity.

An electrostatic field thus appears to be necessary for the

* We are here thinking of *true* ionic reactions, i.e. the formation of an ion-pair (Chap. VII). Reaction (1) is retained in the text in order to clarify the argument, although it is not a true ionic change, since a covalent link is formed.

transformations undergone by organic molecules in solution, and can suitably be furnished by the presence of ions. The general argument in favour of this hypothesis gains support from the following two facts. The reaction between acetic anhydride and water is abnormally slow, but that between the anhydride and hydrogen ion has the normal value (p. 106). The tardiness of the esterification reaction in organic solvents can be accounted for by introducing the idea of ionization (p. 114).

The Attempted Correlation of Velocity Constants with Certain Physical Properties.

The search is being actively carried out for signs that bimolecular velocity constants may be linked in a simple manner with one or other of the physical properties of either the reactants or the solvents.

(1) *Dielectric Constants.* There is a growing belief that the dipole moments of molecules may influence the velocity with which they undergo chemical change, but there is as yet no evidence for this, nor in fact any very clear picture of the mechanism whereby such an effect may be exerted. There are well-known influences which certain groups in the benzene nucleus can exert on the position at which other groups may become attached. It has been shown* that groups which direct ortho and para substitution cause a drift of electrons into the benzene ring: a group which induces substitution into the meta position attracts the electrons away from the ring. The electrical asymmetry of the reacting molecules is thus definitely linked with the seat of reaction, but no comparisons have been made between the velocity of the substitution reactions and the extent of polarization.

The reverse state of affairs has been examined by W. Hückel,† who considers how the dipole moment may be connected with the velocity of intramolecular change. The

* Sutton, *Proc. Roy. Soc.*, **A, 133**, 668, (1932).

† *Leipziger Vorträge*, p. 83, (1925).

velocity of ionization of a simple dipole may be considered proportional to $e^{-E_i/RT}$, where E_i, the heat of ionization, in the simplest case would be $\frac{e^2}{Dr}$; r is the nuclear separation, and D the dielectric constant. The rate of reaction should then be greatest in the solvent with the high dielectric constant. The velocity constants found by Meerwein and Emster* for the isomerization of camphene hydrochloride are quoted in support of the contention. A parallelism is indeed found but this can be interpreted in many other ways, none of which can be of real value until the temperature coefficient has been ascertained. It is open to question whether D for the solvent is the right value to use.

The velocity of formation of tetraethylammonium iodide runs roughly parallel with the dielectric constant of the solvent.† The same regularity has been found to hold for numerous keto-enol transformations and the reverse processes,‡ and seems to be fairly general. Singularly enough, when k does not increase with D, exactly the inverse order is found, i.e. for a series of solvents, k occasionally has the same order as $1/D$. This is true in the case of Dimroth's triazole reaction, where k in chloroform ($D = 4{\cdot}95$) is about 10^4 times as great as in water ($D = 81{\cdot}7$). The most sceptical comment which these results can evoke is that other physical properties of the solvents arrange themselves in a similar order, making possible a variety of interpretations. On the other hand, it is not unreasonable to discern in these regularities evidence that ionization is a factor of the utmost importance in the kinetics of reactions in solution. It is perhaps necessary to point out that the dielectric properties of the medium may influence both the rate of dissociation of the solute dipole and the extent of dissociation. The second effect is clearly the more important.

* *Berichte*, **53**, 1815, (1920); **55**, 2500, (1922).

† Table 20; also Grimm, Ruf, and Wolff, *Z. physikal. Chem.*, **B**, **12**, 301, (1931).

‡ Stobbe, *Annalen*, **326**, 359, (1903).

(2) *Cohesion.* Soper and Williams* note that solvents which accelerate the esterification of acetic anhydride retard the formation of quaternary ammonium salts. They suggest that polar solvents accelerate reactions producing polar products and have the opposite effect when the resultants are less polar than the reactants. The idea is based upon parallelisms between molecular surface energies and velocities determined at single temperatures. The authors have also suggested that slow reactions are those characterized by marked polar differences between reactants and resultants.

(3) *Viscosity.* There have been varying views concerning the possible role played by the viscosity of the medium in determining the rate of bimolecular reactions: viscous solvents have been held to accelerate, to retard, and to have no influence upon the number of binary collisions.† Provided we distinguish clearly between solute-solute collisions and solute-solvent collisions, the answer is unambiguous. The frequency of encounters between molecules of solute cannot be seriously influenced by the viscosity of the medium, whereas the number of collisions between molecules of solvent and molecules of solute is definitely increased by an increase in the viscosity of the solvent. The reason for this has already been given (Chap. I).

Ölander‡ has developed a theory of bimolecular reactions in solution, according to which the collision frequency between dissolved molecules is inversely proportional to the viscosity. The equation deduced makes the number of encounters independent of the masses of the colliding molecules, and is dimensionally incorrect.

* *Trans. Chem. Soc.*, 2297, (1931).

† Moran and Lewis, *Trans. Chem. Soc.*, **121**, 1613, (1922); Scatchard, *J. Amer. Chem. Soc.*, **45**, 1580, (1923); Jowett, *Phil. Mag.*, **8**, 1059, (1929).

‡ *Z. physikal. Chem.*, **A, 144**, 118, (1929).

V

EQUILIBRIA

THERMODYNAMICS, while unable to contribute anything to our knowledge of the speed with which a system approaches its most stable state, yields almost complete information about the stable or equilibrium condition thus attained. For the homogeneous system

$$m_1 A + m_2 B \underset{k_2}{\overset{k_1}{\rightleftarrows}} n_1 C + n_2 D$$

the inter-relation between the concentrations of the participating species at the equilibrium point is given by a well-known theorem as

$$K = \frac{[C]^{n_1} \times [D]^{n_2}}{[A]^{m_1} \times [B]^{m_2}}, \qquad (1)$$

where K, the equilibrium constant, is independent of the relative amounts of the reactants and is determined solely by the temperature. The harmony with data for gaseous systems is too familiar a matter to require comment. The deduction of this expression is based on the assumption that each molecular constituent behaves as an ideal gas, so that its extension to cover cases of equilibria in solution must on theoretical grounds be strictly relegated to the region of high dilution. It is an experimental fact that this equation represents satisfactorily the equilibrium conditions in the majority of cases which have been examined in solution, whether the equilibria refer to ionization, polymerization, or chemical decomposition in the ordinary sense. The expression holds for a large variety of solvents, and, in the form of the distribution law, for equilibria in systems containing two solvents. Even when the reacting species are themselves pure liquids, the expression is sometimes obeyed, due to the proportionality between the concentrations of the pure liquids and the partial vapour pressures of the constituents in the gaseous phase.

A genuine shift in the position of equilibrium indicates that the velocity of either or of both of the opposing reactions has changed, and thus denotes catalysis by the solvent.

The Velocities of Reaction at the Equilibrium Stage.

When equilibrium has been established, the number of molecules of A and B disappearing per unit time ($k_1[A]^{n_1}[B]^{n_2}$) must be equal to the number of these molecules re-formed ($k_2[C]^{n_1}[D]^{n_2}$) by the opposing reaction, so that

$$K = \frac{k_1}{k_2}. \qquad (2)$$

The relative velocities of the two reactions may thus be determined from purely thermodynamic data.

This equation has been verified in a number of instances. From static measurements, the equilibrium constant for the system

$$3HNO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} H^+ + NO_3^- + 2NO + H_2O, \qquad K = \frac{[H^+][NO_3^-][NO]^2}{[HNO_2]^3},$$

has been found to diminish with an increase in dilution, reaching a limiting value of 29* or 31† in aqueous solution at 25° C. The kinetic expressions for the direct and reverse reactions are:

$$-\frac{d[HNO_2]}{dt} = k_1[HNO_2]^4/[NO]^2$$

$$+\frac{d[HNO_2]}{dt} = k_2[HNO_2][H^+][NO_3^-].$$

The ratio (k_1/k_2) of the two velocity constants similarly changes with the dilution, the extrapolated value being about 35.‡

* Abel and Schmid, *Z. physikal. Chem.*, **132**, 56, (1928); **134**, 279, (1928); **136**, 430, (1928).

† G. N. Lewis and Randall, *Thermodynamics*, p. 564, (1923).

‡ Abel, Schmid and Babab, *Z. physikal. Chem.*, **136**, 135, 419, (1928); Abel, Redlich and Lengyel, *ibid.*, **132**, 189, (1928).

Another example is afforded by the work of Roebuck*, Bray,† and Liebhafsky‡ on the following equilibrium:

$$H_3AsO_3+I_3^-+H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} H_3AsO_4+2H^++3I^-.$$

At 0° C., $k_1/k_2 = 0{\cdot}15$, and $K = 0{\cdot}16$. The agreement is as close as the omission of any correction for salt effects will allow. The influence of a varying ionic environment on the equilibrium constant will be discussed in Chapter VII.

Equation (2) is useful in evaluating the rates of reactions which proceed either too slowly or too rapidly, or are in other respects too difficult, to be measured directly. Apparent exceptions to its applicability may be traced to an inaccurate application or to false equilibrium conditions For example, the static analysis of the system

$$\begin{matrix}CH_2Br\\ |\\ CH_2NH_2,\,HBr\end{matrix} +NaOH \rightleftarrows \begin{matrix}CH_2\\ |\quad\diagdown\\ CH_2\quad\diagup\end{matrix}NH,\ HBr+NaBr+H_2O$$

gave an 'equilibrium constant' which could not be reproduced by heating the system and reverting to the original temperature. The disparity between dynamic and static measurements previously believed to exist§ is thus not real.‖

From the ionic product of water at 25° C. we can say that the ions recombine about 4×10^{15} times as fast as the water molecules dissociate, although the absolute speed of either change is not known. Statistical equilibrium is maintained between a small number of hydrogen and hydroxyl ions combining very rapidly and a large number of water molecules dissociating relatively slowly. If we ascribe an average lifetime of about 10^{-13} second to the activated water molecules, it is seen that the rate of combination of the ions is immeasurably rapid. True ionic equilibria are, in fact,

* *J. Physical Chem.*, **6**, 365, (1902).
† *Ibid.*, **9**, 578, (1905). ‡ *Ibid.*, **35**, 1648, (1931).
§ Freundlich and Neumann, *Z. physikal. Chem.*, **87**, 69, (1914).
‖ Freundlich and Kroepelin, *ibid.*, **122**, 39, (1926).

established almost instantaneously. Metallic salts, inorganic acids, and bases, formed by the union of oppositely charged ions, are held together by purely electrostatic forces. As already indicated, no critical energy is required to render these ionic encounters effective, so that the velocity of combination is determined by the speed with which the ions approach one another.

The equilibrium constant K for the system

$$(C_2H_5)_2S+C_2H_5Br \rightleftarrows (C_2H_5)_3SBr$$

in benzyl alcohol solution at 80° C. is $K = [AB]/[A][B] = 1{\cdot}64$ litres per gram molecule.* The unimolecular velocity constant k_1 for the decomposition of triethylsulphonium bromide Corran finds to be $1{\cdot}48\times10^{-5}$ seconds^{-1}, in excellent agreement with von Halban's value of $1{\cdot}50\times10^{-5}$.† It follows that the bimolecular constant k_2 for the combination reaction is $2{\cdot}44\times10^{-5}$ litres/gram molecule-second.‡

The Relation between Critical Increments and Heat of Reaction.

The van 't Hoff isochore expresses the variation with temperature of the equilibrium constant as a function of the decrease $(+U)$ in the total internal energy of the system:

$$\frac{d\ln K}{dT} = -\frac{U}{RT^2}. \qquad (3)$$

The range of temperature to which the investigation of equilibria in solution has hitherto been confined is sufficiently limited to allow us to regard U as being sensibly constant, and equal to the heat (Q) absorbed by the reaction at constant volume, hence,

$$\ln K = \text{const.} - \frac{Q}{RT}.$$

* Corran, *Trans. Faraday Soc.*, **23**, 605, (1927).

† *Z. physikal. Chem.*, **67**, 129, (1909).

‡ I have here corrected an error which appeared in my previous calculations (*Chemical Reviews*, **10**, 241, (1932)).

Let us call the constant $\ln W$, so that

$$K = We^{-Q/RT}. \tag{4}$$

By means of equation (2) we may write

$$K = \frac{k_1}{k_2} = \frac{Z_1 e^{-E_1/RT}}{Z_2 e^{-E_2/RT}} = \frac{Z_1}{Z_2} e^{-(E_1-E_2)/RT},$$

whence it follows that

$$Q = E_1 - E_2 \tag{5}$$

and

$$W = \frac{Z_1}{Z_2}. \tag{6}$$

We will deal in the first place with equation (5), which simply states that the heat of reaction is the difference between the Arrhenius critical increments (not necessarily the energies of activation) of the two opposing reactions. The relation has received inadequate verification.* The nearest approach to a fair test which appears available refers to the equilibrium between ammonium cyanate and urea in aqueous solution. We have seen that Walker and Hambly's value for the critical increment of the reaction $NH_4CNO \rightarrow (NH_2)_2CO$ is 23,200 calories.† The heat absorbed during this change, as measured calorimetrically‡ is 7,500 calories, leading us to expect for the reverse reaction a critical increment of 30,700 calories. From Burrow's and Fawsitt's velocity constants§ for the decomposition of urea

* Hermans (*Z. physikal. Chem.*, **113**, 337, (1924)) has examined the equilibria in acetone-water mixtures of certain diols and acetone on the one hand and the corresponding condensation products and water on the other hand. It would appear at first that the results corroborate completely the conditions predicted by equation (5), for the tabulated values of $(E_2 - E_1)$ are in excellent agreement with the values of Q determined from the variation of K with temperature. On closer inspection, however, it will be appreciated that this is but an arithmetical necessity consequent upon the form of the velocity constant expressions employed. Both reactions are catalysed pseudo-unimolecular changes, the observed unimolecular constant being the sum $(k_1 + k_2)$ of the velocity coefficients for the direct and reverse reactions. To evaluate these separately, it becomes necessary to assume that $K = k_1/k_2$. The introduction of this assumption ensures that $Q = E_1 - E_2$ in the final result.

† *Trans. Chem. Soc.*, **67**, 746, (1895).

‡ Walker, *Z. physikal. Chem.*, **42**, 207, (1902).

§ *Trans. Chem. Soc.*, **105**, 609, (1914).

at 61·1°, 71·3°, and 98·2° C., the observed critical increment is found to be 31,300 calories. Unfortunately, however, this figure refers to aqueous solutions containing 0·1 gram molecule of hydrochloric acid per litre, which detracts somewhat from the value of an otherwise satisfactory agreement. The reaction is definitely not a case of catalysis, for the rate is little affected by the addition of the acid. Moreover, the authors give very good reasons for believing that the chemical change the rate of which is measured is simply the conversion of urea into ammonium cyanate. The function of the acid is to decompose this salt by rapid hydrolysis into ammonia and carbon dioxide.

When a reaction proceeds without any heat effect ($Q = 0$), it is seen from equation (5) that the critical increments of the two opposing reactions must be equal. Highly symmetrical equilibria conform to this requirement, and the relative rates of the two reactions are found to be independent of temperature. The equilibrium between α-glucose and β-glucose in aqueous solution furnishes an example (p. 45).

When the critical increment of one of the opposing reactions is zero, as we assume it to be in the combination of hydrogen ion and hydroxyl ion, the observed heat of reaction is clearly equal to the critical increment of the second reaction. E for the following reaction

$$2H_2O \rightarrow H_3O^{+} + OH^{-}$$

is thus 13,650 calories. The reason for describing the change in this manner is to emphasize the permanent hydration of hydrogen ion in aqueous solution.

The Integration Constant of the van 't Hoff Isochore.

The integration of equation (3) in the simplified form of equation (4) is justified only as an approximation within the very narrow experimental conditions stipulated above. Nevertheless, for our purposes the expression is sufficiently accurate and will henceforth be used as the most convenient formulation of this law. In order to understand the

significance of the term W, it will be necessary to give a brief description of the thermodynamic method employed for the precise integration of the van 't Hoff isochore. This comprises the major portion of the Nernst heat theorem, which finally leads to the expression

$$\ln K = -\left\{\frac{\alpha}{R}\ln T+\frac{\beta}{R}T+\frac{\gamma}{2R}T^2+\ldots-\sum \nu i\right\}-\frac{U_0}{RT}, \qquad (7)$$

in which

U_0 is the heat evolved by the reaction at absolute zero,

α represents the difference between the molecular heats of the resultants and the reactants,

$\beta, \gamma, \ldots$ are the temperature coefficients of this quantity, and

$\sum \nu i$ is the algebraic sum of the integration constants determined from the Clapeyron equation for the variation with temperature of the vapour pressure of each component in the pure phase.

An idea of the magnitudes involved may best be gained by reference to gaseous systems, for which accurate information is available. Bodenstein's expression* for the equilibrium between bromine molecules and bromine atoms ($Br_2 \rightleftarrows 2Br$), obtained from measurements made at temperatures between 800° and 1200° absolute, and given here in terms of concentrations, takes the form

$$\log K = \{0{\cdot}75 \log T+4{\cdot}09\times10^{-4}T+4{\cdot}726\times10^{-8}T^2-0{\cdot}538\}-\frac{10{,}100}{T}.$$

It will be noted that the coefficients β and γ are very small, so that at the low temperatures with which we are concerned these may be completely ignored. Comparison of equations (4) and (7) reveal that the term W is primarily a function of α and $\sum \nu i$, and will thus have a magnitude dependent upon the differences between the specific heats and the chemical constants of the resultants and the reactants. For symmetri-

* *Z. Elektrochem.*, **22**, 327, (1916).

cal equilibria, where there is much similarity in the chemical constitution of the reacting molecules, the quantity $\ln W$ must approximate to zero, W itself being of the order of magnitude unity.

It happens that the simplified equation $K = We^{-E/RT}$ summarizes with quite fair accuracy the data obtained for numerous equilibria even in gaseous systems, although, of course, for all purposes other than the one we have in view the more precise expression is in every way superior. A few figures are quoted in Table 1. The magnitude of the

Table 1

Reference	Equilibrium	K	W	Q
(1)	$H_2 \rightleftharpoons 2H$	$[H]^2/[H_2]$	$1{\cdot}175 \times 10^2$	84,570
(2)	$Cl_2 \rightleftharpoons 2Cl$	$[Cl]^2/[Cl_2]$	$4{\cdot}90 \times 10^3$	57,500
(3)	$Br_2 \rightleftharpoons 2Br$	$[Br]^2/[Br_2]$	$2{\cdot}78 \times 10^3$	46,100
(4)	$I_2 \rightleftharpoons 2I$	$[I]^2/[I_2]$	$1{\cdot}13 \times 10^3$	33,900
(5)	$N_2+O_2 \rightleftharpoons 2NO$	$[NO]^2/[N_2][O_2]$	$4{\cdot}27 \times 10^1$	43,100
(6)	$2NO_2 \rightleftharpoons 2NO+O_2$	$[NO]^2[O_2]/[NO_2]^2$	$4{\cdot}54 \times 10^6$	29,200
(7)	$SbCl_5 \rightleftharpoons SbCl_3+Cl_2$	$[SbCl_3][Cl_2]/[SbCl_5]$	$1{\cdot}89 \times 10^5$	16,320
(8)	$2HI \rightleftharpoons H_2+I_2$	$[H_2][I_2]/[HI]^2$	0·18	2,940

(1) Langmuir, *J. Amer. Chem. Soc.*, **37**, 417, (1915); see also Lewis, *Trans. Chem. Soc.*, **113**, 471, (1918).
(2) Wohl and Kadow, *Z. physikal. Chem.*, **118**, 460, (1925).
(3) Bodenstein, *Z. Elektrochem.*, **22**, 327, (1916).
(4) Bodenstein and Stark, *ibid.*, **16**, 961, (1910).
(5) Briner, Bauer, and Rothen, *J. Chim. Phys.*, **23**, 788, (1926); *Helv. Chim. Acta*, **9**, 634, (1926); *Tables Annuelles*, **7**, 1244, (1930).
(6) Raschig and Prahl, *Z. angew. Chem.*, **42**, 253, (1929).
(7) Braune and Tiedje, *Z. anorg. Chem.*, **152**, 39, (1926).
(8) Bodenstein, *Z. physikal. Chem.*, **29**, 295, (1899); Stegmüller, *Z. Elektrochem.*, **16**, 85, (1910).

term W is evidently capable of variation within very wide limits. The thermodynamic reason for this has already been discussed. We must now seek the kinetic interpretation.

Consider two reversible bimolecular reactions, the velocity of each being given by the equation of Lewis. Since the collision frequencies Z_1 and Z_2 must be of the same order of magnitude, W cannot be very different from unity. These

conditions are fulfilled by the equilibrium between hydrogen iodide, iodine, and hydrogen. From the thermal data given here, W is 5·5, the difference between this and the value of nearly one found from Bodenstein's kinetic results* being due to experimental uncertainty. Consider in the second place an equilibrium reached by a bimolecular process on the one hand and a termolecular process on the other. W now gives the relative probability of successful binary and ternary collisions, and must be of considerable magnitude. This is borne out by the equilibrium data for the system $2NO_2 \rightleftarrows 2NO+O_2$, although complications are known to exist. Let us now assume that the dissociation of the halogens takes place bimolecularly, the recombination of the atoms occurring by ternary collisions involving two atoms and one molecule: $X_2+X_2 \rightleftarrows 2X+X_2$. If this is the true mechanism, the results given in Table 1 enable us to say that the ratio of binary to ternary collisions in these systems is approximately 1,000: 1, which is very similar to Bodenstein's estimate based on a comparison of the mean free path with the molecular diameter. As we are here dealing mainly with the information afforded by thermodynamics concerning the comparative probability of reverse transformations, we have been content with very approximate calculations of both binary and ternary collision frequencies, and have ignored the fact that the former increases slightly while the latter possibly decreases slightly with a rise in temperature.

To return to the kinetics of reactions in solution, it may be stated that there is in general a great similarity in the magnitude of the term W for equilibria in gaseous systems and in dilute solutions although the heat effects observed in solution are naturally small in comparison with those found for atomic processes in gases. In a few simple equilibria, W approximates to unity; for example, K for the polymerization of 9-brom-10-phenanthroxyl in chloroform

* *Z. physikal. Chem.*, **29**, 295, (1899).

solution is $1{\cdot}08\times e^{+885/RT}$.* The constant $[I_2][I^-]/[I_3^-]$ has the value $2{\cdot}746\times e^{-4,470/RT}$, calculated from the electrometric data obtained between 15° and 60° C. by Jones and Kaplan.† The corresponding expression for the equilibrium between bromide ion, bromine, and tribromide ion is $0{\cdot}838\times e^{-1,563/RT}$.‡ Table 2 contains Edgar and Shiver's data§ for the equilibrium in aqueous solution between creatine and creatinine: $K = [\text{creatinine}]/[\text{creatine}]$.



Table 2

$t°$ C.	K (observed)	K (calculated)
25	0·54	0·54
50	1·02	1·02
75	1·60	1·59
100	2·83	2·89

Since the total concentration was 0·01 gram molecule per litre the concentration of water is regarded as constant. The calculated values of K are those given by the equation $K = 2{\cdot}32\times10^3\times e^{-4,944/RT}$.

Only in connexion with one class of equilibria has there been found an inordinately high value for the term W. These refer to the formation of quaternary ammonium salts by combination of amines with alkyl or aryl halides. With dimethylaniline and methyl iodide, for example, in nitrobenzene solution, we have $K = [A][B]/[AB] = 1{\cdot}12\times10^8\times e^{-15,000/RT}$.‖ From kinetic data the critical increment for the bimolecular reaction is 13,020, hence E for the decomposition reaction should be about 28,000 calories. Values lying close to this have in fact been found, though not for this particular

* Goldschmidt, Vogt, and Bredig, *Annalen*, **445**, 123, (1925).
† *J. Amer. Chem. Soc.*, **50**, 1845, (1928).
‡ Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, **28**, 101, (1932).
§ *J. Amer. Chem. Soc.*, **47**, 1179, (1925).
‖ Essex and Gelormini, *ibid.*, **48**, 882, (1920).

reaction, for a number of similar ones.* The abnormal slowness of the combination process has, therefore, not lessened the coherence between the kinetic and the thermodynamic measurements.

Reaction Velocity and Solubility.

The dissolution of a gas, a liquid, or a solid in a solvent is generally associated with energy changes, which may or may not modify the critical energy required by the solute molecules to decompose in their new surroundings. Solids and liquids vaporize into an indifferent gas in accordance with their vapour pressure, but when the pressure of the inert gas is increased to values in the neighbourhood of 100 atmospheres, specific solvent action appears.† At the enormous internal pressures which characterize the liquid state, the effect becomes much more marked, so that even when an inert gas like carbon dioxide dissolves in an inert solvent like carbon tetrachloride powerful attractive forces come into play between solute and solvent molecules, as indicated by the quite considerable heat evolved. In this particular example q is 2,150 calories.‡ Since only minute volume changes accompany the solution of small amounts of solids and liquids, the amount of external work done may be ignored, but varied and complicated changes in the internal energy may set in, possibly associated with material changes such as polymerization, ionization, and solvation. The final solubility is the resultant of all these effects. The question with which we are concerned is how far these influences may be said, on experimental grounds, to govern or alter the rate of reaction in solution.

As a starting-point, we may cite certain thermodynamical considerations advanced by van 't Hoff§ and tested experi-

* von Halban, *Berichte*, **41**, 2417, (1908); Wedekind and Paschke, *Z. physikal. Chem.*, **82**, 314, (1913).

† Nernst, *Theoretical Chemistry*, p. 565, (1923).

‡ Just, *Z. physikal. Chem.*, **37**, 354, (1901).

§ *Lectures on Theoretical and Physical Chemistry*, **1**, 221, (1898).

mentally by Dimroth.* If the equilibrium $A \rightleftarrows B$ be established in the gaseous phase above a given solvent wherein both gases are soluble, we have for the constant relating to the gaseous reaction $K = p_B/p_A$, where p denotes the partial pressure, and is, of course, proportional to the concentration in the gas phase. Henry's law connects this gaseous concentration (p) with the concentration (c) in solution by the relation $p = c/s$, in which s is the solubility of the gas in the solvent, and is usually expressed as the volume of gas dissolved by unit volume of solvent. This experimental equation has clearly a limited range of applicability, for the amount of gas absorbed will increase neither linearly nor indefinitely with increase in pressure of the supernatant gas. For fairly low pressures and solubilities the relation holds, hence

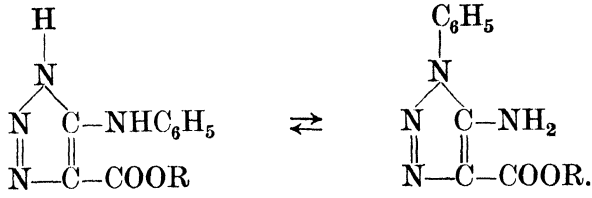
$$K = \frac{c_B/s_B}{c_A/s_A} = K_s\left(\frac{s_A}{s_B}\right). \qquad (8)$$

If, therefore, the concentrations of the solutes in any solvent be expressed as fractions of their solubilities, the resulting equilibrium constant should be independent of the solvent, and numerically equal to the constant for the gaseous reaction. The argument holds for a liquid or solid solute. By measuring the equilibrium concentrations and the solubilities of the isomeric forms of the methyl and ethyl esters of 1-phenyl-5-aminotriazole carboxylic acid in various solvents, Dimroth found K to be sensibly independent of the solvent (Table 3).

Table 3

	Methyl ester			Ethyl ester		
Solvent	c_B/c_A	s_B/s_A	$\frac{c_B/s_B}{c_A/s_A}$	c_B/c_A	s_B/s_A	$\frac{c_B/s_B}{c_A/s_A}$
$(C_2H_5)_2O$	21·7	53·0	0·40	20·7	8·4	2·4
C_2H_5OH	2·3	7·0	0·33	4·56	2·1	2·3
$C_6H_5CH_3$	1·8	4·3	0·33	1·53	0·74	2·1
C_6H_6	1·02	3·2	0·32	1·20	0·60	2·4
$C_6H_5NO_2$	0·80	2·2	0·36	0·85	0·33	2·6
$CHCl_3$	0·32	1·1	0·32	0·32	0·19	1·7

* *Annalen*, **377**, 127, (1910).



The van 't Hoff-Dimroth relation has been shown to hold also for the equilibria between the tautomeric forms of benzoyl camphor* and of ethyl acetoacetate.† It is no doubt universally true.‡ The relative velocities of the two opposing reactions for either of the equilibria in Table 3 varies about sixtyfold when ordinary concentrations are employed. A value of K much nearer unity results with the use of the corrected concentrations. This in itself strengthens the case, for we have seen that the ratio of the velocity coefficients for opposing isomeric changes must usually be of this order of magnitude.

At this stage it will be well briefly to enumerate the factors which govern the solubility of solids in liquids. Saturation may be envisaged as the attainment of equilibrium between the vapour pressure (p) of the solid solute and the partial pressure of the dissolved solute. When p is linearly related to the concentration of the solute, the solution may be regarded as normal; the absolute value of the solubility may be calculated directly from the molecular heat of fusion, the temperature of the system, and the melting-point of the solute.§ This value should be independent of the solvent,

* Dimroth and Mason, *Annalen*, **399**, 91, (1913).

† Meyer, *ibid.*, **380**, 231, (1911).

‡ Meyer (*Berichte*, **47**, 826, (1914)) discovered quite empirically that when two different tautomeric equilibria are established in a series of solvents, the ratio of the two K_t values is independent of the solvent.

§ If π is the vapour pressure of the solid solute, and p that of the supercooled solute at temperature T, the equilibrium constant for the system is π/p. This quantity decreases exponentially with a rise in temperature and with the heat of fusion (q) until at the melting-point (T_0) it becomes equal to unity, so that $-q = \frac{RTT_0}{T_0-T} \ln \frac{\pi}{p}$. (Hildebrand, *Solubility*, p. 35, (1924); Sidgwick, *The Electronic Theory of Valency*, p. 139, (1927).)

and is found experimentally to be so when both solute and solvent are non-polar (e.g. naphthalene dissolved in benzene). Considering the interconversion of two solutes in any solvent behaving in this ideal manner, s_A/s_B will clearly have a value which is independent of the medium, so that the equilibrium constant K_s in all solvents will be the same. In the particular case where both solutes possess the same solubility, and only in this case, the equilibrium constant measured in solution will be identical with K for the gaseous reaction. The natural or 'ideal' solubility is thus seen to be a property of the solute only. When the experimental solubility differs from this, specific solvent effects become observable, and the actual solubility depends on both solute and solvent. The abnormality may be detected by noting that the partial vapour pressure of the solute is no longer linearly related to its concentration. Low solubilities are attributed to a large difference in the internal pressures of solute and solvent. Abnormally high solubilities, on the other hand, can only be explained in terms of some kind of combination between the two components. This conclusion is one of great importance, and has been reached without reference to the study of chemical kinetics.

If the term K_s is replaced by k_A/k_B, equation (8) becomes

$$K = \frac{k_A s_A}{k_B s_B}. \tag{9}$$

Since K is a function of the reaction only, it is of interest to inquire whether the terms $(k_A s_A)$ and $(k_B s_B)$ separately may also be independent of the medium. There is no thermodynamic reason why this should be so, but Dimroth* found that the velocity of conversion of the enol form of the ethyl ester of 1-phenyl-5-hydroxytriazole carboxylic acid into the keto form is in fact nearly inversely proportional to the solubility of the enol in a number of solvents. To a certain extent, however, the agreement suggested by the figures in

* *Loc. cit.*

column 4 (Table 4) is illusory. In order that k_A may preserve its dimensions (t^{-1}) as a unimolecular constant, it is

Table 4

Solvent	k_A at 10° C. (minutes^{-1})	s_A at 10° C. (grams/litre)	$k_A s_A$	$k_A s_A$ (s_A in molar fractions)
CH_3OH	0·00053	218	0·116	4·67
C_2H_5OH	0·00103	97·7	0·101	5·85
$C_6H_5CH_2OH$	0·00110	90·0	0·099	9·12
$(CH_3)_2CO$	0·00527	56·5	0·298	21·7
$CHCl_3$	0·0211	8·8	0·186	14·8
$CH_3COOC_2H_5$	0·0267	12·0	0·320	32·7
$C_6H_5NO_2$	0·0460	6·5	0·299	31·3
$C_2H_5NO_3$	0·0550	3·2	0·176	14·4

necessary to express the solubility as a molar fraction, i.e. as the number of molecules of solute divided by the total number of molecules of solute and solvent. Dimroth's data have accordingly been corrected, although only in an approximate manner, by multiplying $k_A s_A$ by the molecular volume of the pure solvents. This has the effect of diminishing an already rather doubtful regularity. The position may therefore be summed up by stating that the velocity coefficient (k_A) measured in the usual way varies about one-hundredfold in the different solvents, but when the solubility correction is introduced the factor reduces to 7. Closer harmony can hardly be expected when it is recalled that a variation in the solubility of the reactant exerts a possible but by no means an exclusive influence on the rate of reaction. The velocity of the reverse process should show a similar behaviour, but Dimroth's work does not bear this out.

An interesting example of the effect of solubility in the case of two similar, catalysed reactions has been studied by Escolme and Lewis.* In aqueous hydrochloric acid solution, acetyl glycine is hydrolysed more rapidly than benzoyl glycine, k_a/k_b being about 15 and independent of temperature. We should expect the relative solubilities s_b/s_a to

* *Trans. Faraday Soc.*, **23**, 651, (1927).

approximate to this figure if ks has a constant value. Actually, at 25° C. the value is 0·074. This very marked deviation indicates the presence of factors other than solubility, and acting in the opposite way.

If $k_A s_A$ were found to be independent of the medium $(E_{\text{obs}}+q_s)$ should also have a value characteristic of the reaction only, where q_s is the molecular heat absorbed during dissolution. Freundlich and Richards' results* on the velocity of cyclization of ε-chloramylamine into piperidine hydrochloride indicate that this condition is approximately fulfilled. In aqueous solution $E_{\text{obs}} = 20{,}670$ calories and $q_s = 450$; hence $E = 21{,}120$. The corresponding values in tetrachlorethane as solvent are 14,420 and 5,200, giving $E = 19{,}620$. The organic solvent was not dry, so that the latter figure is probably too low. Within the limits of error the sum of the observed critical increment and the heat of solution is independent of the solvent. Further instances of this kind of behaviour, were they to be found, might reasonably be interpreted in the light of the suggestion made by G. N. Lewis regarding the critical increment as an upper limit to the total internal energy of the reacting molecules.

It has been suggested† that the stability of activated intermediate complexes in solution is connected with the solubility. The complex can break up giving the original reactant molecule or it can decompose yielding a molecule of resultant. Soper supposes that the chance of either process taking place depends on the solubility of the molecule that is produced. Considering two opposing unimolecular reactions, and ignoring the possibility of deactivations, we have $k_A \propto \frac{s_B}{s_A+s_B}$ and $k_B \propto \frac{s_A}{s_A+s_B}$, so that $\frac{k_A s_A}{k_B s_B}$ is constant. The assumption is thus equivalent to van 't Hoff's equation (9).

* *Z. physikal. Chem.*, **79**, 681, (1912).

† Soper, *Discussion on the Critical Increment of Homogeneous Reactions*, published by the Chemical Society, p. 45, (1932).

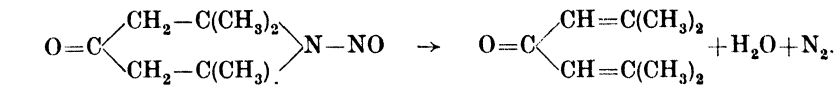
Reaction Velocity and Thermodynamic Activity.

Although not thermodynamically necessary or experimentally secure, let it be supposed that the van 't Hoff-Dimroth equation (9) can be resolved into two terms, each of which is independent of the solvent. If this were so, the velocity constant, expressed not in terms of ordinary concentrations $\left(-\frac{dc}{dt} = k'c\right)$ but in terms of concentrations referred to the solubility as a standard $\left(-\frac{dc}{dt} = k\frac{c}{s}\right)$, would be independent of the solvent, since $k = k's$. Now the thermodynamic activity of a compound is the product of its concentration and its activity coefficient, $a = cf$. In any saturated solution of a given solute its activity must be constant; the activity coefficient is therefore inversely proportional to the saturation concentration: $f \propto \frac{1}{s}$. The assumption is accordingly equivalent to the statement that the velocity of reaction of any solute is governed by its thermodynamic activity. It has been asserted* that this must be so, at least for catalysed reactions in the neighbourhood of the equilibrium point. The introduction of this idea into the study of the kinetics of reactions in solution has, in fact, removed many of the difficulties resulting from the use of uncorrected concentration terms and has revealed certain regularities even in very complicated systems. As will be shown later, the concept can conveniently be embodied into the scheme of things without violating the fundamental idea that the rate of catalysed reactions depends essentially on encounters between substrate and catalyst molecules. We may consider as an example the decomposition of nitrosotriacetonamine, which has been the subject of many investigations, notably by Francis,†

* G. N. Lewis and Randall, *Thermodynamics*, pp. 281, 319, 369, (1923).

† *Trans. Chem. Soc.*, **101**, 2358, (1912); **103**, 1727, (1913); **107**, 1651, (1915).

Brönsted and King,* Kilpatrick,† Colvin,‡ and Goodall and Lewis.§



The decomposition is unimolecular with respect to the amine, and may be followed conveniently by measuring the volume of nitrogen evolved. In the presence of dilute alkali the velocity constant is proportional to the concentration of hydroxyl ion (Francis) and its variation with a change in the reaction medium becomes readily intelligible in terms of the activity theory (Colvin). Successive additions of alkali beyond a concentration of 0·5 molar causes the velocity constant to fall; in the region of high concentrations of alkali the velocity constant is directly proportional to the activity of hydrogen ion. Upon the basis of this observation Goodall and Lewis propose the following mechanism for this instance of hydrogen ion catalysis. The rate of decomposition of nitrosotriacetonamine is assumed to be proportional to the activities of the amine and the hydrogen ions; $-\frac{dc_N}{dt} = ka_N a_{H^+}$. The observed rate is $-\frac{dc_N}{dt} = k_{obs} c_N$, hence $k = k_{obs} \frac{c_N}{a_N a_{H^+}} = k_{obs}/f_N a_{H^+}$. The observed unimolecular constants obtained by Francis bear a constant relation to the product of the activity coefficient of the amine, determined from solubility measurements, and the activity of hydrogen ion, measured electrometrically by Goodall and Lewis, whose table is included below.

The hydrolysis of disaccharides and the condensation of monosaccharides are similarly catalysed by hydrogen ion. The unimolecular constant in each case is proportional to the concentration of the catalysing acid, if this is present in very small amounts. In more concentrated solutions,

* *J. Amer. Chem. Soc.*, **47**, 2523, (1925).
† *Ibid.*, **48**, 2091, (1926). ‡ *Trans. Faraday Soc.*, **22**, 241, (1926).
§ *Z. physikal. Chem.*, **137**, 45, (1928).

Table 5

[KOH]	$10^2 \times k_{obs}$ at 30° C. (minutes^{-1})	$a_{H+} \times 10^{14}$ at 25° C.	f_N	$\frac{k_{obs}}{a_{H+} f_N} \times 10^{-12}$
0·492	9·60	2·37	1·144	3·55
0·588	8·48	2·04	1·161	3·58
0·626	8·05	1·91	1·168	3·62
0·784	6·43	1·48	1·195	3·64
0·815	6·15	1·41	1·200	3·63
0·985	4·80	1·10	1·299	3·56
1·048	4·375	0·997	1·238	3·62
1·176	3·625	0·813	1·257	3·55
1·287	3·175	0·708	1·274	3·52
1·379	2·830	0·661	1·282	3·38

however, k_{obs} becomes closely parallel with the activity of the hydrogen ion as the results given in Table 6 show.*

Table 6

Composition of solution (grams per 100 c.c.)	$k_{obs} \times 10^6$ (seconds^{-1})	a_{H+}	$\frac{k_{obs}}{a_{H+}} \times 10^6$
5 sucrose (at 25° C.)	13·0	0·088	148
5 sucrose + 12·6 glycerol	14·5	0·098	148
5 sucrose + 31·5 glycerol	16·7	0·116	144
10 maltose (at 60° C.)	16·3	0·954	17·1
10 maltose + 10 glucose	18·3	1·091	16·8
10 maltose + 20 glucose	21·6	1·254	17·2
10 maltose + 30 glucose	25·3	1·431	17·7
10 glucose (at 60° C.)	4·20	0·97	4·23
20 glucose	4·76	1·11	4·29
30 glucose	5·51	1·27	4·34
40 glucose	6·39	1·46	4·38
50 glucose	7·66	1·67	4·58

Numerous other instances might be quoted illustrating the method of testing the activity theory of catalysis. The volume concentration of the catalyst is maintained at a constant value (in the present examples hydrochloric acid at concentrations of 0·1 and 1·0 molar were employed), while the activity of the catalyst is varied by the successive additions of an inert substance. As a rule, although not in all cases, the quantity k_{obs}/a_{H+} for any given reaction at

* Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 81, (1929).

a fixed temperature is found to be independent of the nature of the medium within fairly wide ranges of composition. It is always much less sensitive to environmental changes than is the term k_{obs}/c_{H^+}.

Parallelisms of this kind,* however, do not imply that the activity of the catalyst replaces its concentration as the factor *directly* responsible for the instantaneous rate of reaction, dc/dt. Consider the simple reaction $A \rightarrow B$ to be catalysed by C and to proceed in the following stages: $A+C \rightleftarrows AC$; $AC \rightarrow B+C$. The first stage is assumed to be reached very rapidly, the equilibrium conditions being given by

$$K = \frac{a_{AC}}{a_A \times a_C} = \frac{c_{AC}}{c_A \times c_C} \times \frac{f_{AC}}{f_A \times f_C},$$

where a, c, and f represent activities, concentrations, and activity coefficients respectively. The velocity of reaction being governed by the rate of decomposition of the complex, we have $+\frac{dc_B}{dt} = kc_{AC} = kKc_A c_C \frac{f_A f_C}{f_{AC}}$. The experimentally determined velocity constant is $\frac{dc_B}{dt}\frac{1}{c_A}$; hence

$$k_{\text{observed}} = kKc_C \frac{f_A f_C}{f_{AC}}.$$

Even on the assumption, therefore, that the instantaneous velocity is proportional to the *concentration* of the reacting species, the observed velocity coefficient may still be proportional to the activity. Supposing that the activity coefficient (f_{AC}) of the complex remains unaltered, then $k_{obs}/a_C f_A$ must be constant; this appears to be the condition fulfilled in the decomposition of nitrosotriacetonamine in the presence of concentrated alkali. If, in the second place, the ratio f_A/f_{AC} of the activity coefficients of the free and combined substrates does not vary, we should expect the quantity k_{obs}/a_C to be independent of the medium; the

* See also Åkerlöf, *J. Amer. Chem. Soc.*, **51**, 984, (1929); Harned, *ibid.*, **44**, 2193, (1922); Kuhn and Jacob, *Z physikal. Chem.*, **113**, 389, (1924).

hydrolysis of the disaccharides conforms with this requirement.

The intermediate-complex theory has proved to be of great value in the study of enzymic* and ionic† reactions.

The problem which we are here considering may be viewed from another angle, by interrogating how far, in cases of hydrogen ion catalysis for example, we are justified in ignoring all other types of ions and molecules as being without catalytic influence. The necessity felt by Senter, Lapworth, Bredig, Goldschmidt, Acree, and Robertson for ascribing a definite catalytic role to the undissociated acid molecule has given rise to a hypothesis now known as the dual theory of catalysis. Dawson, accepting the view as being in the main true, has extended the original hypothesis, by the analytic treatment of numerous measurements made on certain catalytic processes, to what may conveniently be termed the theory of multiple catalysis. Stated in its simplest form, Dawson's view is that, in any system promoting the velocity of a chemical reaction, each species of molecule and ion present in the system is capable of exerting a specific catalytic influence on the rate of chemical change. For the enolization of acetone at 25° C., it is found that the catalytic coefficients of hydrogen ions, hydroxyl ions, and water molecules are $2{\cdot}85\times10^{-5}$, $4{\cdot}17\times10^{-1}$, and $8{\cdot}33\times10^{-12}$ litres per gram molecule-second respectively.‡ Two aspects of Dawson's work require emphasis at the present juncture. In the first place, there is the very definite conclusion that the catalytic efficiency of the catalyst is often proportional to its concentration, and has no apparent connexion with its thermodynamic activity.§ In the second place, it becomes quite clear that departures from the linear relation between

* Michaelis and Menten, *Biochem. Z.*, **49**, 333, (1913).

† Brönsted, *Z. physikal. Chem.*, **115**, 337, (1925); Bjerrum, *ibid.*, **118**, 251, (1925).

‡ Dawson and Key, *Trans. Chem. Soc.*, 2154, (1928).

§ Dawson and Dean, *ibid.*, 2872, (1926); Dawson and Lowson, *ibid.*, 2146, (1928).

rate of reaction and concentration of reactants can often be completely attributed in a quantitative manner to the influence exerted by the presence of entities other than the catalyst which plays the dominant role.

As already indicated, the two theories in question attempt in different ways to describe the same phenomenon, and there is no real incompatibility between them. According to the theory of multiple catalysis, the observed catalytic effect is considered as due to (1) the part played by the dominant catalyst (say hydrogen ion), and determined by its concentration, plus (2) the part played by all other ions and molecules present in solution. According to the activity theory, the observed rate is determined solely by the activity of the catalyst, e.g. hydrogen ion. This in turn is composite, and entails (1) the concentration of hydrogen ion multiplied by (2) its activity coefficient, which is a function of the solution as a whole, and depends upon the total number of ions of all kinds present, upon their charges, and upon the dielectric properties of the medium. If a hypothetical reaction be considered involving only one type of catalyst, and this at very great dilutions, both theories predict that the rate should be proportional solely to the concentration of hydrogen ion, since factor (2) vanishes in both cases. When greater concentrations of catalyst are employed, with or without the addition of a third body, deviations from the simple behaviour will appear, and k_{observed} will no longer be proportional to [catalyst]. The magnitudes of such deviations are given, according to the activity theory, in terms of the change in the activity coefficient of the catalyst. The theory of multiple catalysis interprets the deviations from normal behaviour in terms of subsidiary catalytic effects. Neither view offers a complete explanation of the facts.

In order to ascertain experimentally whether concentration or activities determine the velocity of reaction, Eyring and Daniels* have measured the rate of decomposition of

* *J. Amer. Chem. Soc.*, **52**, 1472, (1930).

nitrogen pentoxide in the saturated vapour phase and in saturated solutions in two solvents at 15° C. The activity of the reactant is equal in the three systems, so that if this determines the velocity, the instantaneous rate $-dc/dt$, or the number of gram molecules decomposing per second, should be constant. If, on the other hand, the rate of reaction is governed by the concentration, the unimolecular constant should be the same in all cases. Although, as the authors point out, neither view is complete, the weight of evidence lies well over on the side of the concentration hypothesis. As the results in Table 7 show, k varies only

Table 7

	Saturation concentration (gram molecules/litre)	$-\frac{dc}{dt} \times 10^5$	$k\left(=-\frac{dc}{dt}\frac{1}{c}\right) \times 10^5$ (seconds^{-1})
Gas phase	0·0102	0·0080	0·79
Nitromethane	4·38	5·92	1·35
Carbon tetrachloride	4·78	8·75	1·83

about twofold, whereas the instantaneous rate changes over one-thousandfold. The slight difference in k is attributed by Eyring and Daniels to the varying stabilities of the free and solvated nitrogen pentoxide molecules. A fairly small change in the critical increment would likewise completely account for the effect, but E for the reaction in carbon tetrachloride is actually about 800 calories greater than the value for the gaseous reaction, so that one would anticipate the velocity constant to be less in the solvent than in the gas. Quite probably the difference in k is not real. For some unknown reason, the unimolecular constant for the reaction in solution increases very slightly with the initial concentration of nitrogen pentoxide; consequently, in highly attenuated solutions the velocity constant approximates more and more closely to the value characteristic of the gas reaction.

The position may now be described as follows. The study of reactions in solution, including changes undergone by

both ionized and un-ionized molecules, affords evidence for regarding the instantaneous rate of reaction $(-dc/dt)$ as directly dependent upon the concentration of the reactants. If the reactant molecule is engaged in maintaining a state of equilibrium by combination with either the solvent or any other compound, its concentration becomes indissolubly connected with its activity coefficient, which enters into the kinetic scheme solely on account of this circumstance. Accepting this interpretation as correct, we may look upon parallelisms between velocity coefficients and activity coefficients as evidence that the reaction concerned entails the establishment of such equilibria. When the chemical reaction *per se* proceeds to completion, the equilibrium must relate to interaction between reactant and solvent.

A Comparison between Equilibria in the Gaseous Phase and in Solution.

Equation (8) represents the relation between the equilibrium constant K for a gaseous reaction, K_s for the reaction in a given solvent, and the solubilities of the reacting gases in that solvent; $K = K_s(s_A/s_B)$. Differentiating with respect to temperature, and multiplying throughout by RT^2, we have

$$Q = Q_s + (q_A - q_B). \qquad (10)$$

The difference $(Q-Q_s)$ between the heats of reaction in the gas phase and in solution is thus equal to the difference in the molecular heats of solution of reactants and resultants. Consider the dissolution of one gram molecule each of the perfect gases A and B in an ideal solvent wherein they are but slightly soluble and with which they do not react.* If Raoult's law is obeyed, i.e. if the partial vapour pressure of the gas in contact with the solution is proportional to its molar fraction in the liquid phase, the solution is an ideal

* For example, the dissolution of the rare gases in non-aqueous solvents (Tammann, *Z. anorg. Chem.*, **194**, 159, (1930)).

one and the heat of solution becomes equal to the molecular heat of vaporization. The solubility of methane in hexane and in xylene conforms with this requirement. Now it is well known that the latent heat of vaporization for a number of gases, such as nitrogen, oxygen, and air, has a value of about 1,500 calories, while the latent heat of vaporization for compounds with much higher boiling-points, such as ethers, esters, carbon tetrachloride, and chloroform, is usually about 6,500 calories (Trouton's law). The important point to observe is that the difference between λ_m, and consequently between q, for any two substances belonging to either category cannot have a large value. In such ideal cases, the heat of reaction must be very nearly the same in the gaseous phase as in solution. Conversely, when there appears a genuine difference between Q and Q_s, at least one of the solutes will possess an abnormal solubility. We have seen that the most reasonable explanation of this fact is that at least one of the solutes enters into combination with the solvent.

(i) *The Dissociation of Nitrogen Tetroxide*: $N_2O_4 \rightleftarrows 2NO_2$. From Natanson's vapour density measurements at 0° C., it is found that the equilibrium constant for the gaseous dissociation is $K = [NO_2]^2/[N_2O_4] = 7{\cdot}40 \times 10^{-4}$ gram molecules per litre.* The colorimetric data of Cundall† yield, for the corresponding constant in chloroform solution, $K = 5{\cdot}70 \times 10^{-6}$. In this solvent, therefore, K is about 130 times as small as it is in the gas phase—a difference the significance of which was realized by Ostwald.‡ The relative velocities of the two reactions are thus altered to this extent, but whether the rate of dissociation or of combination or both is affected cannot be decided. The behaviour is in striking contrast with the decomposition of nitrogen pentoxide in these two systems.

* *Ann. Physik*, **27**, 606, (1886).
† *Trans. Chem. Soc.*, **59**, 1076, (1891).
‡ *Ibid.*, **61**, 242, (1892).

Schreiber,* from a review of numerous results, quotes 13,600 calories as the best value for the heat absorbed during the gaseous dissociation at constant pressure between 0° and 100° C. Q is accordingly 13,000 calories, in good agreement with the value calculated by van 't Hoff from specific heat data.† The effect of temperature upon the dissociation equilibrium in various solvents has been extensively examined by Cundall,‡ from whose results the following figures have been calculated.

Table 8

Solvent	$K_{20°C.}$ (gram molecules/litre)	Q_s (calories/gram mol.)
Gas	382	13,000
$SiCl_4$	17·8	20,470
CS_2	13·3	19,400
CCl_4	8·05	18,840
$CHCl_3$	5·53	21,210
C_2H_5Br	4·79	20,490
C_6H_5Br and C_6H_5Cl	3·70	19,350
C_6H_6	2·23	22,180

The colorimetric method of investigation adopted by Cundall must, in the light of manipulative refinements which have subsequently been made possible, be regarded as somewhat crude. Although possibly accurate enough for the comparative purpose to which they are here submitted, a repetition of the work, perhaps by measuring absorption coefficients, is very desirable. Assuming, however, the figures as quoted to be trustworthy, they leave no doubt as to the reality of the solvent effect, for the magnitude of the difference between Q and Q_s is not such as can reasonably be attributed to a difference in the heats of dissolution of the two oxides. We therefore conclude that definite reaction sets in between one of these and the solvent with an approximate heat effect of $(Q_s - Q)$. It would appear that

* *Z. physikal. Chem.*, **24**, 651, (1897).
† *Studies in Chemical Dynamics*, p. 154, (1896).
‡ *Trans. Chem. Soc.*, **67**, 794, (1895).

nitrogen peroxide (NO_2) is responsible for the major part of the heat effect. From a few fragmentary data given by Cundall, it is found that the heats absorbed when one gram molecule of liquid nitrogen tetroxide dissolves in chloroform and in carbon tetrachloride are 413 and 669 calories respectively. These figures lie sufficiently close to the free energy of expansion at 20° C. (which under ideal conditions would be $RT = 580$ calories) to indicate that no heat effect can be detected calorimetrically when nitrogen tetroxide dissolves in these solvents. One point remains to be mentioned. Lewis and Randall* have shown that the equilibrium constant for this dissociation, expressed in terms of molar fractions, is approximately independent of the composition of the solution from 100 per cent. liquid nitrogen tetroxide to nearly 100 per cent. chloroform. The solution is thus nearly perfect. This is difficult to reconcile with the conclusion which we have drawn concerning complex formation. If, however, the solvated molecule, like the free NO_2 molecule, is colourless, Cundall's results at any one temperature would clearly give no clue to its presence. Its existence has here been inferred from the change in the heat of reaction. Complex formation is often so elusive that even its detection is a matter of difficulty.

(ii) *The Dissociation of Ethylene Iodide*:

$$CH_2I.CH_2I \rightleftarrows CH_2:CH_2+I_2.$$

This equilibrium has not been examined very carefully, but since it appears to be the only other case available for comparison the results will be of interest in spite of their approximate character. The constants for the gaseous reaction at temperatures of 11–65° C. have been determined by Mooney and Ludlam.† The total pressure of the system was measured statically, that of ethylene iodide by a streaming method, and that of iodine by difference. Under these conditions the value of K cannot refer to the homo

* *Thermodynamics*, p. 303, (1925). † *Proc. Roy. Soc. Edin.*, **49**, 160, (1929).

geneous equilibria, as is borne out by the discontinuity observed at 40° C. in the curve found by plotting $\ln K$ against $1/T$. Above this temperature the results are considered by the authors to be fairly trustworthy, and from the slope of the curve the heat of dissociation is found to be 22,300 calories. Scanty data for the corresponding equilibrium in carbon tetrachloride solution are also available, Polissar* finding Q to be 11,300 calories in the neighbourhood of 137° C. These figures, despite a not inconsiderable uncertainty, probably represent a genuine difference in the thermal effects for the two systems.

(iii) *Equilibrium in Various Solvents.* Other instances are lacking, but evidence of a similar nature is to be found in the variation of the position of equilibrium and the heat of reaction for a given chemical process in different solvents. From measurements of the extinction coefficient, Goldschmidt and Bader† have determined the degree of polymerization of $\alpha\alpha'$-diphenyl-*p*-benzoyl hydrazyl, and have given values for the constants $[X]^2/[X_2]$ in various solvents at about four temperatures covering a range of 30° C. Their results (Table 9) reveal marked changes in K and Q from

Table 9

Solvent	$K_{-32\cdot4°\,C.} \times 10^5$	Q
$(C_2H_5)_2O$	0·95	9,400
$C_6H_5CH_3$	3·3	10,500
$(CH_3)_2CO$	5·8	6,800
$CHCl_3$	120	5,200

solvent to solvent. We may, perhaps, regard the first two values as approximating to those for the gaseous reaction, whence it appears that chloroform influences this equilibrium to much the same extent as it does the dissociation of nitrogen tetroxide.

For a given reaction in two similarly constituted solvents, K and Q should not exhibit a wide variation. Cundall's results

* *J. Amer. Chem. Soc.*, **52**, 956, (1930). † *Annalen*, **473**, 137, (1929).

(Table 8) confirm this view. So also do the experiments of von Halban* on the combination of allyl bromide and *p*-brom-dimethylaniline in tetrachlorethane and in chloroform solution, for which the heat evolved is 19,090 and 18,940 calories respectively. The heat of dissociation of hexaphenylethane has a fixed value in six somewhat similar solvents.†

Complex Formation and Reaction Velocity.

The foregoing comparison between equilibria in gaseous systems and in solution makes it desirable, if not necessary, to postulate the formation of complexes produced by the union of solute and solvent molecules. It will be recalled that the abnormally high solubility of solids in liquids can be understood best by making a similar supposition. The existence of such molecular compounds, which has long been recognized, is thus found to be a much commoner item in chemistry than had hitherto been supposed. Nitro-compounds are well known for the ease with which they form molecular compounds with hydrocarbons and amines, but even the so-called chemically inert compounds, such as carbon tetrachloride, have lately been shown to be capable of forming complexes with other molecules. By spectrometric analysis, von Halban and Zimpelmann‡ have studied the equilibrium conditions governing the union, in chloroform solution, of picric acid and the dinitrobenzenes on the one hand with naphthalene and anthracene on the other. Concordant equilibrium data for the formation, in the same solvent, of compounds between symmetrical trinitrobenzene and dimethylaniline and dimethyl-*p*-toluidine have been obtained by Ley and Grau§ by photometric, ebullioscopic, and solubility measurements. Wyatt's cryoscopic results‖ demonstrate that chloroform (and occasionally carbon tetrachloride) forms molecular compounds with ethers,

* *Z. physikal. Chem.*, **67**, 129, (1909); **72**, 719, (1911).

† Ziegler and Ewald, *Annalen*, **473**, 163, (1929).

‡ *Z. physikal. Chem.*, **117**, 461, (1925).

§ *Berichte*, **B, 58**, 1765, (1925). ‖ *Trans. Faraday Soc.*, **25**, 43, (1929).

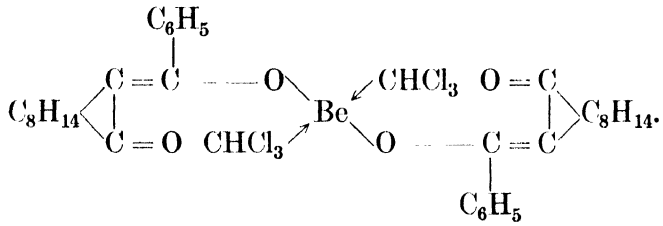
esters, and alcohols. Schulze,* by assuming that the partial pressure of acetone and of chloroform over the liquid solution is proportional to the molar fraction of each, has calculated the equilibrium relations involved at various temperatures in the mixed solvent.

These facts are understood in the light of the electronic theory of valency. The constituents in a molecular compound are held together by a coordinate linkage, wherein previously unshared electrons of one component contribute to the formation of a more complete and stable electronic arrangement in the second component. The oxygen atom in ethers and esters, for example, having two pairs of unshared electrons, is able to donate these (by forming a complex) to an acceptor molecule such as chloroform or carbon tetrachloride, which can accommodate a larger number of electrons than those already present in the outer octet of each chlorine atom. The study of these and of similar electronic rearrangements lies outside the scope of this book, but it is essential to seek the possible bearing of such considerations upon the subject of the kinetics of reactions in solution. In passing, it is to be noted that an etheric oxygen atom is a more powerful donor than a ketonic oxygen atom; chlorine atoms in chloroform are better acceptors than chlorine atoms in carbon tetrachloride.

Direct experimental proof that complexes between solute and solvent play a definite part in determining the rate of reaction is hard to find, although the necessity for postulating such behaviour frequently arises. An interesting example is afforded by the work of Lowry and Traill† on the mutarotation of beryllium benzoylcamphor. Dissolved in carbon tetrachloride or in cyclohexane, the α and β forms have almost the same stability, so that at equilibrium they are present in equal amounts ($K = \frac{c_\alpha}{c_\beta} = \frac{k_\beta}{k_\alpha} = 1$). In chloroform

* *Z. physikal. Chem.*, **93**, 370, (1919).
† *Proc. Roy. Soc.*, **A, 132**, 398, (1931).

solution, the ratio becomes 2 : 3 approximately, indicating, as the authors point out, that this solvent is not only able to combine with the α and β forms of beryllium benzoyl-camphor, but by selective combination with the β form to favour the formation of this variety at the expense of the less soluble α isomeride. The intermediate compound has been isolated by Burgess and Lowry* as a crystalline solvate with two molecules of chloroform; from the value of its optical rotation, the following symmetrical structure has been ascribed to it:



Since the racemization of an optically active compound usually proceeds through the formation of an intermediate compound of higher symmetry, the complex thus formulated provides an ideal mechanism for the reaction. From a knowledge of all the specific rotations involved, Lowry and Traill have shown that 46 per cent. of the α form and 64 per cent. of the β form are combined with the solvent. Experiments prove that these figures account quantitatively for the lessened catalytic activity of pyridine in chloroform, as compared with solutions in carbon tetrachloride, where the whole of the solute is apparently free to interact with the catalyst instead of being bound in part to the solvent. These investigations have accordingly given us a description —possibly as clear and precise as it is possible to expect— of the definite part played by a well-defined intermediate compound in the mechanism of chemical change in solution.

A similar explanation may be accepted for the slightly differing environmental influence exerted by carbon tetra-

* *Trans. Chem. Soc.*, **125**, 2081, (1924).

chloride and chloroform on the reactivity of other solutes. In fact, the intermediate-complex theory has much to commend it as the basis for a general treatment of the kinetics of reactions in solution. It is sufficiently comprehensive to take into account many if not most of the diverse phenomena of solvent and of catalytic action. The energy changes which must be associated with the formation of such complexes offers a ready means of understanding how the solvent, by altering the observed energy of activation, may exert an effect at once profound and specific, causing the experimental rate to exceed the ideal rate when the complex is formed endothermally (as in the experiments of Ley and Grau) or to fall short of the ideal value when the complex is produced with evolution of heat (as in the experiments of Schulze and of von Halban and Zimpelmann). Relatively minor difficulties, such as the apparently erratic catalytic behaviour of nitrobenzene, become intelligible when viewed in this light. The most cogent argument, however, for adopting the hypothesis—which may ultimately prove to be not very different from van 't Hoff's solubility theory—is the fact that the observed variation in the critical increments for reactions in solution is of the same magnitude as the thermal effect which accompanies the production of the complex.

VI

UNIMOLECULAR REACTIONS

THE distinction between unimolecular and bimolecular reactions is one of degree only. 'The essential difference is merely one in the time elapsing between activation and reaction, and therefore in the importance of deactivation of active molecules by subsequent collision before chemical transformation has occurred. In general we may say: rate of activation $= k_1c^2$; rate of deactivation $= k_2ca$, where a is the concentration of active molecules; rate of chemical transformation $= k_3a$. For a stationary concentration of active molecules, $k_1c^2 = k_2ca+k_3a$, whence the rate of reaction is $k_3a = k_1c^2\Big/\left(1+\frac{k_2}{k_3}c\right)$. According as the ratio k_2/k_3 is great or small, the reaction approximates to the classical unimolecular or bimolecular type.'*

By including terms to allow for the influence of the solvent, we may apply similar considerations to reactions in solution. Let

c = concentration of solute,
s = concentration of solvent, and
a = concentration of activated molecules of solute.

Then

rate of activation $= k_1cs+k_2c^2$,
rate of deactivation $= k_3as+k_4ac$, and
rate of chemical reaction $= k_5a$.

The condition for a stationary concentration of active molecules is $k_1cs+k_2c^2 = k_3as+k_4ac+k_5a$. The velocity of chemical change is thus

$$-\frac{dc}{dt} = k_5a = \frac{k_5(k_1cs+k_2c^2)}{k_3s+k_4c+k_5}. \qquad (1)$$

This is the general form of the equation for uncomplicated reactions of the first and second order in solution. Of the five constants which it contains, three are primarily char-

* Hinshelwood, *Annual Reports for* 1931, p. 41, (1932).

acteristic of the reaction itself and two (k_1 and k_3) are functions of the solvent also. The relative magnitudes of these constants determine the order of reaction and the extent of the solvent effect. No reaction has yet been met with in solution which, under varying concentrations, changes gradually from the first to the second order, or vice versa. This is a consequence of the fact that s is always a fixed quantity, and c can vary only within the usually narrow limits imposed by the solubility of the solute.

In a completely inert solvent, active molecules of solute can be neither formed nor destroyed by collisions with solvent molecules (i.e. $k_1 = 0$ and $k_3 = 0$). Under these conditions

$$\text{rate} = \frac{k_5 k_2 c^2}{k_4 c + k_5}. \qquad (2)$$

Two special cases must be discussed. When the chance of an active solute molecule losing its energy by collision with a normal solute molecule is small, the expression reduces to $k_2 c^2$, and the rate is a simple bimolecular one. The decomposition of chlorine monoxide in carbon tetrachloride solution furnishes an example.* When collisions between active and normal solute molecules are highly efficient in the deactivating sense ($k_4 \gg k_5$), the expression becomes $\frac{k_5 k_2}{k_4} c$, and the rate is a simple unimolecular one. The decomposition of nitrogen pentoxide and the isomerization of pinene in carbon tetrachloride solution conform with these conditions.† The experimental observation that the velocities of these reactions are the same in the gaseous phase as in solution in this solvent shows that not only has k_5 remained unchanged, as might be expected, but that the ratio of the constants k_2 and k_4 also is unaffected by the solvent. Both these depend upon collision frequencies, which must therefore be the same in the gas as in carbon tetrachloride solution.

* *Proc. Roy. Soc.*, **A, 131,** 177, (1931).

† Daniels and Johnston, *J. Amer. Chem. Soc.*, **43,** 53, (1921); Lueck, *ibid.*, **44,** 757, (1922); see Chapter III.

Positive and negative catalytic solvents are those in which active molecules of solute may be generated or destroyed by collisions with molecules of the solvent. When solute-solvent collisions predominate over solute-solute collisions (i.e. $k_2 \simeq 0$ and $k_4 \simeq 0$),

$$\text{rate} = \frac{k_5 k_1 cs}{k_3 s + k_5} \tag{3}$$

and the reaction is unimolecular. Two special cases again arise. In the true unimolecular reaction, when the vast majority of active molecules lose their energy before being transformed ($k_3 \gg k_5$), the rate becomes $\frac{k_5 k_1}{k_3} c$. The observed unimolecular constant is thus the product of the true reactivity (k_5) and the ratio of two constants which denote the activating and deactivating efficiency of the solvent. Most complicated molecules undergoing unimolecular change in solution probably do so by this mechanism. The other case is that in which there are no deactivations ($k_3 = 0$): the rate then becomes essentially bimolecular, although unimolecular with respect to the solute:

$$\text{rate} = k_1 cs. \tag{4}$$

Ozone in carbon tetrachloride, carbonyl sulphide in water, and numerous other fairly simple molecules are transformed in this way, each activating collision between a solute molecule and a solvent molecule leading to chemical change. The rate at which any given reaction of this type proceeds as well as the critical increment will vary from solvent to solvent.

Based upon the simple assumption that all the molecular species in a liquid system collide with varying activating and deactivating efficiencies, equation (1) and the simpler equations derived from it are sufficiently elastic to cover a large number of the phenomena of solvent action. By ascribing a relatively long life to a pair of molecules in collision, the scheme can be extended to include complex formation.

The problem thus becomes as interesting from the theoretical aspect as it is difficult from the practical side. Progress in the elucidation of the precise mechanism of unimolecular reactions in solution awaits the appearance of more experimental results characterized by accuracy and variety. The two outstanding facts which may already be regarded as established are: (1) broadly, there exists between unimolecular reactions in the gaseous phase and in solution a marked similarity, which amounts to identity in certain cases; (2) the solvent effect, when it does appear, may be of great magnitude and is always specific with respect to the system.

The Influence of the Solvent.

Table 1 summarizes the results at present available on the influence of the solvent upon the kinetics of unimolecular reactions. Inert solvents have been fully discussed in Chapter III. The most striking results of this table are those referring to the decomposition of trichloracetic acid and trinitrobenzoic acid, for which the critical increment varies by 10,000 calories from one solvent to another. The lesser variations observed by von Halban may now be safely accepted as genuine although small. There are clear indications from the results quoted in the table that solvents of similar chemical nature exert similar effects and that nonpolar solvents allow a faster rate than the polar solvents. It is, however, unwise to base any generalizations upon such limited information.

The investigation of a few of these reactions has been confined to a narrow temperature range, and the solvents used have been of questionable purity. The results given in Table 1 are therefore not of uniform value.

The catalytic properties of some solvents—particularly nitrobenzene—are extremely sensitive to the presence of impurities, the most insidious one being water. The effect of temperature upon the physical properties of this solvent

Table 1

Reference	Reactant	Solvent	E	$\ln Z$
(1)	Nitrogen pentoxide	Gas	24,700	31·45
(2)	,, ,,	CCl_4	25,470	31·61
(2)	,, ,,	$CHCl_3$	24,450	31·22
(3)	,, ,,	N_2O_4	25,000	32·82
(3)	,, ,,	CH_3CHCl_2	24,900	32·56
(3)	,, ,,	$C_2H_4Cl_2$	24,400	31·42
(3)	,, ,,	C_2HCl_5	25,000	32·35
(3)	,, ,,	Br_2	24,000	30·61
(3)	,, ,,	CH_3NO_2	24,500	31·13
(3)	,, ,,	HNO_3	28,300	34·11
(3)	,, ,,	$C_3H_6Cl_2$	28,300	35·72
(4)	Camphorcarboxylic acid	$C_6H_5COCH_3$	28,960	30·56
(4)	,, ,,	H_2O	29,640	30·02
(4)	,, ,,	C_6H_6	27,800	28·88
(5)	Triethylsulphonium bromide	$C_5H_{11}OH$	33,140	37·84
(5)	,, ,,	C_3H_7OH	33,120	36·87
(5)	,, ,,	$C_6H_5CH_2OH$	32,180	34·70
(5)	,, ,,	CH_3COOH	31,060	33·01
(5)	,, ,,	$CHCl_3$	33,010	41·57
(5)	,, ,,	$C_2H_2Cl_4$	30,350	37·70
(6)	,, ,,	$C_2H_2Cl_4$	30,410	37·87
(5)	,, ,,	$C_6H_5NO_2$	28,290	34·44
(6)	,, ,,	$C_6H_5NO_2$	28,870	35·14
		$\begin{cases} C_6H_5CH_2OH \\ +x \text{ per cent.} \\ C_6H_5CH_3 \end{cases}$		
		x		
(7)	,, ,,	0	35,900	40·23
(7)	,, ,,	25	34,800	39·41
(7)	,, ,,	50	33,100	37·86
(7)	,, ,,	75	32,700	38·56
(8)	Benzylhydroxytriazole-carboxylic acid ester	$CHCl_3$	36,270	48·77
(8)	,, ,,	C_2H_5OH	30,670	36·09
(8)	,, ,,	$(CH_3)_2CO$	29,000	35·46
(8)	,, ,,	CH_3OH	26,530	29·16
(9)	Acetonedicarboxylic acid	C_2H_5OH	26,600	37·54
(9)	,, ,,	C_3H_7OH	25,800	37·26
(9)	,, ,,	C_4H_9OH	23,200	32·25
(9)	,, ,,	*iso*C_3H_7OH	22,200	30·83
(9)	,, ,,	*iso*$C_5H_{11}OH$	22,100	30·63
(9)	,, ,,	*iso*C_4H_9OH	21,500	29·63
(9)	,, ,,	HOH	23,200	32·29

Reference	Reactant	Solvent	E	$\ln Z$
(10)	Benzenediazonium chloride	HOH	27,030	36·01
(11)	,, ,,	CH_3OH	27,130	36·72
(11)	,, ,,	C_2H_5OH		
(11)	,, ,,	C_4H_9OH	26,930	36·34
(11)	,, ,,	*iso*C_4H_9OH		
(11)	,, ,,	CH_3COOH	27,310	35·99
(11)	,, ,,	C_2H_5COOH		
	β-Bromethylamine	H_2O + x per cent. CH_3OH		
		x		
(12)	,,	0	24,710	34·39
(13)	,,	25	19,920	26·05
(13)	,,	50	20,210	25·11
(13)	,,	75	21,380	25·80
(14)	Trichloracetic acid	C_5H_5N	28,350	33·82
(15)	,, ,,	H_2O	37,050	45·00
(16)	Trinitrobenzoic acid	H_2O	29,970	32·85
(16)	,, ,,	$C_6H_5OCH_3$	30,730	31·13
(16)	,, ,,	$C_6H_5NO_2$	34,990	33·75
(16)	,, ,,	$C_6H_5COCH_3$	25,450	24·23
(16)	,, ,,	$C_6H_5CH_3$	31,600	27·68

(1) Daniels and Johnston, *J. Amer. Chem. Soc.*, **43**, 53, (1921).
(2) Lueck, *ibid.*, **44**, 757, (1922).
(3) Eyring and Daniels, *ibid.*, **52**, 1473, (1930).
(4) Bredig and Balcom, *Berichte*, **41**, 740, (1908); Fajans, *Z. physikal. Chem.*, **73**, 25, (1910).
(5) von Halban, *ibid.*, **67**, 129, (1909).
(6) Essex and Gelormini, *J. Amer. Chem. Soc.*, **48**, 882, (1926).
(7) Corran, *Trans. Faraday Soc.*, **23**, 605, (1927).
(8) Dimroth, *Annalen*, **373**, 367, (1910).
(9) Wiig, *J. Physical Chem.*, **32**, 961, (1928); **34**, 596, (1930).
(10) Brandsma, *Thesis*, Delft (1925); see *Tables Annuelles* (1930).
(11) Pray, *J. Physical Chem.*, **30**, 1477, (1926).
(12) Freundlich and Neumann, *Z. physikal. Chem.*, **87**, 69, (1914).
(13) Freundlich and Kroepelin, *ibid.*, **122**, 39, (1926).
(14) Goldschmidt and Bräuer, *Berichte*, **39**, 109, (1906).
(15) Kappanna, *Z. physikal. Chem.*, **A, 158**, 355, (1932).
(16) Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **A, 131**, 186, (1931).

has been said to be anomalous, in that a discontinuity appears in the temperature-property curve,* and attempts

* Williams and Daniels, *J. Amer. Chem. Soc.*, **46**, 903, (1924); Mazur, *Nature*, **127**, 893, (1931).

have not unnaturally been made at correlating this with its apparently exceptional solvent activity.* Recent work has shown, however, that the ordinary physical properties of nitrobenzene, when pure, are quite normal,† and there are no real grounds for supposing the solvent action of the pure liquid to be exceptional.‡

Although there is little prospect at present of ascertaining with certitude which of the many mechanisms of solvent action is at work in any particular instance, some of the more obvious possibilities may be recapitulated. The solvent may affect the velocity of chemical change of a solute by (1) combining with it to form a complex of greater or smaller reactivity than the unsolvated molecule; (2) generating or destroying active molecules of the solute; (3) varying the degree of ionization of those solutes which decompose in the ionic form; and finally (4) by modifying the number of internal degrees of freedom which contribute to the energy of activation. This last possibility will be referred to at a later stage.

The Molecular Statistics of Unimolecular Reactions.

The fact that the decomposition of ozone, which is bimolecular in the gaseous phase, is unimolecular in carbon tetrachloride solution suggests that in the liquid system collisions between ozone molecules and solvent molecules are chemically effective. Calculation shows that 22 molecules of ozone (or 10 molecules, if the correction for the persistence of velocity is included) decompose for each collision with a solvent molecule with the appropriate energy.§ This is a significant result in view of the experimental observation that 1 molecule of solvent is destroyed for every 17 molecules

* See, for example, Essex and Gelormini, *J. Amer. Chem. Soc.*, **48**, 882, (1926).

† Massey, Warren, and Wolfenden, *Trans. Chem. Soc.*, 91, (1932).

‡ *Proc. Roy. Soc.*, **A, 131,** 186, (1931).

§ *Trans. Chem. Soc.*, 95, (1932); fuller information will be obtained in this paper concerning all the examples discussed in this section.

of ozone which disappear. Whether, therefore, we are dealing with a chain reaction of a small number of cycles or simply with a bimolecular reaction at an enormous (and constant) pressure, the results are consistent with the view that solute-solvent collisions are the determining factor. This we shall see is true also for the mutarotation of glucose in water (p. 233). Since on general chemical grounds it is quite reasonable to regard many other reactions in the same light, we must consider in some detail the calculations upon which these conclusions are based.

By equation (7) of Chapter I, the total number of collisions occurring per second between n molecules of solute (diameter $= \sigma$; mass $= m$) and molecules of solvent (viscosity $= \eta$) is

$$Z = n \frac{3\pi\sigma\eta}{2m}. \tag{5}$$

Assuming that each collision with energy equal to E' (calories per gram molecule) results in chemical transformation, the rate becomes

$$\frac{dn}{dt} = n \frac{3\pi\eta\sigma}{2m} e^{-E'/RT},$$

giving a unimolecular constant equal to

$$k = \frac{3\pi\eta\sigma}{2m} e^{-E'/RT}. \tag{6}$$

The conditions imagined are those corresponding to equation (4), i.e. there are no deactivations. Since

$$k/\eta = \text{const.} \times e^{-E'/RT},$$

the energy of activation can be found by plotting $\ln(k/\eta)$ against $1/T$. Alternately it may be found by making use of Andrade's equation* for the temperature coefficient of the viscosity of unassociated liquids:

$$\eta = a \times e^{b/T}.$$

* *Nature*, **125**, 309, (1930).

Combination with the Arrhenius equation gives us the relation

$$E' = E_A + Rb; \qquad (7)$$

R is the gas constant (in calories per degree), b is one of the viscosity constants of the solvent, and E_A is the Arrhenius critical increment. In applying equation (6) to hydrolytic reactions in aqueous solution, allowance should strictly be made for the diminution in the concentration of the solvent, but since in dilute solutions only one molecule of solvent in several hundreds is used up, the correction can be neglected.

Equation (6) accounts satisfactorily for the velocity of decomposition of dibromsuccinic acid,* the conversion of chloropurpureochromichloride into roseochromichloride,† and numerous other reactions to be discussed below. The hydrolysis of carbonyl sulphide, however, is faster than that predicted by this equation.‡ The disparity becomes negligible when the correction for the persistence of velocity is introduced. This term should properly be included in all the present calculations. It has been omitted in the following examples for reasons which will be evident.

The Arrhenius critical increment (26,310 cals.) for the hydrolysis of monochloracetic acid, $CH_2Cl.CO_2H + H_2O \rightarrow CH_2(OH).CO_2H + HCl$, is lower by 3,370 calories than the value obtained for the energy of activation when allowance has been made for the variation of the collision number with temperature. The diameter of the monochloracetic acid molecule being taken as $5{\cdot}4 \times 10^{-8}$ cm. [Chap. I], equation (6) gives calculated rates which are greater by a factor of 2·5 (see Table 2) than those determined experimentally by Buchanan.§ The reaction appears to be fairly free from complications.‖

Olivier** has measured the rate of hydrolysis of a large

* van 't Hoff, *Studies in Chemical Dynamics*, London, (1896).
† Freundlich and Pape, *Z. physikal. Chem.*, **86**, 458, (1914).
‡ Buchböck, *ibid.*, **23**, 123, (1897).
§ *Berichte*, **4**, 340, (1871); see van 't Hoff, *op. cit.*, p. 130.
‖ See, however, Dawson and Dyson, *Trans. Chem. Soc.* 49, (1933).
** *Rec. trav. chim. Pays-bas*, **41**, 301, 646, (1922); **42**, 516, 775, (1923).

Table 2

Temp.°C	$\eta \times 10^3$	Unimolecular velocity constants (secs.$^{-1}$) Obs.	Calc.
80	3·56	$8·52 \times 10^{-7}$	$2·13 \times 10^{-6}$
90	3·16	$2·31 \times 10^{-6}$	$6·00 \times 10^{-6}$
100	2·84	$6·64 \times 10^{-6}$	$1·63 \times 10^{-5}$
110	2·56	$1·67 \times 10^{-5}$	$4·23 \times 10^{-5}$
120	2·32	$4·03 \times 10^{-5}$	$1·03 \times 10^{-4}$
130	2·14	$9·10 \times 10^{-5}$	$2·50 \times 10^{-4}$

number of substituted benzyl chlorides in 50 per cent. aqueous alcoholic mixtures at 30° and 83°. Within this range, the temperature coefficients of the viscosity of ethyl alcohol and water are not very different, so that values for water have been used in correcting the Arrhenius *E*'s; the effect is in all cases to increase this by 3,425 calories. Table 3

Table 3

Reactant	*E* (Arrhenius)	$\sigma \times 10^8$	$k_{30°} \times 10^7$ (secs.$^{-1}$) Obs.	Calc.	k_{calc}/k_{obs}
$C_6H_5.CH_2Cl$	19,900	5·3	18·5	125	6·8
o-$CH_3.C_6H_4.CH_2Cl$	19,790	5·5	91·7	140	1·5
m- ,,	20,190	5·5	24·0	73·6	3·1
p- ,,	20,390	5·5	173	52·0	0·4
o-$NO_2.C_6H_4.CH_2Cl$	22,250	6·3	0·867	2·18	2·5
m- ,,	21,780	6·3	1·05	4·76	4·5
p- ,,	21,990	6·3	0·818	3·37	4·1
m-$CO_2H.C_6H_4.CH_2Cl$	21,350	5·7	3·15	8·89	2·8
p- ,,	21,560	5·7	2·02	6·29	3·1
o-$Br.C_6H_4.CH_2Cl$	21,110	6·5	3·93	12·7	3·2
m- ,,	21,870	6·5	2·45	3·58	1·5
p- ,,	21,550	6·5	7·62	6·08	0·8
2:6-$Br_2C_6H_3.CH_2Cl$	22,460	7·0	1·19	1·04	0·9
2:4- ,,	22,490	7·0	1·82	0·99	0·6
3:5- ,,	22,450	7·0	0·53	1·04	1·8

indicates that equation (6) predicts rates which are always within a small factor of the observed values, the absolute rates varying about three-hundredfold. The same degree of agreement holds, of course, for the results obtained at the higher

temperature, where the velocities are usually about 200 times greater. Only approximate values for the molecular diameters have been employed, their magnitudes being given by equation (4) of Chapter I or by comparison with the diameters of similarly constituted molecules. All isomerides are assumed to have the same radii, i.e. any possible steric influence has been ignored in these calculations.

The velocity coefficients of these reactions at any one temperature should be proportional to the viscosity of the medium. Where such substances as urea and glycerol have been added, the increase in viscosity has, in fact, been attended by an increase in k, but to an extent exceeding that demanded by theory. The difficulty is, as usual, to effect a change in one property of the solution without causing the concomitant adjustment of another.

The instances examined so far have been either decompositions of very simple molecules or elementary changes in more complex molecules; the agreement between calculated and observed velocity coefficients has justified our assumption that the rates of activation and reaction have been equal. When more complicated chemical changes are considered, these two quantities need not be the same. For reactions of the true unimolecular type, the rate of activation which still depends, of course, on the number of suitable collisions is often considerably greater than, and does not determine, the velocity of reaction. The rate of chemical change is now governed by the frequency of interatomic vibrations, and by other factors, and cannot be evaluated without a fuller knowledge of the dynamics of activated molecules. The immediate problem is to account, on a collision mechanism, for a rate of activation great enough to sustain a sufficient fraction of the total number of molecules in an energized state. This becomes possible if the energy of activation is regarded as being distributed between a number of internal degrees of freedom of the reacting molecule. Adopting the expression of Hinshelwood, the rate of

production of activated molecules by collision becomes

$$\frac{dn}{dt} = n\frac{3\pi\eta\sigma}{2m}e^{-E/RT}\left(\frac{E}{RT}\right)^F\frac{1}{F!}.$$

For the kind of reaction with which we are concerned, $E = E'+FRT$, where F is one less than the number of degrees of freedom involved. If this be equated to the observed rate of chemical change

$$dn/dt = kn,$$

it becomes possible to evaluate the minimum number of degrees of freedom which must be concerned in the activation process:

$$k = \frac{3\pi\eta\sigma}{2m}e^{-E/RT}\left(\frac{E}{RT}\right)^F\frac{1}{F!}. \qquad (8)$$

The values of F thus found for a number of unimolecular reactions in solution are given in Table 4.

The observed critical increment (E_A) and the corrected value (E') have been determined by plotting the logarithm of k and of k/η respectively against $1/T$. On an average, each of these reactions has been investigated at five temperatures over a range of 40°, the actual temperatures having varied from 0° to 140°. With one or two exceptions, the energy of activation is considered to be accurate to within about ±500 calories. The viscosity data have been taken from the *International Critical Tables*, vol. vii, 1930. The correction introduced into the critical increment by allowing for the temperature coefficient of the collision frequency depends not only on the solvent but also on the temperature at which the kinetic measurements were made. The magnitude of this viscosity correction ($E'-E_A$) varies from 880 calories for chloroform at 40–70° to 5,680 calories for acetophenone at 70–140°. The numbers in the last column of Table 4 are the nearest integers which will satisfy equation (8) when the observed velocity coefficients are substituted for k; k_{calc} is the value assumed by k when this value of F is used in the same equation.

Table 4

Reference	Reactant	Solvent	E (Arrhenius)	E'	$\eta_{60°} \times 10^3$	$k_{60°}$ Obs.	$k_{60°}$ Calc.	F
(1)	Triethylsulphonium bromide	$PhNO_2$	28,290	31,340	10·94	$2·11 \times 10^{-4}$	$2·96 \times 10^{-4}$	4
		$C_2H_2Cl_4$	30,350	33,180	9·90	$2·19 \times 10^{-4}$	$1·66 \times 10^{-4}$	6
		$CHCl_3$	33,010	33,890	4·50	$2·07 \times 10^{-4}$	$9·84 \times 10^{-5}$	7*
		$Pr^{\alpha}OH$	33,120	37,600	9·16	$1·53 \times 10^{-6}$	$2·14 \times 10^{-6}$	7
		CH_2CO_2H	31,060	33,820	7·16	$8·51 \times 10^{-7}$	$5·43 \times 10^{-7}$	3
(2)	2:4:6-Trinitrobenzoic acid	H_2O	29,970	33,080	4·69	$3·33 \times 10^{-6}$	$3·91 \times 10^{-6}$	4
		PhCOMe	25,450	31,130	10·80	$5·79 \times 10^{-7}$	$4·39 \times 10^{-7}$	2
		$PhNO_2$	34,990	37,120	10·94	$4·07 \times 10^{-9}$	$8·61 \times 10^{-9}$	3
		$PhCH_3$	31,600	33,620	3·80	$1·62 \times 10^{-9}$	$4·20 \times 10^{-9}$	1
(3)	Camphorcarboxylic acid	PhCOMe	28,960	32,620	10·80	$1·59 \times 10^{-6}$	$2·39 \times 10^{-6}$	3
		H_2O	29,640	32,690	4·69	$3·31 \times 10^{-7}$	$2·18 \times 10^{-7}$	2
(4)	Trichloracetic acid	$PhNH_2$	28,350	32,950	15·40	$1·05 \times 10^{-4}$	$9·44 \times 10^{-5}$	5
(5)	Acetonedicarboxylic acid	H_2O	23,320	27,240	4·69	$5·48 \times 10^{-2}$	$2·05 \times 10^{-2}$	4
(6, 7)	Malonic acid	,,	28,820	31,620	4·69	$1·41 \times 10^{-7}$	$2·11 \times 10^{-7}$	1
(7)	Allylmalonic acid	,,	27,970	30,820	4·69	$2·46 \times 10^{-7}$	$5·03 \times 10^{-7}$	1
(7)	Diethylmalonic acid	,,	33,430	36,250	4·69	$2·00 \times 10^{-8}$	$4·34 \times 10^{-8}$	4
(7)	Mesoxalic acid	,,	33,700	36,330	4·69	$1·82 \times 10^{-8}$	$1·33 \times 10^{-8}$	3
(8)	Benzenediazonium chloride	,,	23,360	27,110	4·69	$3·43 \times 10^{-3}$	$6·70 \times 10^{-3}$	3
(8)	*o*-Toluenediazonium chloride	,,	23,440	27,310	4·69	$8·97 \times 10^{-3}$	$5·00 \times 10^{-3}$	3
(8)	*m*-Toluenediazonium chloride	,,	22,800	26,670	4·69	$8·89 \times 10^{-3}$	$1·22 \times 10^{-2}$	3
(8)	*p*-Toluenediazonium chloride	,,	27,680	31,150	4·69	$5·20 \times 10^{-4}$	$5·51 \times 10^{-4}$	5
(9)	Phenylbenzylmethylallylammoniumbromide	$CHCl_3$	29,960	31,620	4·50	$1·04 \times 10^{-3}$	$1·38 \times 10^{-3}$	7

(1) von Halban, *Z. physikal. Chem.*, **67**, 129, (1909).
(2) Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **A**, **131**, 186, (1931).
(3) Fajans, *Z. physikal. Chem.*, **73**, 25, (1910); also private communication from Professor Freudenberg.
(4) Goldschmidt and Bräuer, *Berichte*, **39**, 109, (1906).
(5) Wiig, *J. Physical Chem.*, **34**, 596, (1930); **32**, 961, (1928).
(6) Bernouilli and Wege, *Helv. Chim. Acta*, **2**, 511, (1919).
(7) Knaus, *Thesis*, Bâle, (1923); vide *Tables Annuelles*, (1928).
(8) Cain and Nicoll, *Trans. Chem. Soc.*, **81**, 1412, (1902).
(9) von Halban, *Berichte*, **41**, 2417, (1908).

It will be seen from this table that the velocities of these reactions can be accounted for if a small number—from 2 to 8—of internal degrees of freedom of the reacting molecules come into play during collisional activation. It should, however, be emphasized that these may not be the actual numbers involved; they are the minimum values which make it possible for the observed rate to be maintained. At the same time, it is not improbable that some of them actually represent the numbers of degrees of freedom which are operative. The number marked with an asterisk indicates both the minimum value of F which will account for the observed rate and the value of F which corresponds to the

maximum rate of activation. In other words, if F were taken as 8, k_{calc} would be lower than that given in the table. It is a consequence of the Hinshelwood-Fowler-Rideal equation that such a maximum should exist. Unless the collision term used is very much in error, it can therefore be concluded that 8 degrees of freedom (7+1) come into play when triethylsulphonium bromide decomposes in chloroform solution. Values of F for the gaseous decomposition of simple ethers, aldehydes, and triazenes vary from about 2 to 15.

It will be observed that for one and the same reaction in different solvents, the minimal number of degrees of freedom which must be invoked often varies from solvent to solvent. The role of the solvent in chemical kinetics has not yet been definitely correlated with any physical properties and seems to belong to the category of specific chemical effects, which range from the formation of complexes, on the one hand, to an apparently inert or purely diluent influence on the other. The suggestion has been made that the varying values of F from solvent to solvent may indicate in a quasi-quantitative manner the extent to which the solvent enters into partnership with the reactant for purposes of decomposition.

Many alternative theories, as we have seen, are possible and will have to be tested in due course. Provided the rate of activation exceeds that of reaction, the medium effect may be associated with the variable deactivating influence of the solvent molecules.

The Influence of Substitution and of Dilution upon the Kinetics of Unimolecular Reactions.

These two aspects of the subject have received very inadequate attention.

The introduction of a new group into a reactant molecule usually alters its reactivity, the magnitude of the effect being comparable for unimolecular and bimolecular

reactions. The data in Table 5 have been compiled from the results of Knaus* and of Bernouilli and Wege† on the decomposition of substituted malonic acids. These figures

Table 5

Acid	E	$\ln Z$
Malonic	28,820	27·96
Diethylmalonic	33,430	32·99
Allylmalonic	27,970	27·20
Phenylmalonic	29,050	33·69
Meso-oxalic	33,700	33·29

should be compared with those obtaining for the gaseous unimolecular decomposition of ethers‡ and imides§ and with the bimolecular benzylation of amines in solution.‖ The substitution of a bromine atom for a hydrogen atom in camphorcarboxylic acid reduces the critical increment for the decomposition in acetophenone solution from 28,960 calories** to 20,090 calories.†† On the other hand, the critical increments for the decomposition in water of *p*-brombenzenediazonium chloride‡‡ and *p*-methylbenzenediazonium chloride§§ are almost equal. As might be expected, the effect of substitution is highly specific.

The velocity of decarboxylation of trichloracetic acid in water increases continuously with an increase in dilution from 0·2 to 1,000 litres per gram molecule,‖‖ but the variation

* *Thesis*, Bâle, (1923); *Tables Annuelles*, (1928).

† *Helv. Chim. Acta*, **2**, 511, (1919); see also Burk and Daus, *J. Physical Chem.*, **35**, 1461, (1931).

‡ Hinshelwood and Askey, *Proc. Roy. Soc.*, **A, 115**, 215, (1927); Hinshelwood, *ibid.*, **A, 114**, 84, (1927); Glass and Hinshelwood, *Trans. Chem. Soc.*, 1805, (1929).

§ Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1495, (1927); **50**, 714, (1928); **51**, 2134, (1929).

‖ Peacock, *Trans. Chem. Soc.*, 2177, (1925).

** Fajans, *Z. physikal. Chem.*, **73**, 25, (1910).

†† Creighton, *ibid.*, **81**, 543, (1913).

‡‡ 27,000 calories; Euler, *Annalen*, **325**, 292, (1902).

§§ 27,680 calories, Cain and Nicoll, *Trans. Chem. Soc.*, **81**, 1412, (1902).

‖‖ Kappanna, *Z. physikal. Chem.*, **A, 158**, 355, (1932).

is no greater than with bimolecular reactions. This behaviour is probably quite general. Of the many explanations which may be offered, that based upon a change in extent of ionization is the least probable, since hydrogen ion exerts little influence on this reaction.

Empirical Relations

The variety of chemical changes and the range of conditions under which they occur make possible an almost unlimited diversity of kinetic phenomena. In the nature of things, it is therefore unlikely that any simple mathematical relation can describe more than a limited number of reactions. The restricted applicability of the theoretical equations which are used in this book is being repeatedly emphasized and need be stressed no further. Similarly confined in scope are the empirical formulae which have recently been advanced and may be considered briefly here.

Most of the attempts have been directed at correlating the two constants S and E of the Arrhenius equation: $k = Se^{-E/RT}$.* Many of the equations can be expressed in the general form

$$k = Je^{E/C}e^{-E/RT}.$$

The hydrolysis of sugars and glykosides by acids conform with an equation of this type, J being unity and C being a constant dependent upon the type of glykoside; for glucosides, $C = 857$ calories; for fructosides, $C = 743$ calories. All the members of one group are thus hydrolysed at unit rate ($k = 1$) at the same temperature, which is equal to C/R.† J is also unity for some unimolecular reactions.‡ The kinetics of the decomposition of alcohols at the surface of solids are given by the same relation, C now being a constant for a group of similarly constituted catalysts.§ It

* See, for example, Boeseken, *Rec. trav. chim. Pays-bas*, **46**, 574, (1927); Gapon, *Ukraine Chem. J.*, **5**, 169, (1930).

† Moelwyn-Hughes, *Thesis*, Liverpool, p. 88, (1928).

‡ Syrkin, *Z. anorg. Chem.*, **199**, 28, (1931).

§ G. M. Schwab, *Z. physikal. Chem.*, **B**, **5**, 406, (1929).

has been suggested that C in the case of bimolecular reactions in solution is a function of the solvent.* Another generalization referring to a special class of chemical changes—the formation of quaternary ammonium salts—has recently been disclosed.† Polissar‡ takes the view that the relation is equivalent to arithmetical accident conditioned by the experimental restrictions under which investigations have to be carried out. From an examination of a totally different set of reactions, D. T. Lewis and Huddleston§ express a similar opinion, which cannot, however, be wholly true. The fallacious argument that the constants E and S of the Arrhenius equation must be related simply because only reactions with moderate speeds can be measured is refuted by the experimental results discussed in Chapter IV. Normal bimolecular reactions, it will be recalled, have velocities differing by a factor of 10^{47}, i.e. while E undergoes a wide variation, the term S is virtually the same for all. When S has not its normal value, it is in fact found that $\ln S$ often varies proportionately with E. There is no doubt that this relation has a physical meaning, but the truth which it attests is deeply hidden, and when revealed may not have the same complexion in all cases. With the growth of the subject other empirical formulae will unquestionably appear. For example, the velocity of decomposition of a number of different carboxylic acids in water is given with fair accuracy by the general equation

$$k = 2{\cdot}3 \times 10^{14} \times e^{-E/RT},$$

as the results given in Table 6 indicate. When dealing with *uni*molecular reactions, a constancy in S is seldom found accompanied by such a wide variation in E, and may indicate a common interatomic frequency characteristic of the carboxyl group.|| At present, however, it is wisest to

* Holdzschmidt, *Z. anorg. Chem.*, **200**, 82, (1931).

† *Chemical Reviews*, **10**, 240, (1932).

‡ *J. Amer. Chem. Soc.*, **54**, 3105, (1932).

§ *Trans. Chem. Soc.*, 1398, (1932).

|| Cf. Polanyi and Wigner, *Z. physikal. Chem.*, 'Haber-Band', 439, (1928).

Table 6

Acid	E	$\ln S$
Meso-oxalic	33,700	33·3
Diethylmalonic	33,430	33·0
Trinitrobenzoic	29,970	32·9
Phenylmalonic	29,050	33·7
Acetonedicarboxylic	23,200	32·3

recall the facts that the equation is quite empirical and of a strictly limited applicability (see Table 5). Like the other empirical relations discussed here, its immediate value lies in its utility and suggestiveness.

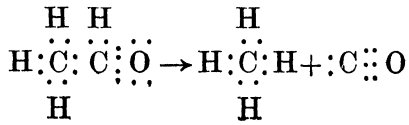
VII

IONIC REACTIONS

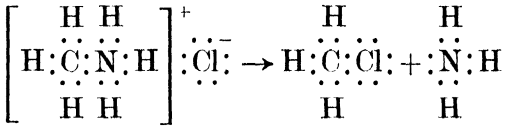
CHEMICAL transformations are either preceded or accompanied by a diminution in the attractive forces which hold together the constituent atoms or groups within the reacting molecule. In other words, a chemical bond is either loosened or entirely ruptured. The velocity of chemical change is accordingly dependent, among other things, upon the rate at which the reacting molecules can acquire the critical energy necessary to loosen or break the bond in question. There are three types of linkages which have to be dealt with. (1) The electrovalent linkage. When barium sulphate is formed in solution in the familiar analytical reaction,

$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4,$$

the rate of formation is simply the rate at which the barium ions and sulphate ions come together and subsequently fit into the crystal lattice of the precipitated salt. In the crystalline, fused, or dissolved state the sub-molecular constituents of such salts are the ions, which are held together by electrostatic forces. No critical energy is required to render the chemical change complete. True ionic reactions, as we have seen, are to all intents instantaneous, and the study of the kinetics of such processes is quite beyond the reach of experiment at present. (2) The covalent linkage. The single bond between two carbon atoms consists of two electrons, one electron being contributed by each atom. Such linkages are said to be covalent: they usually hold the constituents together very firmly. When acetaldehyde, for example, decomposes into methane and carbon monoxide, a considerable amount of energy must be absorbed before the covalent bond is broken.



The velocity of reaction is thus very slow, and becomes conveniently measurable only at high temperatures. (3) When two atoms or groups are held together by a pair of electrons contributed solely by either atom or group, the linkage is termed a coordinate one. Thus in the case of methylamine-hydrochloride, the two electrons constituting the bond between the carbon and nitrogen atoms belong to the nitrogen atom, and appear as a lone pair in the molecule of ammonia produced by decomposition:



When a coordinate linkage is broken, there is always a change in electrovalency, which in the present example has been reduced from one to zero.

All these types of transformations, and of course the corresponding reverse changes, are met with in the study of reactions in solution. As already indicated, the almost instantaneous rate of the purely ionic reaction of the type $A^{+z}+B^{-z} \rightarrow AB^0$ explains the absence of data in cases of this kind. On the other hand, the fairly high energy of activation required to disrupt the stable covalent bond implies a slow rate of reaction at the fairly low temperatures to which investigations in liquid media are confined. When the critical increment is relatively small (as in the decomposition of nitrogen pentoxide, chlorine monoxide, urea, and carboxylic acids) the velocity becomes measurable, and is found to be not very sensitive to the nature of the solvent, provided no chemical union sets in. Coordinate linkages are more easily broken, and a considerable number of coordination reactions have been investigated kinetically since their theoretical importance was discovered a few years ago. These changes, as we have seen, are attended by electrostatic disturbances within the molecule, and are therefore more likely to be influenced by a change in the medium

than are the decompositions of covalent compounds, since an electrical environment (altered by using solvents of varying dielectric capacities or by adding electrolytes) may make itself felt without allowing of any definite chemical interaction between solute and solvent such as is postulated to account for the influence of the solvent on the decomposition of covalent compounds.

A distinction must now be drawn between what we have termed true ionic reactions and ionic reactions as the term is more generally understood. A purely ionic reaction involves the combination of ions the mutual affinity of which is wholly electrostatic. In the more general sense, an ionic reaction is taken to mean a chemical change, perhaps of a profound character, between two or more molecular species of which at least one possesses an electrical charge. An example is afforded by the conversion of chloropurpureochromichloride into roseochromichloride in aqueous solution —a reaction which was followed by Freundlich and Pape* by measuring the power of the cation to coagulate arsenic sulphide sol:

$$[Cr(NH_3)_5Cl]^{++}+H_2O \rightarrow [Cr(NH_3)_5H_2O]^{+++}+Cl^-.$$

This reaction is seen to be in reality a coordination reaction; although ionic in the sense that charged molecules participate, the chemical change is quite as radical as, and in fact very similar to, the combination of amines with alkyl halides. It is with reactions of this kind that we have now to deal. The major part of the information available is concerned with the manner in which the velocity of such chemical changes is influenced by the electrical environment, which in aqueous solutions may be suitably modified by the introduction of electrolytes. For this purpose it will be necessary to give a brief outline of recent views on the nature of electrolytic solutions. At a later stage the absolute rates of ionic reactions will be compared with those calculated from

* *Z. physikal. Chem.*, **86**, 458, (1914).

first principles. The result of the comparison, it may be well to emphasize here, is to show that the electrical environment is but one of the factors governing the rate of reaction.

The Interionic-Attraction Theory of Electrolytic Solutions.

Deviations of the behaviour of ions in solution from that of neutral molecules have their origin in the forces of electrical attraction and repulsion exerted between the ions. This is the fundamental idea underlying the modern theory of solutions of electrolytes, which, originating in the work of Milner* and of Bjerrum,† has been incorporated into physical chemistry in the form given it by Debye and Hückel.‡ It is beyond the scope of this book to examine the theory in detail, and reference will therefore be made only to those aspects of it which will be of direct service to us.§ The basic postulate of the theory is that, owing to electrical forces, the ions in solution are not uniformly distributed, there being on the average in the neighbourhood of any ion more ions of unlike than of like sign.|| On the assumption—which experiment shows to be nearly though not quite valid—that the electrolyte is completely dissociated, Debye and Hückel have shown that the value of the mean electrical potential ϕ_A at a distance r from the ion A, due to the uneven distribution of the ions, is

$$\phi_A = \frac{z_A \epsilon}{Dr} e^{-\kappa r} \frac{e^{\kappa a}}{1+\kappa a}, \qquad (1)$$

where z_A is the valency of ion A, ϵ is the electronic charge, D is the dielectric constant of the medium, a is the closest

* *Phil. Mag.*, **23**, 551, (1912).

† *Z. Elektrochem.*, **24**, 321, (1918).

‡ *Physikal. Z.*, **24**, 185, (1923); **25**, 97, (1924).

§ For a simplified presentation of the theoretical treatment reference may be made to the work of A. A. Noyes (*J. Amer. Chem. Soc.*, **46**, 1080, (1924)). Its examination in the light of experiment is given by Davies (*The Conductivity of Solutions* (Chapman and Hall, (1930)).

|| It is more accurate to say that the motion of any given ion in solution sets up an electrostatic field which tends to oppose the motion.

distance of approach of other ions to an A ion, and κ is given by the now familiar expression

$$\kappa = \sqrt{\left(\frac{4\pi\epsilon^2 \sum cz^2}{1{,}000\, DRT}\right)}. \qquad (2)$$

c is the total concentration of the surrounding ions, expressed in gram ions per litre, so that the term $\sum cz^2$ is equal to twice the ionic strength μ.

The activity coefficient of an ion of valency z in a medium of uniform dielectric constant D at temperature T, when the ionic strength is μ, is given by the Debye-Hückel theory as

$$-\ln f = \frac{N_0^2 \epsilon^3 \sqrt{(2\pi/1000)}}{R^{1.5}} \times \frac{z^2\sqrt{\mu}}{(TD)^{1.5}}. \qquad (3)$$

The first term in this expression is seen to be a universal constant, which, on substituting $6{\cdot}06\times10^{23}$ for N_0, $4{\cdot}77\times10^{-10}$ e.s.u. for ϵ, and $8{\cdot}315\times10^7$ for R, is found to be $4{\cdot}166\times10^6$. In a medium of unvarying dielectric capacity at a fixed temperature we have

$$-\ln f = \alpha z^2\sqrt{\mu}, \qquad (4)$$

where α is a constant. The theory, therefore, states that the activity coefficient of an ion is an exponential function of the square root of the ionic strength, its absolute value being independent of any specific property of the ion and determined solely by its ionic type, i.e. by the sign and magnitude of the charge z.

Equation (4) has been deduced on the assumptions that the ions may be regarded as point charges and that the dielectric constant of the medium is the same at all distances from a given ion and is, moreover, independent of the ionic strength. By assuming D to be a linear function of μ, it has been shown that

$$-\ln f = \alpha z^2\sqrt{\mu} - \beta\mu, \qquad (5)$$

where β is a constant characteristic of both solute and solvent, and varies approximately inversely with the radius of the ion.* It is only in very dilute solutions—say, for

* E. Hückel, *Physikal. Z.*, **26**, 93, (1925).

example, below an ionic strength of 0·002—that the constant β may be entirely ignored and the limiting expression (4) becomes strictly applicable.

The application of these principles to the kinetics of reactions in solution is due in large measure to Brönsted, whose theory of the influence of added electrolytes on the velocity of chemical change occurring between ions in solution must now be considered.

The Intermediate-Complex Theory of Bimolecular Reactions.

Following the line of argument given on p. 139, the transformation of molecules A and B in a bimolecular reaction $A+B \rightarrow C+D$ may be imagined to take place *via* the formation of an intermediate complex X, with which the reactants are in thermodynamic equilibrium, $A+B \rightleftarrows X$. By the law of mass action we have

$$K = \frac{a_X}{a_A a_B} = \left(\frac{c_X}{c_A c_B}\right)\left(\frac{f_X}{f_A f_B}\right).$$

The rate of reaction being proportional to the concentration of the complex,

$$v = k'c_X = k'Kc_A c_B\left(\frac{f_A f_B}{f_X}\right), \tag{6}$$

or, putting $k'K = k_0$,

$$v = k_0 c_A c_B\left(\frac{f_A f_B}{f_X}\right). \tag{7}$$

Nothing is known about the nature of the intermediate complex. Bjerrum* assumes it to decompose unimolecularly, the rate of chemical change being determined by its specific reactivity k'; K is assumed to be independent of temperature. Brönsted,† on the other hand, regards the rate of formation of the complex, or the rate of attainment of the equilibrium stage, as determining the velocity, so that the influence of temperature upon the reaction is a displacement of the equilibrium; k' is taken to be independent of

* *Z. physikal. Chem.*, **108**, 82, (1924).

† *Ibid.*, **102**, 109, (1922); **115**, 337, (1925).

temperature. Both hypotheses are equally valid: if the lifetime of the complex is great compared with the time elapsing between two successive activating collisions, the conditions postulated by Bjerrum will result. Alternatively, if the complex has a life which is short in comparison with the time taken to traverse the mean free path, the state of affairs will correspond with Brönsted's supposition. The two views therefore represent extreme cases, the choice between the two being governed by the relative complexity of the chemical change concerned. The whole problem has been regarded from another angle by Christiansen,* who, without making any assumptions about the intermediate complex, recalls the possibility that the factors governing its formation may be complicated by variable deactivating influences.

Equation (7) has, in fact, been derived in a variety of ways, starting with assumptions concerning the complex which are equally plausible but experimentally indistinguishable. Since nothing is definitely known about its true nature, there is clearly no advantage to be gained by comparing the various assumptions. It will be recalled that this equation reduces to the experimental relations found by Lewis, Harned, Åkerlöf, and others, when the activity coefficient of one or more of the reacting solutes is either independent of, or changes in a simple manner with, the total concentration. The important point is that the velocity v at constant temperature is a function of the ratio $(f_A f_B/f_X)$ of the activity coefficients—a term which Brönsted calls the kinetic activity factor (F). Since the observed bimolecular constant is $\frac{dc}{dt}\frac{1}{c_A c_B}$, we have

$$k_{\text{observed}} = k_0\left(\frac{f_A f_B}{f_X}\right) = k_0 F. \qquad (8)$$

The kinetic activity factor is thus a quantitative indication of the extent to which the experimental velocity deviates

* *Z. physikal. Chem.*, **113**, 35, (1925).

from the ideal value k_0. At infinite dilution, the activity coefficients of all solutes are unity, and the two rates become equal; but it must not be overlooked that k_0 is still a composite term.

Brönsted's Theory of the Electrolyte Effect.

The presence of neutral salts has long been known to influence the velocity of reactions in aqueous solution. The rate of change may be increased or decreased by the addition of electrolytes, and may be a simple linear function or a more complicated function of the total salt concentration. Brönsted's theory* has brought coherence into many of the apparently chaotic observations that have been made from time to time. The theory distinguishes between two definite effects which added salts may exert. Primarily, their mere presence may alter the activity coefficients of the solutes, whether these be ions or neutral molecules. Such an influence is termed the primary salt effect, and is represented by a change in the value of F. Secondly, the presence of the added salt may vary the position of the equilibrium governing the formation of the complex, and thus alter the actual concentration of one or more of the reacting species. This is termed the secondary salt effect. An example will serve to illustrate these ideas. When sucrose is hydrolysed in aqueous solution by 0·1 molar hydrochloric acid, k is found to increase about 4 per cent. on addition of 0·1 molar potassium chloride. The degree of dissociation of the acid has remained sensibly constant, and the increase in k can be attributed entirely to the enhancement of the activity coefficient of the hydrogen ion; we are therefore dealing with the primary electrolyte effect. When, however, the catalyst is 0·1 molar acetic acid, the addition of the same concentration of sodium acetate causes k to decrease about 40 per cent.; in this case also the activity coefficient of the

* *Loc. cit.*; also, *Chemical Reviews*, **5**, 231, (1928); *Trans. Faraday Soc.*, **24**, 630, (1928).

hydrogen ion has increased slightly, but its effect on the velocity has been completely masked by the suppression in the dissociation of the acid, and the consequent serious diminution in the concentration of the catalyst; the salt effect is therefore secondary. The primary electrolyte effect is by far the commoner. The secondary effect appears when one of the reactants is a weak electrolyte, i.e. when its dissociation at moderately high dilutions is not complete and varies with the total concentration.

The Primary Electrolyte Effect; The Principle of Ionic Type.

The general solution is given by equation (7), in the derivation of which it is important to observe that the instantaneous rate (v) of reaction has, upon all hypotheses, been assumed to be directly proportional to the concentration—and not the activity—of the participants, i.e. the velocity constant k' retains its usual significance as the number of molecules reacting per unit time in a system containing unit concentration of reactants. Now let us consider the ionic bimolecular reaction $A^{Z_A}+B^{Z_B} \rightarrow X^{Z_X}$, where Z denotes the electrical charge on the various ions. By equation (4), we have

$$-\ln f_A = \alpha Z_A^2 \sqrt{\mu}$$

$$-\ln f_B = \alpha Z_B^2 \sqrt{\mu}, \text{ etc.}$$

Combining with equation (7), and noting that $Z_A+Z_B = Z_X$:

$$v = k_0 c_A c_B e^{2\alpha Z_A Z_B \sqrt{\mu}} \tag{9}$$

or

$$k_{\text{observed}} = k_0 e^{2\alpha Z_A Z_B \sqrt{\mu}} \tag{10}$$

or

$$\ln\left(\frac{k_{\text{obs}}}{k_0}\right) = 2\alpha Z_A Z_B \sqrt{\mu}. \tag{11}$$

The velocity of ionic reactions is thus an exponential function of the ionic type (represented by the charges Z_A and Z_B) and of the square root of the ionic strength. No departure from ideal behaviour will be apparent when either of the reacting species is uncharged, since $k_{\text{obs}} = k_0$ when

either Z_A or Z_B is zero. When the two reacting ions have charges of the same sign, the addition of electrolyte will cause an increase in the velocity; when the ions are oppositely charged, an increase in the total concentration of electrolyte will diminish the velocity; if one of the reactants is a neutral molecule, k_{obs} should be independent of μ. Finally, the curves found by plotting values of $\ln k_{obs}$, for all ionic reactions, against the square root of the ionic strength should be linear, the tangents of the curves being integral multiples, positive or negative, of 2α.

If, in the expression for the activity coefficient of an ion, common logarithms be employed, $\log_{10} f = \alpha' Z^2 \sqrt{\mu}$, where $\alpha' = \alpha/2{\cdot}303$. Equation (11) then becomes

$$\log_{10}\left(\frac{k_{obs}}{k_0}\right) = 2\alpha' Z_A Z_B \sqrt{\mu}.$$

The absolute magnitude of α', as we have seen, is dependent upon the dielectric constant of the medium and upon the temperature. It happens that for water at 25° C., $\alpha' = 0{\cdot}505$, so that as an approximation we may write

$$\log_{10}\left(\frac{k_{obs}}{k_0}\right) = Z_A Z_B \sqrt{\mu}. \qquad (12)$$

When, therefore, the common logarithm of the observed velocity coefficient for a bimolecular ionic reaction in dilute aqueous solution at 25° C. is plotted against $\sqrt{\mu}$, the intercept should be $\log_{10} k_0$ and the gradient should be $\theta = \tan^{-1} Z_A Z_B$. With the values of k_0 so obtained, the quantity $\log_{10}\left(\frac{k_{obs}}{k_0}\right)$ may be plotted as a function of $\sqrt{\mu}$; the slopes under these special conditions should be very nearly +1, +2, +3, etc., 0, −1, −2, −3, etc. The principle is exemplified well by the accompanying figure, which is due to La Mer.*

Such excellent agreement with the theory of Brönsted is

* *Chemical Reviews*, **10**, 179, (1932).

found to be limited, not only to very dilute solutions, but to ionic reactions where the charges are fairly low. The

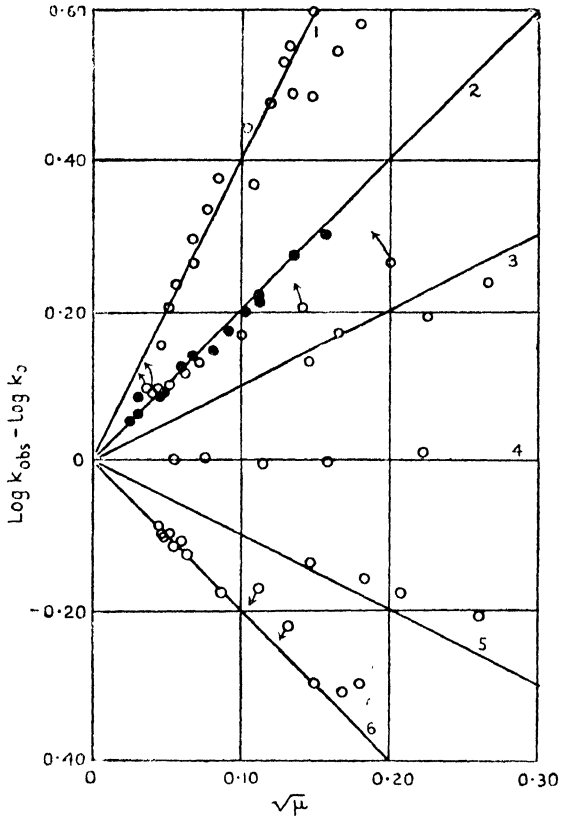


FIG. 1.—The influence of ionic strength on the velocity of ionic reactions.

1. $2[Co(NH_3)_5Br]^{++}+Hg^{++}+2H_2O \rightarrow 2[Co(NH_3)_5H_2O]^{+++}+HgBr_2$ (Bimolecular).
2. Circles. $CH_2BrCOO^- + S_2O_3^{--} \rightarrow CH_2S_2O_3COO^- + Br^-$.
   Dots. $S_2O_8^{--} + 2I^- \rightarrow I_2 + 2SO_4^{--}$ (Bimolecular).
3. $[NO_2{=}N{-}COOC_2H_5]^- + OH^- \rightarrow N_2O + CO_3^{--} + C_2H_5OH$.
4. $C_{12}H_{22}O_{11} + OH^- \rightarrow$ Invert Sugar
5. $H_2O_2 + H^+ + Br^- \rightarrow H_2O + Br_2$.
6. $[Co(NH_3)_5Br]^{++} + OH^- \rightarrow [Co(NH_3)_5OH]^{++} + Br^-$.

failure of the curves to reach the theoretical limiting slope may be traced to the inapplicability of the simple expression (equation (3)) deduced by Debye and Hückel for the

activity coefficient.* The activity coefficient of certain tervalent ions, determined by means of solubility measurements, is found to be linearly related to $\sqrt{\mu}$ only when the anion of the added salt is univalent. When ions of higher valency are present, the experimental limiting slope of the $-\log f$–$\sqrt{\mu}$ curve is between two and three times as great as that predicted by equation (3). The precise formula for the activity coefficient of salts of the unsymmetrical valency type ($A^{Z_A}B^{Z_B}$, where $Z_A \neq Z_B$) is somewhat complicated,† but even with these electrolytes there is a parallelism between activity coefficient and reaction velocity in their relation to the ionic strength.

Reactions between Ions and Neutral Molecules.

Chemical reactions of the type ($A^0+B^Z \rightarrow$ Products) deserve a more detailed treatment on account of their prevalence. In very dilute solutions, the velocity should be independent of the total concentration of electrolyte. This is seen to hold for the reaction between monoiodoacetic acid and the thiocyanate ion in the presence of a strong acid (Table 1):

$$CH_2I.COOH+CNS^- \rightarrow CH_2(CNS).COOH+I^-.$$

In neutral solutions, the iodoacetic acid is largely ionized, so that under these conditions the reaction between the iodoacetate ion and the thiocyanate ion should come into

Table 1

$[H^+]$	$[K^+]$	k
0·10	0·10	5·71
0·10	0·05	5·69
0·10	0·025	5·79
0·05	0·05	5·67
0·025	0·025	5·76
0·10	0·20	5·71
0·05	0·20	5·75

* La Mer and Mason, *J. Amer. Chem. Soc.*, **49**, 363, 410, (1927); La Mer and Cook, *ibid.*, **51**, 2622, (1929); La Mer and Goldman, *ibid.*, **51**, 2632, (1929).

† La Mer, Gronwall, and Grieff, *J. Physical Chem.*, **35**, 2245, (1931).

prominence. Since the term $Z_A Z_B$ of equation (11) has now increased from zero to unity, there should be a primary salt effect. Holmberg's observations* are consistent with this.† Another striking example is afforded by the work of Kilpatrick,‡ who investigated the velocity of the reaction between water and hexa-urea chromium ion:

$$6H_2O+Cr\left(Co\langle^{NH_2}_{NH_2}\right)_6^{+++} \rightarrow Cr(H_2O)_6^{+++}+6Co\langle^{NH_2}_{NH_2}.$$

The change is almost certainly not as simple as its unimolecular character would indicate, but this is probably irrelevant. Using a constant initial concentration of the complex ion of 0·0025 gram ion per litre, k was found not to vary when by addition of potassium nitrate the ionic strength was brought up to 0·0402 (Table 2). Attention

Table 2

$[KNO_3]\times 10^3$ (gram mol./litre)	$k_{22\cdot5°C.}\times 10^{-6}$ (seconds^{-1})
0	1·86
25	1·84
50	1·87
100	1·85
150	1·85
200	1·83

has been directed by Brönsted§ to a number of other reactions of zero ionic type, where the primary salt effect amounts to no more than the limit of experimental error. Mention may be made of the reduction of ferric ion by hydroxylamine||

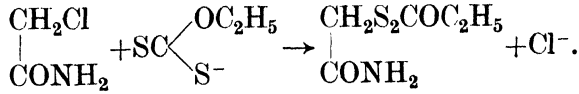
$$2Fe^{+++}+2NH_2OH \rightarrow 2Fe^{++}+N_2O+H_2O+4H^+,$$

the decomposition of chlorine peroxide by chloride ion:**

$$2ClO_2+H_2O+Cl^- \rightarrow 2HClO_2+ClO^-,$$

* *Z. physikal. Chem.*, **92**, 134, (1921). † Brönsted, *ibid.*, **102**, 169, (1922).
‡ *J. Amer. Chem. Soc.*, **50**, 359, (1928).
§ *Loc. cit.* || Raschig, *Annalen*, **241**, 188, (1887).
** Bray, *Z. physikal. Chem.*, **54**, 569, (1906).

and the reaction between chloracetamide and potassium xanthogenate:*



As indicated on p. 40, when the concentration of one of the reacting species in a bimolecular reaction is maintained at a constant value, the reaction appears to be unimolecular. The majority of the known cases of catalysed reactions in aqueous solution belong to this class, so that the catalytic coefficient (i.e. observed unimolecular constant/concentration of catalyst) should, in dilute solutions, not alter with the concentration of the reactants. This has already been shown (p. 41) to be true in the classic instance of catalysis by hydrogen ion.† Similar behaviour is recorded by Brönsted and Grove‡ for the hydrolysis of ethylene acetal (Table 3). Other familiar examples of catalysis by hydrogen

Table 3

$[H^+] \times 10^3$ (gram ion/litre)	$k_{20°C.} \times 10^3$ (minutes^{-1}; $\log_{10}$)	$\frac{k}{[H^+]}$
5	0·912	0·182
10	1·82	0·182
25	4·62	0·185
50	9·38	0·188

ion in which no primary electrolyte effect is observed are: the inversion of sucrose;§ the hydrolysis of esters;‖ and the mutarotation of glucose.** Among those reactions which are catalysed by hydroxyl ion, no change in the catalytic coefficient with dilution has been found for the hydrolysis

* Holmberg, *ibid.*, **88**, 385, (1914).

† Bredig and Fraenkel, *Z. Elektrochem.*, **11**, 525, (1905); *Z. physikal. Chem.*, **60**, 202, (1907); Spitalsky, *Z. anorg. Chem.*, **54**, 278, (1907).

‡ *J. Amer. Chem. Soc.*, **52**, 1394, (1930).

§ Arrhenius, *Z. physikal. Chem.*, **4**, 226, (1889); Palmaer, *ibid.*, **22**, 492, (1897); Euler, *ibid.*, **32**, 348, (1900).

‖ Poma, *Meddelanden Vetenskap. Nobelinstit.*, **2**, 11, (1912); Taylor, *ibid.*, **2**, 34, (1913).

** Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, **49**, 2554, (1927).

of γ-valerolactone,* the polymerization of acetone,† and the inversion of sucrose.‡ A salt effect amounting to about 10 per cent. is observed when esters are saponified by alkalis in 0·1 molar solutions, but below this concentration k is definitely independent of the dilution, as the following results of Arrhenius prove:

[NaOH]	0·05	0·025	0·0125	0·00625	0·003125
$k_{24·7°\,C.}$	6·76	6·52	6·48	6·58	6·65

The reaction between hydrogen peroxide and the iodide ion in aqueous solutions has been very fully investigated.§ The complete absence of any electrolyte effect is brought out clearly by the results of Walton, which are quoted in Table 4. With potassium iodide as catalyst, the average

Table 4

$[NaI] \times 10^3$ (gram mol./litre)	$k_{25°\,C.} \times 10^3$ (minutes^{-1}; log$_e$)	$\frac{k_{obs}}{[NaI]}$
6·16	8·13	1·32
9·21	11·99	1·30
12·26	16·21	1·32
18·40	24·19	1·31
24·52	31·95	1·30
30·60	39·47	1·29
36·80	48·10	1·31

value of the catalytic coefficient at 25° C. is 1·33 litres per gram molecule per minute.

The dynamical interpretation of these results is simply that the frequency of collisions between ions and neutral molecules in dilute solution is not appreciably influenced by the presence of added electrolytes.

The Secondary Electrolyte Effect.

Let us consider a reaction which is catalysed by hydrogen ion. As the source of the catalyst we will use, in turn, two

* Henry, *Z. physikal. Chem.*, **10**, 96, (1892); Holmberg, *ibid.*, **80**, 587, (1912).

† Koelichen, *ibid.*, **33**, 129, (1900).

‡ Arrhenius, *ibid.*, **1**, 111, (1887); La Mer, *Chemical Reviews*, **10**, 179, (1932).

§ Walton, *Z. physikal. Chem.*, **47**, 185, (1904); Brode, *ibid.*, **49**, 208, (1904); Harned, *J. Amer. Chem. Soc.*, **40**, 1461, (1918).

weak electrolytes so that the concentration of hydrogen ion may be varied by the addition of a neutral salt. With acetic acid as the first source of the catalyst we have

$$HA \rightleftarrows H^+ + A^-$$

and
$$K_a = \frac{a_{H^+} \times a_{A^-}}{a_{HA}} = \frac{c_{H^+} \times c_{A^-}}{c_{HA}} \frac{f_{H^+} \times f_{A^-}}{f_{HA}}.$$

If f_{HA} may be regarded as invariant,

$$K' = \frac{c_{H^+} c_{A^-}}{c_{HA}} f_{H^+} f_{A^-}.$$

Both activity coefficients decrease with the addition of neutral salts, so that an increase in c_{H^+} is anticipated, and the secondary salt effect should be positive. As our second source of hydrogen ion we will use the hexa-aquo chromic ion, the first stage in the dissociation of which is

$$Cr(H_2O)_6^{+++} \rightleftarrows Cr\overset{OH^{++}}{(H_2O)_5} + H^+.$$

Like the ammonium ion, this complex ion is a true acid in the sense that it is able to part with a proton. As before, the equilibrium is defined by the relation

$$K_a = \frac{c_{H^+} c_{Cr^{++}}}{c_{Cr^{+++}}} \frac{f_{H^+} f_{Cr^{++}}}{f_{Cr^{+++}}}.$$

By means of equation (4) it is seen that the kinetic activity factor in this case is $e^{\frac{1}{2}\alpha\sqrt{\mu}}$, i.e. it increases with the concentration, so that c_{H^+} may be expected to decrease with the addition of neutral salts; the secondary salt effect should thus be negative.

These considerations have been applied by Brönsted and Teeter* to the catalytic decomposition of diazoacetic ester by hydrogen ion. They find (Table 5) that the addition of potassium nitrate causes the velocity to increase when acetic acid (0·05 molar) furnishes the catalyst, and to decrease when hexa-aquo chromic ion (0·0105 molar) supplies

* *J. Amer. Chem. Soc.*, **28**, 579, (1924).

Table 5

The Effect of the Addition of Potassium Nitrate upon the Velocity of Decomposition of Diazoacetic Ester Catalysed by Hydrogen Ion.

Hydrogen ions from acetic acid				Hydrogen ions from hexa-aquo chromic ions			
$[KNO_3]\times10^3$	$k\times10^3$	$[H^+]\times10^4$	$K_c\times10^5$	$[KNO^3]\times10^3$	$k\times10^3$	$[H^+]\times10^4$	$K_c\times10^5$
0	1·27	9·52	1·85	0	1·39	10·4	1·26
5	1·31	9·77	1·95	—	—	—	—
10	1·35	10·07	2·07	10	1·38	10·0	1·16
20	1·37	10·27	2·15	20	1·29	9·7	1·09
50	1·42	10·62	2·30	50	1·21	9·0	0·94
100	1·46	10·90	2·44	100	1·12	8·4	0·82

the catalyst. The concentration of hydrogen ion has been obtained by means of the relation $k_{\text{observed}} = k''[H^+]$, where k'' is the catalytic coefficient of Bredig and Fraenkel (see Table 6, Chap. II). The equilibrium constant K_c is thus $\frac{[H^+]^2}{0{\cdot}05-[H^+]}$, and is found to vary with the dilution in conformity with Brönsted's supposition.

Precisely the same argument holds for the catalysis of reactions by weak bases. The decomposition of nitrosotriacetonamine is catalysed by hydroxyl ion: with piperidine as the base, addition of sodium chloride increases the rate of reaction, but with sodium phosphate as base, addition of the same salt decreases the rate.* The lowering in the rate of hydrolysis of ethyl acetate when ammonium chloride is added to a solution of the ester containing ammonia may be explained in the same way.†

The classification of salt effects into primary and secondary is one of convenience only and is not fundamental. In both cases the added electrolyte influences one or more of the factors in terms of which thermodynamic equilibrium is defined. In the primary salt effect, it is the equilibrium between two reactants which is disturbed; in the secondary effect, it is the equilibrium between one of the reactants and a third body, usually a constituent of a weak electrolyte.

* Brönsted and King, *J. Amer. Chem. Soc.*, **47**, 2523, (1925).

† Arrhenius, *Z. physikal. Chem.*, **2**, 284, (1888).

Linear and Exponential Electrolyte Effects.

Hitherto we have confined attention to the influence of ionic environment upon the velocity of reactions in very dilute solutions, for which the limiting law of Debye and Hückel (equation (4)) expresses with sufficient accuracy the change in activity coefficient with total concentration of electrolyte. The factors at work in solutions of higher ionic strength are but little understood; progress in this direction is partly empirical, and depends upon the validity of approximations which have to be introduced. The greatest advance has been made in the study of reactions of zero kinetic type: $A^0+B^z \rightarrow$ Products. According to the hypothesis of the intermediate complex, the velocity of reaction is given by equation (7). It is therefore necessary to find expressions for the activity coefficients of both ions and neutral molecules which are applicable to solutions of high ionic strength.

Theoretical investigations on the manner in which the activity coefficient (f_A) of a non-electrolyte is influenced by ionic environment have been made by Debye and MacAulay* and by Scatchard.† It has been shown that, provided the dielectric constant of the solution of the non-electrolyte falls off with an increase in concentration, $\ln f_A$ increases linearly with respect to μ:

$$\ln f_A = b\mu. \qquad (13)$$

b is a constant depending upon the value of the ionic radii. Experimental confirmation of this equation has been given by Belton‡ for the change in the activity coefficient of N-chloracetanilide in the presence of various salts. Using common logarithms, the numerical values of b in aqueous solution at 25° C. are 0·372, 0·164, and 0·275 for sodium chloride, barium chloride, and magnesium sulphate respectively. In the same way, the activity coefficients of iodine

* *Physikal. Z.*, **26**, 22, (1925). † *Trans. Faraday Soc.*, **23**, 454, (1927).
‡ *Proc. Leeds Phil. Soc.*, **iv**, 178, (1932).

in aqueous salt solution are exponentially related to the ionic strength.* To an approximate degree this is true also for solutions of phenyl-thiourea† and *o*-nitrobenzaldehyde.‡ As a working hypothesis it may be assumed that in general the activity coefficient of a non-electrolyte is given by an equation of this form.

The activity coefficient of an ion is given by equation (5), which accounts for the well-known minimum through which the activity coefficient passes during a change in concentration. Combining equations (7), (5), and (13), we obtain for the kinetic activity factor:

$$\ln\left(\frac{k_{\text{obs}}}{k_0}\right) = \mu(b+\beta_B-\beta_X). \qquad (14)$$

For reactions between ions and neutral molecules, therefore, $\ln k$ should be directly proportional to the ionic strength up to very considerable concentrations. In dilute solutions, this has been verified by Brönsted and Wynne-Jones§ for the hydrolysis of acetal by 0·0008N hydrochloric acid at 20° C.

$$CH_3CH(OC_2H_5)_2+H_2O \rightarrow CH_3CHO+2C_2H_5OH.$$

The reaction is sensitive to hydrogen ion but not to other ions. This fact, coupled with the slowness of the uncatalysed hydrolysis and the electrical neutrality of the participants, renders it very suitable for the purpose in hand. Using a dilatometric method, the figures in Table 6 have been

Table 6

Added electrolyte	Concentration of electrolyte	$k \times 10^2$ (minutes^{-1}; $\log_{10}$)	$2+\log_{10} k$	
None	0·00	1·53	0·185	0·027
KNO_3	0·05	1·63	0·212	
NaCl	0·10	1·72	0·238	0·025
NaCl	0·15	1·84	0·265	0·027
KNO_3 or NaCl	0·20	1·94 (average)	0·288	0·023

* Carter, *Trans. Chem. Soc.*, **127**, 2861, (1925).
† Rothmund, *Z. physikal. Chem.*, **33**, 401, (1900).
‡ Goldschmidt and Sunde, *ibid.*, **56**, 1, (1906).
§ *Trans. Faraday Soc.*, **25**, 59, (1929).

obtained, from which it is clear that log k is proportional to μ. It will be noticed that the primary electrolyte effect is quite considerable—a fact which rather suggests that the absence of any such effect for those other reactions of zero kinetic type which have been discussed may be due, not to the applicability of expression (4), but to the cancelling out of the β terms in the more accurate expression (5). As already indicated, equation (14) should hold up to moderate concentrations. In view of this fact, it is unfortunate that the scope of the inquiry has been so limited.

It is an experimental fact that the velocity constant for certain reactions of zero kinetic type, particularly hydrolytic changes catalysed by hydrogen ion, is linearly (rather than exponentially) related to the ionic strength. The hydrolysis of ethylene acetal is a case in point.* When catalysed by perchloric acid, or by mixtures of this with either acetic acid or monochloracetic acid, the unimolecular constant is directly proportional to $[H^+]$, at least up to concentrations of 0·05 gram molecule per litre. When uni-univalent salts are added to a solution containing a fixed concentration of acid, k is found to increase linearly with the total salt concentration, as shown in Table 7, where relative values of k are given taking the velocity in a salt-free solution as unity. The slope of the curve found by plotting k against [Salt] is constant in all cases, but assumes different values for different uni-univalent salts. The velocity is actually decreased by the addition of sodium picrate.

Table 7

Concentration of added electrolyte	Relative velocity of hydrolysis of ethylene acetal	
	In the presence of $NaClO_4$	In the presence of $NaNO_3$
0·00	1·000	1·000
0·05	—	1·039
0·10	1·165	1·080
0·15	1·239	1·123
0·20	1·326	1·172

* Brönsted and Grove, *J. Amer. Chem. Soc.*, **52**, 1394, (1930).

Marked specific effects have been observed also by Dawson and Key* in the study of the enolization of acetone in the presence of lithium, sodium, and potassium chlorides. The reaction between thiocyanate ions and monochloracetate ions is not influenced to an equal extent by potassium and sodium ions.†

Brönsted offers the following explanation for the proportionality between k and μ, and for the specificity of the salt effect. Considering the terms $(b+\beta_B-\beta_X)$ of equation (14), where b refers to the unionized solute, β_B to the hydrogen ion, and β_X to the complex, it can be seen that, if the term within the brackets is small,

$e^{\mu(b+\beta_B-\beta_X)}$ is nearly $1+\mu\,(b+\beta_B-\beta_X)$, hence

$$\frac{k_{\text{obs}}}{k_0} = 1+\mu\,(b+\beta_B-\beta_X). \qquad (15)$$

Now b is usually positive, and β for any ion is approximately inversely proportional to its radius, hence in hydrogen ion catalysis β_B will be greater than β_X, and a (linear) positive salt effect is to be anticipated. This expectation, as we have seen, is fulfilled in certain instances. Adopting the same argument, a linear and positive salt effect should be manifest in zero type reactions which are catalysed by hydroxyl ion. Generally speaking, this is not found.‡

The specificity of the electrolyte effect has been recorded in an empirical observation made by Grube and Schmid§ upon the hydrolysis of cyanamide by acids in concentrated salt solutions. They found that $\frac{k_{\text{obs}}}{k_0} = e^{Gc}$, where c is the concentration of salt, and G is a constant, specific for each electrolyte. This is formally similar to equation (14), and

* *Trans. Chem. Soc.*, 1239, 1248, (1928).

† Holmberg, *Z. physikal. Chem.*, **97**, 134, (1921).

‡ Cf. The depolymerization of diacetone—Koelichen, *ibid.*, **33**, 129, (1900); the decomposition of nitrosotriacetonamine—Francis and Geake, *Trans. Chem. Soc.*, **104**, 1722, (1913).

§ *Z. physikal. Chem.*, **119**, 19, (1926).

reduces to $k_{obs} = k_0(1+Gc)$ for small values of c (cf. equation (15)).

It will be already appreciated that the theory of Brönsted offers considerable latitude in the matter of interpretation. A comparison of the results given in Tables 1, 2, 3, and 4 with those of Tables 6 and 7 indicates that even in dilute solutions (not exceeding 0·2 molar) the effect produced upon the velocity of reaction by increasing the total concentration of electrolyte may be zero, exponential, or linear. The slight departures from the zero effect given in Table 3 suggest the existence of intermediate cases. In conjunction with this, it must be remembered that different uni-univalent electrolytes exert unequal influences on one and the same reaction. The case is therefore not yet proved that the extent of the disturbance in these reactions, even in very dilute solutions, depends solely upon the ionic strength. It would be very surprising in fact, if, contrary to experience, such were found to be the case; the electrical environment is but one of the conditions which can alter the velocity, and specific influences are bound to enter. Among other effects, the relative complexity of the reactants has been mentioned. The rate of hydration of hexa-urea chromic ion, for example, involving a series of changes in a complicated molecule, is probably governed by the stability of the activated ion, i.e. the Bjerrum condition may be expected to hold. It is not surprising, therefore, that the presence of small amounts of neutral salts has no effect on the velocity of this chemical change. The hydrolysis of ethylene acetal is more likely to depend upon the frequency of collisions between hydrogen ion and the solute—a quantity which is susceptible to the presence of ions of varying sizes and degrees of hydration. In solutions not so dilute as those with which we have been dealing, the specific influence of foreign ions is satisfactorily explained by the terms b, β_B, and β_X of equation (15).

An alternative explanation of the linear salt effect becomes possible if the anion, as well as hydrogen ion, exercises

a catalytic effect on these reactions. The results of Dawson and Lowson, however, on the rate of hydrolysis of ethyl acetate catalysed by mixtures of sodium chloride with hydrochloric acid and with monochloracetic acid show that this explanation is not sufficient.* By the theory of multiple catalysis, we have $v = k_{H^+}[H^+]+k_{HAc}[HAc]+k_{Ac^-}[Ac^-]$ for the rate of reaction in the presence of the organic acid. k_{HAc} has a value of $9{\cdot}0\times10^{-6}$ at 25° C., and may be assumed constant at all dilutions. Independent experiments show that k_{Ac^-} is negligibly small. The values of k_{H^+} computed upon this basis are given in Table 8. Up to an ionic strength of 0·063, this quantity is independent of the amount of added electrolyte, thus furnishing another example of a reaction of zero kinetic type for which the primary salt effect is nil. Beyond this point, k_{H^+} increases almost linearly

Table 8

0·1 N Hydrochloric acid		0·1 N Monochloracetic acid	
[NaCl]	$k_{H^+}\times10^3$	[NaCl]	$k_{H^+}\times10^3$
0	6·47	0	6·50
—	—	0·01	6·52
—	—	0·02	6·53
—	—	0·03	6·55
—	—	0·04	6·57
0·05	6·57	0·05	6·58
0·10	—	0·10	6·66
0·20	6·87	0·20	6·82
0·30	—	0·30	6·98
0·50	7·35	0·50	7·32
1·00	8·09	1·00	8·14
2·00	9·85	2·00	9·90
3·00	11·80	3·00	11·80
4·00	14·10	4·00	14·10

with the total concentration of salt, at least up to a concentration of 2 gram molecules per litre. These results are in excellent agreement with equation (15). Dawson's work on the acetone-iodine reaction reveals a similar behaviour until an ionic strength of about 3 is reached.

* *Trans. Chem. Soc.*, 393, (1929).

A linear salt effect is not infrequently met with in reactions between ions and neutral molecules, but several instances are known of carefully investigated reactions in this category for which there appears to be no clear connexion between velocity and ionic strength.*

Review of Brönsted's Theory.

The work of Brönsted and his collaborators deals with the part played by electrolytes in altering the velocity of ionic reactions in aqueous solution. The theory postulates the formation of a charged intermediate complex, which exists in thermodynamic equilibrium with the reactants. Expressions for the velocity of reaction are then deducible in terms of the activities of the reactants, for determining which the theory of Debye and Hückel is introduced. By predicting the direction (and in many cases the magnitude) of the electrolyte effect, by distinguishing between primary and secondary disturbances, and by establishing the principle of ionic type, Brönsted has brought a long-delayed theoretical illumination on to a large mass of experimental material. The theory is admittedly incomplete in that it ignores all non-thermodynamic factors. Furthermore, its validity rests largely on assumptions made concerning the activity coefficient of a fugitive complex which eludes direct investigation.

The theory treats comprehensively of the factors which modify the velocity of an ionic reaction from that 'normal' value which it would possess in an ideally dilute solution, but tells us nothing about its absolute magnitude. This aspect of the problem must now be discussed.

The Statistical Mechanics of Ionic Reactions.

The problem of ionic bimolecular reactions has been approached from the point of view of statistical mechanics

* Åkerlöf, *Z. physikal. Chem.*, **98**, 260, (1921); Garrett and Lewis, *J. Amer. Chem. Soc.*, **45**, 1091, (1923).

by Christiansen.* As shown in Chapter IV, the instantaneous velocity v of a bimolecular reaction in an inert solvent at great dilutions is

$$v = c_A c_B Z_{AB} \sqrt{T}\, e^{-E/RT}, \tag{16}$$

where v is the number of gram molecules decomposing per second per litre, and Z_{AB} is a constant characteristic of the reaction and numerically equal to

$$\sigma_{AB}^2 \frac{N_0}{1000} \sqrt{\left\{8\pi R\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}}.$$

Ignoring the effects due to orientation and to deactivations, we must now inquire how this expression must be modified for the case where the reacting molecules are electrically charged.

In the deduction of the collision formula by the kinetic theory of gases, it is assumed that the concentration of molecules B in the neighbourhood of any given molecule A is the same as that in the bulk of the gas—an assumption which cannot be true when ions in solution rather than neutral molecules in gases are considered. The theory of strong electrolytes, as we have seen, is based upon the recognition of an uneven distribution of ions. When thermodynamic equilibrium is attained in the immediate vicinity of any ion, the Boltzmann distribution law states that the mean 'concentration' c of ions B at a distance r from an ion A is

$$c = c_B e^{-(z_B \epsilon / kT)\phi_A}, \tag{17}$$

where ϕ_A is the average electrostatic potential at the distance r from the central ion A, c_B is the bulk concentration of ions B, z_B their valency, and ϵ the electronic charge. The distribution, moreover, of translatory energy is uniform throughout the solution, since the motion of a swarm of molecules into a field of force alters the density but not the kinetic energy of the swarm.† It follows that the number

* *Z. physikal. Chem.*, **113**, 35, (1924).

† Jeans, *The Dynamical Theory of Gases*, 4th ed., p. 96, (1925).

of collisions between ions A and B will be given by the gas collision formula, corrected by the term $e^{-(z_B\epsilon/kT)\phi_A}$. The velocity of reaction then becomes

$$v = c_A c_B Z_{AB} \sqrt{T} e^{-E/RT} e^{-(z_B\epsilon/kT)\phi_A}. \qquad (18)$$

Z_{AB}, as before, is a constant characteristic of the masses and diameters of the ions.

Two conditions must be fulfilled before chemical reaction can set in. In the first place, the ions must approach each other to within a certain critical distance, which is the lower limit of r. Now this depends upon the total concentration of electrolyte, so that the collision frequency will vary with the ionic strength. In the second place, the kinetic energy of the colliding molecules must equal or exceed the energy of activation; this is not influenced by the ionic strength.

By inserting into equation (17) an approximate expression for the electrical potential ϕ_A, Christiansen has shown that the collision theory, modified in this way, is in agreement with Brönsted's theory. The treatment outlined above, however, makes no allowance for the possible formation of a stable complex, although the conditions holding in the case of an unstable complex are covered in Christiansen's fuller treatment by including the probability of deactivation. Equation (17) accordingly gives us the upper limit to the velocity of reaction which is possible under the most favourable conditions of translatory activations. It will be shown later that the observed rates of certain reactions are greater even than this.

The following deduction of the Brönsted relation from a statistical mechanical basis is due to Scatchard.* It has certain advantages over Christiansen's earlier derivation, although yielding finally the same result. It is immaterial whether we think of the complex as a physical constellation or as an activated chemical compound. Provided the probability of its existence, while small, differs but slightly

* *Chemical Reviews*, **10**, 229, (1932).

from that of other complexes, the concentration of the complex is given by the relation

$$c_X = K'' c_A c_B e^{-(z_B \epsilon / kT)\phi_A}. \tag{19}$$

The rate of reaction being proportional to c_X (equation (6)), we have

$$v = k' c_X = k' K'' c_A c_B e^{-(z_B \epsilon / kT)\phi_A} e^{-E/RT}, \tag{20}$$

which is similar to equation (18) except that it does not identify the proportionality factor with the collision frequency. Using the value given by equation (1) for the electrostatic potential, we have

$$c_X = K'' c_A c_B e^{\{-(\epsilon^2 z_A z_B / DkTr) e^{-\kappa r}(e^{\kappa a}/1+\kappa a)\}}. \tag{21}$$

At infinite dilution ($\kappa = 0$), the concentration of each species is equal to its activity, and the exponential term reduces to $-\epsilon^2 z_A z_B / DkTr$, so that

$$a_X = K'' a_A a_B e^{-\epsilon^2 z_A z_B / DkTr}. \tag{22}$$

Remembering the definition of the activity coefficient as $f = a/c$,

$$\ln \frac{f_A f_B}{f_X} = \ln \frac{c_X}{c_A c_B} - \ln \frac{a_X}{a_A a_B} = \frac{\epsilon^2 z_A z_B}{DkTr}\left[1 - \frac{e^{-\kappa r} e^{\kappa a}}{1+\kappa a}\right]. \tag{23}$$

We may now either expand in series, omitting higher terms, or make the assumption that a and r must be very nearly equal. It is in all probability justifiable to assume that the distance (r) of approach of two ions which characterizes the formation of a complex cannot differ much from the closest distance (a) of approach of other ions to an A ion. When $r = a$, we have

$$\ln \frac{f_A f_B}{f_X} = \frac{\epsilon^2 z_A z_B}{DkT} \frac{\kappa}{1+\kappa a}. \tag{24}$$

A further approximation becomes legitimate, since we may ignore the term κa in comparison with unity, and write

$$\ln \frac{f_A f_B}{f_X} = \frac{\epsilon^2 z_A z_B}{DkT} \kappa. \tag{25}$$

Combining with (7), which is the general equation of the intermediate-complex theory,

$$v = k_0 c_A c_B e^{(\epsilon^2 z_A z_B/DkT)\kappa}$$

or

$$\ln \frac{k_{\text{obs}}}{k_0} = \frac{\epsilon^2 z_A z_B}{DkT} \kappa.$$

Employing the value of κ given by equation (2), it follows that

$$\ln \frac{k_{\text{obs}}}{k_0} = 2\alpha z_A z_B \sqrt{\mu}, \tag{26}$$

where α, as before, is

$$\frac{N_0^2 \epsilon^3}{(DRT)^{1.5}} \sqrt{\left(\frac{2\pi}{1000}\right)}.$$

This is identical with equation (11), as might have been anticipated from the fact that the Debye-Hückel expression for the electrostatic potential has been incorporated in the thermodynamic treatment of Brönsted and in the statistical mechanical treatment of Christiansen.

Reactions between ions and non-electrolytes, in solutions containing low concentrations of each, have been dealt with along similar lines by Scatchard.* By means of relations deduced by Gross† and by Debye‡ for the influence of an electrolyte (A) upon the activity of a non-electrolyte (B), it can be shown that the concentration (C_r) of the non-electrolyte at a distance r from an ion is

$$C_r = C_\infty^{-R^4/r^4}. \tag{27}$$

C_∞ is the concentration at an infinite distance:

$$R^4 = \frac{\epsilon^2 z_A^2 \delta_B}{8\pi N_0 kT D_0^2} \tag{28}$$

and

$$\delta_B = \frac{D - D_0}{c_B}. \tag{29}$$

* *Loc. cit.* † *Monatsh.*, **53**, 445, (1929).
‡ *Z. physikal. Chem.*, **130**, 56, (1927).

Since R is independent of the concentration of the electrolyte, we have, for the concentration of the complex,

$$C_X = K'C_A C_r = K'C_A C_\infty e^{-R'/r^2} = KC_A C_\infty = KC_A C_B f_B. \quad (30)$$

The change in rate of a reaction between an ion and an uncharged molecule caused by the addition of an electrolyte should thus be equal to the change in the activity coefficient of the uncharged molecule. This is identical with Brönsted's conclusion (equation (14)), since in dilute solutions β_B and β_X are probably equal.

To the question of how the velocity of a completely non-ionic reaction is influenced by the presence of electrolytes, the answer given by the statistical mechanical inquiry is that $\ln k$ should vary as an approximately linear function of the ionic strength. Reference will be made later to experiments which confirm this conclusion in a striking manner.

Scatchard has approached the problem of solvent action by attempting to discover the manner in which the velocity of a reaction is changed when the sole variant is the dielectric constant of the medium. The inquiry leads to interesting conclusions, but it is difficult to conceive of experimental conditions complying with the assumptions upon which the calculations are based.

The Relation between Critical Increment and Ionic Strength.

The effect of temperature on the velocity of an ionic reaction will in general be a profound one. Regarded from the standpoint of thermodynamics, a change in temperature will shift the position of equilibrium and will modify the activity coefficients in terms of which the equilibrium is defined. From the point of view of statistical mechanics, the effect of a change in temperature is to alter the number of activated molecules, in the Arrhenius sense, and by an adjustment of the most probable distribution of the ions to modify the collision frequency also. Now although ions of

opposite sign congregate near one another as a result of electrostatic attraction, they do not collide with any greater violence than they would in the absence of electrostatic attraction. This, as we have seen, is a salient point in Christiansen's theory of ionic reactions. It has been rightly emphasized* that its omission violates an important principle of statistical mechanics. Accepting as an hypothesis that activation in ionic reactions is due to the translatory energy of the colliding ions, it follows that the energy of activation must be independent of the ionic strength. Whether the observed critical increment will prove to be so remains to be seen.

The problem may be suitably approached by considering the equation of Brönsted which applies to solutions so dilute that the limiting law of Debye and Hückel holds good.

$$\ln k_{\text{obs}} = \ln k_0 + 2\alpha z_A z_B \sqrt{\mu}. \qquad (11)$$

k_0 is simply the extrapolated value of the velocity constant corresponding to zero ionic strength; α has its usual significance. Differentiating with respect to T, and multiplying each term by RT^2:

$$E_{\text{obs}} = E_0 - 3\alpha z_A z_B \sqrt{\mu}\left\{RT^2 \frac{d \ln D}{dT} + RT\right\}. \qquad (31)$$

Reactions between ions and neutral molecules (z_A or z_B is zero) should therefore have a critical increment independent of the ionic strength. There is a large mass of data which might be quoted as vindicating this conclusion. Many examples have been given in earlier chapters. The effect seems to be fairly general even when the total concentration of electrolyte far exceeds that for which the limiting law can be expected to apply. Table 9 shows that the addition of large amounts of univalent salts does not change the critical increment of the lactonization of γ-hydroxyvaleric acid.

* La Mer, *Chemical Reviews*, **10**, 179, (1932): Brönsted, *ibid.*, **5**, 231, (1928); Wynne-Jones, *Trans. Chem. Soc.*, 1230, (1928).

Table 9

Lactonization of γ-Hydroxyvaleric Acid, Catalysed by 0·5 N Hydrochloric Acid in the Presence of Salts

KCl	$E_{25\text{-}36°\,C.}$	LiCl	$E_{25\text{-}35°\,C.}$
0	15,220	0·391	15,030
0·671	15,020	0·781	15,170
1·341	14,880	1·172	14,790
2·012	15,000	1·562	15,440
2·682	15,000	1·953	15,240

Garrett and Lewis, *J. Amer. Chem. Soc.*, **45**, 1091, (1923).

Returning to equation (31), it will be observed that when both reactants are charged, E_{obs} will vary with $\sqrt{\mu}$ in a way which depends, in the first place, upon the relative magnitudes of the terms $RT^2(d \ln D/dT)$ and RT. Since the dielectric constant decreases with a rise in temperature, these terms will be opposite in sign. In the case of water at 25° C., they are roughly −930 calories and +590 calories, hence as a special case we may write

$$E_{\text{obs}} = E_0 + 3\alpha z_A z_B \sqrt{\mu} \text{ (340).} \qquad (32)$$

The critical increment should thus increase or decrease with increasing concentration, according as the ions are similarly charged or oppositely charged. α for water at 25° C. has a numerical value of 1·158. The difference between the critical increment at infinite dilution and the value at an ionic strength of 0·2 is consequently $530 z_A z_B$ calories. This falls within the limit of experimental error when $z_A z_B$ is 1, and possibly 2, but should be detectable experimentally for reactions of higher ionic types.

The influence of temperature upon the velocity of ionic reactions has been very inadequately studied. As far as the work hitherto accomplished allows us to decide, these expectations are confirmed by experiment. Kappanna* gives the following results for the reaction between thiosulphate ions and monobromacetate ions (Table 10). Taking 15,900

* *J. Indian Chem. Soc.*, **6**, 451, (1929); Kappanna and Patwardhan, *Rec. trav. chim. Pays-bas*, **51**, 379, (1932).

Table 10

$S_2O_3^{--}+CH_2Br.COO^- \rightarrow CH_2(S_2O_3)^-.COO^-+Br^-$.

μ	$E_{30\text{-}50°C.}$
0·0025	15,660
0·0050	16,290
0·0070	16,120
0·0085	15,920
0·0100	15,520

calories as the average value of E, the maximum experimental deviation from this is $\pm$400 calories, which is greater than the variation of 225 calories predicted by equation (31). Over a wider range of concentration, similar effects have been found in the case of chloracetate-thiosulphate reaction.*

Table 11

Total ionic concentration	$k_{60°C.}/k_{50°C.}$	$k_{70°C.}/k_{60°C.}$
0·02	1·98	2·09
0·04	1·96	1·99
0·08	2·02	2·04
0·10	2·02	2·08
0·15	2·04	2·02

It does not appear that the combined influence of temperature and ionic strength has been studied in the case of reactions of higher ionic type.

The temperature coefficient of the following non-ionic reaction

$$3HNO_2 \rightarrow HNO_3+2NO+H_2O$$

has been carefully measured over a wide range of electrolyte concentration by Abel, Schmid, and Römer,† whose results are summarized in the form

$$\log_{10}k = -\frac{6,250}{T}+22·65+0·078j.$$

The total ionic concentration (j) was varied from 0·6 to 4·0. Within this fairly wide region, then, there is an invariant

* Kappanna, *J. Indian Chem. Soc.*, **5**, 293, (1928).

† *Z. physikal. Chem.*, **148**, 337, (1930).

(and composite) critical increment of 28,500 calories. At each temperature, $\log k$ is proportional to the ionic strength—as predicted by the statistical mechanical theory.

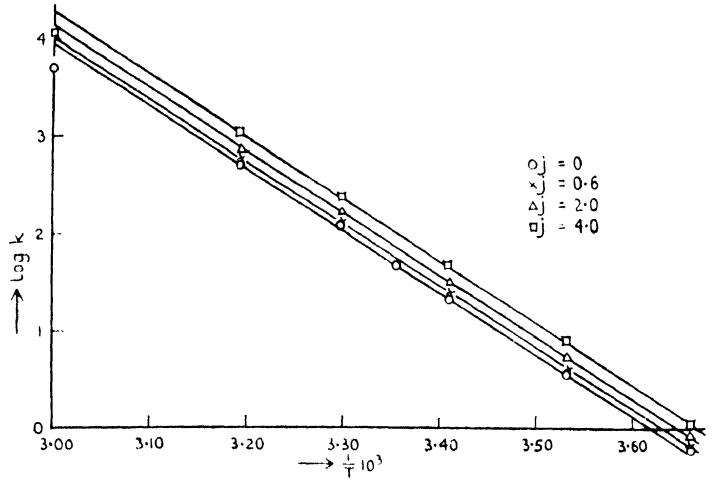


FIG. 2.

It has been found that, just as E for non-ionic reactions is uninfluenced by the addition of electrolytes, so E for reactions involving ions is frequently not influenced by the addition of non-electrolytes (Table 12).

Table 12

Reaction	Non-electrolyte added	E
Hydrolysis of acetyl-glycine by 0·5 N hydrochloric acid (Escolme and Lewis, *Trans. Faraday Soc.*, **23**, 651, (1927))	None	22,300
	12·6% glycerol	21,800
	31·5% glycerol	21,700
	50·4% glycerol	21,800
	8·1% propyl alcohol	22,500
	20·2% propyl alcohol	21,900
	32·3% propyl alcohol	21,900
Hydrolysis of raffinose by 0·1 N hydrochloric acid (Stothart, *Thesis*, Liverpool, (1928))	None	25,330
	12·6% glycerol	25,510
	31·5% glycerol	25,270
	50·4% glycerol	25,210
	10·0% glucose	25,510
	20·0% glucose	25,580
	30·0% glucose	25,570

Less Simple Ionic Reactions.

Most of the reactions hitherto considered have been those which follow a fairly straightforward bimolecular course in dilute solutions. Ionic reactions are usually much more complicated; the number which has been studied is very large. All that is possible here is to demonstrate, by examining a few illustrative examples, the general principles upon which all the others are interpreted. We shall treat of the action of halogens, in aqueous solution, upon oxalic acid, arsenious acid, hydrogen peroxide, and phenylpropiolic acid. These are all retarded by hydrogen ion, a fact which at once suggests that the active agent is not the free halogen molecule, but one or more of the products of hydrolysis: $X_2+H_2O \rightarrow HXO+X^-+H^+$. This contention has been substantiated in all the following instances.

A. *The Reaction between Bromine and Oxalic Acid.*

$$(COOH)_2+Br_2 \rightarrow 2HBr+2CO_2.$$

Roloff* discovered that the rate of reaction was retarded by bromide ions and by hydrogen ions, and concluded that the bromine molecules were attacked by oxalate ions. Berthoud and Bellenot,† by replacing oxalic acid by neutral oxalates, arrived at the same conclusion, and showed, further, that the velocity had the exceptionally high temperature coefficient of 5·99. From a study of the inhibitive action of various acids, examined under a great range of experimental conditions, Jozefowicz‡ inferred that the measurable reaction is

$$HC_2O_4^-+HOBr \rightarrow H_2O+2CO_2+Br^-.$$

His rather incomplete analysis of the kinetic data, however, led to certain inconsistencies in the final results, which were not removed until the whole matter was reinvestigated by Griffith, McKeown, and Winn.§ These authors agree with

* *Z. physikal. Chem.*, **13**, 346, (1894).
† *J. Chim. physique*, **21**, 308, (1924).
‡ *Rocz. Chem.*, **8**, 123, (1928). § *Trans. Faraday Soc.*, **28**, 107, (1932).

Jozefowicz in regarding the velocity of reaction as being due entirely to the change written above. In their hands, this relatively simple mechanism has been shown to account fully for all the experimental facts. Rates have been measured at three temperatures, and in solutions of varying composition for which μ ranged from 0·8 to nearly zero.

The kinetic equations are very complicated, yielding finally the bimolecular constants given in Table 13. These values refer to 21·5° C., and are given in litres per gram molecule per minute. There is a pronounced linear salt effect, and a specific influence of sodium and potassium ions.

Table 13

μ	In presence of KBr $k \times 10^{-4}$.	In presence NaBr $k \times 10^{-4}$.
0·00	(1·89)	(1·89)
0·01	1·90	1·90
0·05	1·945	1·90
0·1	2·01	1·92
0·2	2·11	1·945
0·3	2·195	1·99
0·5	2·41	2·16

The high temperature coefficient recorded by Berthoud and Bellenot is shown to be a composite value involving the equilibrium constant (K) for the hydrolysis of bromine. The product Kk was found by Griffith, McKeown, and Winn to increase 5·95 times for a rise of 10°, this value being independent of the total concentration of electrolyte. Since the temperature coefficient of K is 2·42,* that for k must be 2·52, which corresponds to a critical increment of 15,400 calories.

B. *The Reaction between Chlorine and Oxalic Acid.* An analogous mechanism has been found to apply to this reaction,† the velocity of which is governed by the bi-

* Jones and Hartman, *Trans. Amer. Electrochem. Soc.*, **30**, 295, (1916); Bray and Conolly, *J. Amer. Chem. Soc.*, **33**, 1485, (1911).

† Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, **28**, 518, (1932).

molecular process

$$HC_2O_4^- + HOCl \rightarrow H_2O + 2CO_2 + Cl^-.$$

The specific rate is about 28 times as slow as that of the bromine-oxalate reaction; E is 15,000 calories.

C. *The Reaction between Iodine and Oxalic Acid.* Depending on the relative concentrations of iodine and potassium iodide, the rate of the thermal oxidation of oxalic acid by iodine is unimolecular or semimolecular with respect to the halogen. The varied and interesting observations which have been made are best interpreted by postulating the existence of two independent, concurrent reactions.* The unimolecular component is in all respects analogous to the reaction between oxalic acid and the other halogens, the measurable process being

$$HC_2O_4^- + HOI \rightarrow H_2O + 2CO_2 + I^-.$$

Rather surprisingly, the critical increment (18,550) is greater than that for the two other reactions, and the velocity is somewhat lower. The mechanism of the semimolecular process indicates that the active agent is the iodine atom, as in the photo-oxidation of oxalic acid. The simplest kinetic interpretation of the results is that a chain reaction takes place in the following manner:

$$I + C_2O_4^{--} \xrightarrow{k'} I^- + C_2O_4^-$$
$$C_2O_4^- + I_2 \rightarrow 2CO_2 + I + I^-.$$

Calculation of the velocity of this reaction necessitates a knowledge of the degree of dissociation of iodine in aqueous solution, which is not at present available. Griffith and McKeown have estimated that the approximate value of k' at 45° C. is $7{\cdot}5 \times 10^4$ seconds, E' being 17,800 calories. Chains of about a million cycles are thus indicated.

Reference may here be made to another example of a *thermal* reaction in solution involving free atoms.† The

* Griffith and McKeown, *ibid.*, **28**, 752, (1932).

† Polissar, *J. Amer. Chem. Soc.*, **52**, 956, (1930).

uncatalysed decomposition of ethylene iodide in carbon tetrachloride solution at temperatures ranging from 40° to 150° C. is negligibly slow:

$$CH_2I.CH_2I \rightarrow CH_2{:}CH_2+I_2.$$

The reaction, however, is autocatalytic, and over a very wide range of iodine concentration the velocity is expressed by the equation

$$\frac{d[I_2]}{dt} = k[C_2H_4I_2]\,[I_2]^{\frac{1}{2}}.$$

Several mechanisms might be suggested, all of which, as Polissar points out, indicate the action of iodine atoms. Expressed in minutes, k is equal to $4{\cdot}4\times10^{12}\times\sqrt{T}\times e^{-29,500/RT}$.

Assuming the heat of dissociation of iodine in this solvent to be equal to the value in the gas phase, it can be shown that Polissar's hypothesis leads to calculated rates lying close to the observed values. The energy of activation for the reaction involving iodine atoms is about 12,500 calories.

D. *The Reaction between Iodine and Arsenious Acid.*

$$H_3AsO_3+I_3^-+H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} H_3AsO_4+2H^++3I^-. \qquad (a)$$

Roebuck* and Bray,† from a study of this reaction at 0° C., have shown that

$$-\frac{d[H_3AsO_3]}{dt} = k_1\frac{[H_3AsO_3][I_3^-]}{[H^+][I^-]^2} \qquad (b)$$

and

$$+\frac{d[H_3AsO_3]}{dt} = k_2[H_3AsO_4][H^+][I^-]. \qquad (c)$$

The ratio k_1/k_2 was found to be 0·15, agreeing closely with the value of 0·16 determined for the equilibrium constant

$$K = \frac{[H^+]^2[I^-]^3[H_3AsO_4]}{[I_3^-][H_3AsO_3]}. \qquad (d)$$

Bray‡ accepts the mechanism of Roebuck as the only

* *J. Physical Chem.*, **6**, 365, (1902); *ibid.*, **9**, 727, (1905).
† *Ibid.*, **9**, 578, (1905).
‡ *Chemical Reviews*, **10**, 161, (1932).

reasonable one. This assumes the two following equilibria to be reached very rapidly,

$$I_2+H_2O \rightleftarrows HIO+I^-+H^+; \qquad K_1=\frac{[HIO][I^-][H^+]}{[I_2]} \qquad (e)$$

$$I_3^- \rightleftarrows I_2+I^-; \qquad K_2=\frac{[I_2][I^-]}{[I_3^-]}, \qquad (f)$$

and the observed rate to be governed entirely by the bimolecular reaction between arsenious acid and hypoiodous acid:

$$H_3AsO_3+HIO \xrightarrow{k} H_3AsO_4+H^++I^-. \qquad (g)$$

According to this mechanism,

$$-\frac{d[I_3^-]}{dt}=-\frac{d[H_3AsO_3]}{dt}=k[H_3AsO_3][HIO]$$

$$=kK_1\frac{[H_3AsO_3][I_2]}{[H^+][I^-]}=kK_1K_2\frac{[H_3AsO_3][I_3^-]}{[H^+][I^-]^2}. \qquad (h)$$

By comparing equations (*b*) and (*h*), we see that $k=k_1/K_1K_2$, so that it becomes possible to evaluate the bimolecular coefficient (k) from a knowledge of the observed coefficient (k_1) and the equilibrium constants K_1 and K_2. Liebhafsky* takes K_1 at 0° C. to be 9×10^{-15}, and K_2 to be $7{\cdot}2\times10^{-4}$.† Using Roebuck and Bray's figure for k_1, which is $1{\cdot}57\times10^{-5}$ litres per gram molecule-second, k becomes $2{\cdot}42\times10^{12}$. This, as Liebhafsky points out, is of the same order of magnitude as the collision frequency calculated by means of the formula for gases—a result very similar to that obtained by him in the case of the reaction between hydrogen peroxide and the iodate ion‡—and indicates that every collision between the reacting molecules results in chemical change, independent of any energetic restrictions. Another interesting feature of this reaction is that, upon approximate estimates, it appears to have a negative temperature

* *J. Physical Chem.*, **35**, 1648, (1931).
† Jones and Kaplan, *J. Amer. Chem. Soc.*, **50**, 1845, (1928).
‡ *Ibid.*, **53**, 896, (1931).

coefficient, the Arrhenius E being about $-7{,}700$ calories. Unfortunately, these figures are not very reliable, so that a discussion based upon them at this stage is premature. It is reassuring to learn that Liebhafsky's investigations are being continued, for they have every prospect of affording interesting information on the frequency of collisions in liquid systems. In the meantime, it may be mentioned that the results as they stand at present are not difficult of interpretation. If the measurable reaction is determined by collisions between water molecules and molecules of the complex H_3AsO_3,HIO, a theoretical collision frequency somewhat greater than $2{\cdot}42\times10^{12}$ becomes possible, and a negative temperature coefficient is also to be expected.

E. *The Reaction between Bromine and Hydrogen Peroxide.* The manner in which bromine attacks hydrogen peroxide in aqueous solution is given by the stoichiometric equations

$$H_2O_2+2Br^-+2H^+ \rightarrow Br_2+2H_2O \qquad (a)$$

$$H_2O_2+Br_2 \rightarrow O_2+2Br^-+2H^+. \qquad (b)$$

The velocities of these reactions have been found to be*

$$-\frac{d[H_2O_2]}{dt} = +\frac{d[Br_2]}{dt} = k_1[H_2O_2][Br^-][H^+] \qquad (c)$$

and

$$-\frac{d[H_2O_2]}{dt} = -\frac{d[Br_2]}{dt} = k_2\frac{[H_2O_2]\,[Br_2]}{[Br^-][H^+]}. \qquad (d)$$

The decomposition of hydrogen peroxide is thus catalysed by both bromine ions and bromine molecules. The concentration of bromine molecules, by reaction (a), increases with time, and by reaction (b) decreases with time. The reverse is true of bromine ions. A certain stage will consequently be reached at which these opposing influences exactly balance one another, and the composition of the catalyst will attain a stationary value. This condition has been termed the steady state, and the reactions which lead

* Bray and Livingston, *J. Amer. Chem. Soc.*, **45**, 1251, (1923); *ibid.*, **50**, 1654, (1928); Livingston and Bray, *ibid.*, **45**, 2048, (1923); Livingston, *ibid.*, **48**, 53, (1926).

to it have been termed compensating reactions.* At the steady state, the two rates given by equations (*c*) and (*d*) must be equal, hence

$$\frac{k_1}{k_2} = R = \frac{[Br_2]}{[Br^-]^2[H^+]^2}. \qquad (e)$$

This relation has been verified at 25° C., where k_1 and k_2, corrected for salt effects, are $3{\cdot}7\times10^{-4}$ and $3{\cdot}0\times10^{-4}$ respectively (units of seconds and gram molecules per litre). k_1/k_2 is thus 1·23; R was found to be *ca.* 1·45. It will be observed that, at the steady state, the reaction must be unimolecular with respect to the hydrogen peroxide, since the effective concentration of catalyst is fixed. The reaction itself, however, is anything but unimolecular. A totally unsuspected complexity here lies concealed under an apparent kinetic simplicity. It indicates the fallacy of ascribing an order to a reaction by seeing with which of the kinetic equations the results fit best. Expressing the hydrolysis of bromine in the usual way,

$$Br_2+H_2O \rightleftarrows HBrO+Br^-+H^+; \quad K = \frac{[HBrO][Br^-][H^+]}{[Br_2]}, \quad (f)$$

we complete the experimental relations which are necessary in formulating the kinetics of this reaction. If the measurable reaction $H_2O_2+H^++Br^- \rightarrow HBrO+H_2O$ be followed by the rapid attainment of stage (*f*), the velocity of reaction (*a*) can be accounted for. The stoichiometric and kinetic equations (*b*) and (*d*) can be reconciled by postulating the process which determines the rate to be

$$H_2O_2+HBrO \xrightarrow{k_3} O_2+Br^-+H^++H_2O. \qquad (g)$$

This gives us

$$-\frac{d[H_2O_2]}{dt} = -\frac{d[HBrO]}{dt} = k_3[H_2O_2][HBrO] = k_3K\frac{[H_2O_2][Br_2]}{[Br^-][H^+]},$$

* Bray, *loc. cit.*; Abel, *Z. Elektrochem.*, **14**, 598, (1908).

from which, as in the previous instance, it is possible to evaluate the bimolecular velocity constant (k_3). At 25° C., we have $k_3 = k_2/K = 3{\cdot}0\times10^{-4}/5{\cdot}2\times10^{-9} = 5{\cdot}8\times10^{+4}$ litres per gram molecule-second.

F. *The Reaction between Iodine and Hydrogen Peroxide.* The work of Brode,* Magnanini,† Noyes,‡ and Abel,§ indicates that the very simple relationship established by Walton (Table 4) for the kinetics of this reaction holds only in neutral solutions of iodides. In the presence of acid, the velocity at any instant is a complicated function of the concentrations. Without entering into a full discussion of the mechanism which is at present accepted, it may be mentioned that there is evidence for believing that at least three catalysts affect the decomposition of hydrogen peroxide in the presence of aqueous iodine. They are

$$H_2O_2+I^- \rightarrow H_2O+IO^- \qquad (a)$$

$$H_2O_2+IO^- \rightarrow H_2O+I^-+O_2 \qquad (b)$$

$$H_2O_2+HIO \rightarrow H_2O+H^++I^-+O_2. \qquad (c)$$

The velocity constants, determined indirectly, at 25° C. are (l./g.m.s.)

$$k_b = ca.\ 1{\cdot}7\times10^9$$

$$k_c = 5{\cdot}5\times10^3.$$

The difference in catalytic activity of hypoiodous acid and its anion is rather striking, and, as far as can be ascertained, has no parallel. But it is admitted by the investigators that neither of these values is very reliable. A reinvestigation by Liebhafsky‖ has yielded the following results:

$$k_b = 2\times10^{11};\ k_c = 2{\cdot}2\times10^3.$$

It seems quite clear that the reaction measured by Walton was reaction (*a*), followed by a second and fast change, which is perhaps reaction (*b*). In other words, the reaction

* *Loc. cit.* † *Gazz. chim. ital.*, **21**, 476, (1891).

‡ *Z. physikal. Chem.*, **19**, 601, (1896).

§ *Ibid.*, **136**, 161, (1928); *ibid.*, **96**, 1, (1920); *Z. Elektrochem.*, **14**, 598, (1908).

‖ *J. Amer. Chem. Soc.*, **54**, 3499, (1932).

between hydrogen peroxide and the iodide ion in neutral solution is a chain reaction of two cycles. This is probably the explanation for the inapplicability of the Arrhenius equation to Walton's results (Table 14). The published value of the Arrhenius term A is 6,864, which corresponds to $E = 13{,}590$. This, however, is just the mean of three values which definitely fall with a rise in temperature.

Table 14

$t°$ C.	$k_{observed} \times 10^3$ (minutes^{-1} g.m./l.)	$E_{Arrhenius}$
15	6·35	14,240
25	14·12	13,580
35	30·00	12,490
45	62·50	

The thermal decomposition of hydrogen peroxide has many of the features of a chain reaction, and it is a matter for surprise that it has not been studied from this angle. The uncatalysed decomposition is exothermic, Q being 23,060 calories per gram molecule,* and exhibits many kinetic irregularities, among which may be noted the sensitiveness of the rate to the presence of dust particles, the nature of the walls of the vessel, and adventitious impurity.† The high photon efficiency‡ and the action of inhibitors§ establish the chain character of the photochemical reaction.

G. *The Reaction between Chlorine and Hydrogen Peroxide.* There is much similarity between this and the case of bromine. A stationary concentration of the halogen molecules and ions is reached, and a steady rate of decomposition sets in. Budge‖ has substantially confirmed the earlier work of Livingston and Bray,** and finds a temperature coefficient

* Thomsen, *Thermochemistry*, p. 194, London (1908).

† See p. 34; also Clayton, *Trans. Faraday Soc.*, **11**, 164, (1915); J. Williams, *ibid.*, **24**, 245, (1928); Pana, *ibid.*, **24**, 486, (1928).

‡ Kornfeld, *Z. wiss. Phot.*, **21**, 66, (1921).

§ Anderson and Taylor, *J. Amer. Chem. Soc.*, **45**, 1210, (1923).

‖ *Ibid.*, **54**, 1792, (1932).

** *Ibid.*, **47**, 2069, (1925).

for the reaction, in the presence of concentrated hydrochloric acid, of 20,750 calories. If this is any indication of the energy required in the separate stages, it is seen that a molecule of hydrogen peroxide in decomposing liberates more than enough energy to activate a fresh molecule, and a reaction chain becomes possible. The limiting value of the velocity constant of the following reaction is not known,

$$H_2O_2+HClO \rightarrow O_2+Cl^-+H^++H_2O,$$

but in the presence of 4·8N hydrochloric acid at 25°, k is $1{\cdot}3\times10^4$ (l./g.m.s.).

H. *The Reaction between Iodine and β-Phenylpropiolic Acid.* In the presence of potassium iodide, this reaction is bimolecular with respect to the acid and the total iodine.* It appears, however, that molecular iodine does not add on to the acid, the reaction at ordinary concentrations taking place between the tri-iodide ion and the organic acid or its anion:†

$$C_6H_5C{\equiv}C.COO^-+I_3 \rightarrow C_6H_5CI{=}CI.COO^-+I^-.$$

At dilutions exceeding about 400 litres per gram molecule, there comes into prominence a very rapid reaction, apparently initiated by collisions between molecules of hypoiodous acid and phenylpropiolate ions. The kinetics of the reaction are summarized by the equation

$$-\frac{d[I_2]}{dt} = k_1[A][I_3^-]+k_2[A][HOI].$$

k_1 is smaller than, and k_2 is greater than, the normal values.

Molecular halogens are reluctant to attach themselves to unsaturated compounds by a simple mechanism. Bromine is not added on directly to cinnamic acid, but hypobromous acid has been suspected of playing a role in the bromination in acetic acid solution.‡

Collecting the evidence afforded by the foregoing examples,

* James and Sudborough, *Trans. Chem. Soc.*, **91**, 1037, (1907).
† Moelwyn-Hughes and Legard, *ibid.*, 424, (1933).
‡ Williams, *ibid.*, 979, (1932).

it may be said that most of the facts may be suitably interpreted by regarding the active agent as the molecule HXO or its anion (X represents a halogen atom). The velocities of the reactions between HXO and oxalic acid, arsenious acid, hydrogen peroxide, and β-phenylpropiolic acid are so great that they lend themselves to measurement only by indirect means. A complete comparison of the various rates is not yet possible, since the temperature coefficient has not been determined for each reaction, but sufficient data are available to show that the catalytic activity of the halogens diminishes in the order $I > Br > Cl$. The decomposition of di-isopropyl ether in the gaseous state is catalysed by iodine, and to a smaller extent by bromine; chlorine has little influence.* As already pointed out (p. 96), this order of catalytic efficiency is persistently encountered whether the halogen atom is free or combined.

The Effect of Substituent Groups on the Velocity of Ionic Reactions.

The change in the rate of ionic reactions attending the introduction of new groups into one or both of the reacting molecules has been studied by a large number of investigators. In fact, this approach to the problem has long been one of the most popular from the experimental side. Lengfeld, for example, measured the 'stability' of alkyl halides by comparing the rates at which they react with alkalis and with silver nitrate.† For reasons which have already been given, conclusions drawn from a comparison of velocity measurements carried out on a homologous series of reactions at one temperature only are apt to be misleading. If the influence of substitution upon the kinetics of the reactions is the aim of the research, complete and accurate determinations over a range of temperature are absolutely necessary (p. 93). Then it may become possible to decide whether

* Clusius and Hinshelwood, *Proc. Roy. Soc.*, **A, 128**, 75, (1930).

† *J. Amer. Chem. Soc.*, **11**, 40, (1889).

'weighting' the molecules alters the critical increment, or whether, in a more mechanical way, it interferes with the frequency of effective collisions by obstructing the smaller molecule (or ion) from hitting the larger one on the right spot.

Rather than omit entirely any reference to the abundance of material which is available, we may cite a few of the most carefully studied cases. They show effects qualitatively similar to those found for non-ionic reactions. Table 15* illustrates the effects of interchanging the halogen atom (X) and the inorganic ion (B^- or B^{--}) in the following reaction:

$$X.CH_2.COO^- + B^{--} \rightarrow B^-CH_2.COO^- + X^-.$$

The figures are relative values of the bimolecular constants.

Table 15

Substituent in the acetate ion	Reacting ion		
	CNS^-	SO_3^{--}	$S_2O_3^{--}$
Cl	1	22	41
Br	110	2,160	4,230
I	154	3,780	6,300

The influence of lengthening the chain of carbon atoms is shown in Table 16, from which it would appear that internal rearrangement of one of the reacting molecules brings about

Table 16

Relative Velocities of Homologous Reactions

	Total number of carbon atoms in the molecule†					Temperature of comparison
	2	3	4	5	6	
$S_2O_3^{--} + HCHBr.COO^-$	101	30·5	1	0·53	0·33	25·0‡
$OH^- + HCH_2.COOCH_3$	1·24	1·14	1	0·60	..	9·4§
$C_6H_5O^- + HCH_2I$	2·79	1·07	1	0·43	0·96	42·5‖
$H_3O^+ + H.CONH_2$	13·8	0·83	1	0·51	0·13	61·4††

* La Mer, *Chemical Reviews*, **10**, 179, (1932).

† The chains are lengthened by substituting for the hydrogen atom shown in heavy type. The series are normal or straight-chained.

‡ Backer and van Mels, *Rec. trav. chim. Pays-bas*, **49**, 457, (1930); La Mer, (*loc. cit.*). § Reicher, *Annalen*, **228**, 275, (1885); van 't Hoff, *Studies*, p. 116, (1896).

‖ Segaller, *Trans. Chem. Soc.*, **105**, 106, (1914).

†† Crocker, *ibid.*, **91**, 593, (1907).

a slightly greater change in velocity in reactions of high than in those of low ionic type. On the whole, however, the successive introduction of —CH_2— groups has much the same effect on the different reactions. The first member of a homologous series is usually 'abnormal' in the velocity with which it reacts, as it is in most of its other properties. This is the reason for the standard adopted in Table 16.

Esters containing a halogen atom are attacked by the thiosulphate ion more readily than are ions containing the same halogen atom. This fact has been turned to good account by La Mer,* who has been able to calculate from it the nearest distance of approach of the ions during collisions which lead to chemical change. Let us consider the two following reactions:

$$BrCH_2.COOCH_3 + S_2O_3^{--} \rightarrow (S_2O_3^-)CH_2.COOCH_3 + Br^-$$

and

$$BrCH_2.COO^- + S_2O_3^{--} \rightarrow (S_2O_3^-)CH_2.COO^- + Br^-.$$

The concentration of the complexes thio-ester and thio-ion are given by equations (22) and (30). Considering the conditions which hold at infinite dilution, and assuming that the equilibrium constant for the two systems is the same, we have

$$\mu = 0 \begin{cases} [\text{thio-ion}] &= K'' c_A c_B e^{-\frac{\epsilon^2 z_A z_B}{DkTr}} \\ [\text{thio-ester}] &= K'' c_A c_B. \end{cases}$$

Hence

$$\log_{10}\left(\frac{k_{\text{ester}}}{k_{\text{ion}}}\right)_{\mu=0} = \frac{\epsilon^2 z_A z_B}{2{\cdot}303\, DkTr}. \qquad (33)$$

Substituting numerical values for the constants relating to water at 25° C., the expression becomes $z_A z_B \times \frac{3{\cdot}066 \times 10^{-8}}{r}$.

The limiting value of the ratio $\frac{k_{\text{ester}}}{k_{\text{ion}}}$ determined experimentally by La Mer† is 58, whence $r = 3{\cdot}47 \times 10^{-8}$ cm. The corresponding value using α-bromopropionic acid is 131, giving r a value of $2{\cdot}88 \times 10^{-8}$ cm. Ingold‡ from measurements

* *Loc. cit.* † *J. Amer. Chem. Soc.*, **51**, 3341, (1929).
‡ *Trans. Chem. Soc.*, 1375, (1930).

of the velocity of hydrolysis of dicarboxylic acid esters, has been able to evaluate the distance separating the two carboxyl groups. These are rather striking results of molecular magnitudes determined from purely kinetic data.

The influence of polar substituents upon the velocity of hydrolysis of ethyl esters ($XCH_2.COOC_2H_5$) has been examined by Ingold.* To eliminate the steric factor the ratio $\left(\frac{k_{OH}}{k_H}\right)$ of the velocities under the influence of hydroxyl ions and hydrogen ions is considered. This relative velocity should be independent of the shape of the ester, but not of the polarity. It is in fact found that $\left(\frac{k_{OH}}{k_H}\right)$ increases as X is H—, Cl← or NH_3^+←.

The Absolute Magnitude of the Velocities of Ionic Reactions.

The combined influence of temperature and of added electrolytes upon the rate of ionic reactions has been rather inadequately studied. The data available are summarized in Table 17, which contains the results obtained by La Mer,

Table 17

Reaction	$k_{\mu=0}$ at 25° C. (litres/gram mol.-sec.)	Z	E
$CH_2Cl.COO^- + S_2O_3^{--} \rightarrow$	$4{\cdot}47 \times 10^{-5}$†	$1{\cdot}13 \times 10^{7}$	*ca.* 15,500‡
$CH_2Br.COO^- + S_2O_3^{--} \rightarrow$	$4{\cdot}38 \times 10^{-3}$	$2{\cdot}20 \times 10^{9}$	15,900
$2[Co(NH_3)_5Br]^{++} + Hg^{++} + 2H_2O \rightarrow$	$1{\cdot}21 \times 10^{0}$	$1{\cdot}28 \times 10^{8}$	12,280§
$HClO + HOOC.COO^- \rightarrow$	$1{\cdot}61 \times 10^{+1}$	$1{\cdot}77 \times 10^{12}$	15,000
$HBrO + HOOC.COO^- \rightarrow$	$4{\cdot}35 \times 10^{+2}$	$9{\cdot}30 \times 10^{13}$	15,400
$[Co(NH_3)_5Br]^{++} + OH^- \rightarrow$	$7{\cdot}29 \times 10^{0}$	$1{\cdot}63 \times 10^{18}$	23,570§
$C_6H_5C{:}C.COO^- + I_3^- \rightarrow$	$1{\cdot}01 \times 10^{-3}$	$1{\cdot}39 \times 10^{8}$	15,500

* *Trans. Chem. Soc.*, 1032, (1930).

† Computed by assuming the ratio k_{Br^-}/k_{Cl^-} (= 98 in 0·1 molar solutions) not to vary with dilution.

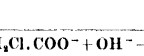
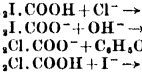
‡ The Arrhenius equation is not accurately obeyed; the values at two temperatures differ by 1,500 calories.

§ Velocities were measured at two temperatures only, hence it is not clear whether the Arrhenius equation holds good.

Kappanna, Griffith, McKeown, Winn, Brönsted, Livingston, Legard, and Moelwyn-Hughes, rearranged into common units. Each reaction is kinetically bimolecular, the velocity constant corrected for salt effects being given by the expression $k = Ze^{-E/RT}$ litres per gram molecule-second. These reactions have rates differing widely from those we should expect if they were simple bimolecular processes deriving the energy of activation from two square terms only. To go beyond this stage is admittedly speculative but will serve to exemplify the principles which have been outlined in the preceding portions of this work. We will consider the reaction between hypobromous acid and the monoxalate ion only. In principle, the following three possibilities present themselves as explanations of this very fast velocity. Quantitative agreement with theory results if (1) reaction chains of 450 cycles are set up, or if (2) a complex is formed with a heat effect of 3,600 calories, or if (3) three internal degrees of freedom contribute to the energy of activation. Of these, the chain mechanism is perhaps the least plausible, so that we may go one stage nearer the solution by ascribing the rapid rate of this reaction to either or both of the other influences. It would perhaps appear that the intermediate-complex theory is the more probable explanation, in that it conforms with the theory of ionic reactions as developed by Brönsted, but this is really not true, for we have seen that Brönsted's equations may be derived without postulating the existence of a complex (i.e. by Christiansen's method, which simply combines equation (1) of Debye and Hückel with the collision formula (18) modified by the Maxwell-Boltzmann factor). The problem must accordingly be left open. In this connexion it may be remarked that valuable evidence in favour of the intermediate-complex view would result if a reaction were discovered of a non-chain character possessing a velocity exceeding any which might be calculated from equations (6) and (11) of Chapter I.

Since (by equation (21)) the critical increment of ionic reactions does not vary with the ionic strength when one of the reactants is an uncharged molecule, and changes but slightly when both ions are charged, we are justified in supplementing these data with results found without paying any special regard to salt effects beyond keeping the concentration low and fixed over the complete temperature range (Table 19). Out of about thirty reactions now before us, nine have rates that are normal in the sense that they agree with the values calculated by the equation of Lewis, allowing an error of about 1,800 calories in the value of E. Just as in the general case for bimolecular reactions (Chap. IV), the most probable velocity of a bimolecular ionic reaction is

Table 19

Reference.	Reaction	E	Z
(1)	$CH_2Cl.COO^- + OH^- \rightarrow$	25,850	$4{\cdot}55 \times 10^{11}$
(2)	$NH_4CNO \rightarrow (NH_2)_2CO$	23,160	$4{\cdot}69 \times 10^{12}$
(3)	$CH_2I.COOH + Cl^- \rightarrow CH_2Cl.COOH + I^-$	23,850	$7{\cdot}9 \times 10^{11}$
	$CH_2I.COO^- + OH^- \rightarrow CH_2OH.COO^- + I^-$	22,370	$6{\cdot}3 \times 10^{11}$
	$CH_2Cl.COO^- + C_6H_5O^- \rightarrow$	21,010	$4{\cdot}0 \times 10^{10}$
	$CH_2Cl.COOH + I^- \rightarrow$	19,770	$1{\cdot}3 \times 10^{10}$
	$CH_2I.COO^- + CN^- \rightarrow$	17,030	$2{\cdot}0 \times 10^{9}$
	$CH_2I.COO^- + SCN^- \rightarrow$	16,580	$6{\cdot}3 \times 10^{8}$
(4)	$CH_2OH.CH_2Cl + OH^- \rightarrow$ $+ Cl^- + H_2O$	19,870	$2{\cdot}55 \times 10^{12}$
	$C(CH_3)_2OH.CH_2Cl + OH^- \rightarrow$	18,050	$2{\cdot}94 \times 10^{13}$
	$CCl_3OH.CH_2Cl + OH^- \rightarrow$	21,270	$2{\cdot}96 \times 10^{15}$
(5)	$2ClO^- \rightarrow Cl^- + ClO_3^-$	22,460	$9{\cdot}19 \times 10^{8}$
(6)	$+ OH^- \rightarrow NO_2.C_6H_4.COO^- + NH_3$	12,830	$2{\cdot}82 \times 10^{5}$
	 $+ OH^- \rightarrow$	11,310	$4{\cdot}14 \times 10^{4}$
(7)	$CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$	11,210	$1{\cdot}66 \times 10^{7}$
	$iso CH_3COOC_5H_{11} + OH^- \rightarrow$	11,040	$1{\cdot}08 \times 10^{7}$
(8)		12,500	$4{\cdot}17 \times 10^{12}$
(9)	$AsO_3^{--} + TeO_4^{--} \rightarrow AsO_4^{--} + TeO_3^{--}$	14,380	$1{\cdot}95 \times 10^{6}$

(1) Schwab, quoted by van 't Hoff, *Studies in Chemical Dynamics*, pp. 15 and 129, (1896).
(2) Walker, *Trans. Chem. Soc.*, **67**, 746, (1895).
(3) Wagner, *Z. physikal. Chem.*, **115**, 121, (1925).
(4) Evans, *ibid.*, **7**, 337, (1891).
(5) Foerster, *Z. Elektrochem.*, **23**, 137, (1917); Giordani, *Gazz. chim. ital.*, **54**, 844, (1924).
(6) Reid, *J. Amer. Chem. Soc.*, **21**, 281, (1899).
(7) L. Smith and Olsson, *Z. physikal. Chem.*, **118**, 99, (1925).
(8) Tasman, *Thesis*, Leiden, (1927); *vide Tables Annuelles*, (1931).
(9) Straup and Meloche, *J. Amer. Chem. Soc.*, **53**, 3331, (1931).

given approximately by the collision formula in its simple form. As far as this not very extensive evidence goes, the next most probable velocity is definitely lower than the normal value. The slowness of the arsenite-tellurate reaction has been attributed by the investigators to the transfer of an oxygen atom, i.e. to the breaking of a coordinate link.

One or two minor matters call for comment. (i) Among those reactions which have roughly the normal rates are cases (1) and (8), the absolute velocities of which, under comparable conditions, differ by a factor of 10^{10}. (ii) The presence of iodine, in the combined or ionic state, again ensures the relative rapidity of the process in which it takes part. (iii) Wagner's experiments were carried out at two temperatures differing by 10°, and are therefore more liable to error than the others, most of which have covered a good range.

The Order of Ionic Reactions.

Ionic reactions have occasionally been found to be of a higher kinetic order than is now regarded as possible. The explanation of this is adequately given in terms of the electrolyte effect.

Donnan and Le Rossignol* concluded that the reduction of the ferricyanide ion by the iodide ion was a reaction of the fifth order:

$$2Fe(CN)_6^{+++} + 3I^- \rightarrow 2Fe(CN)_6^{++++} + I_3^-.$$

The velocity was measured by adding successive amounts of sodium thiosulphate, and noting the time taken for the iodine produced to colourize starch. The ionic strength was thus continually changing. The reaction is bimolecular with respect to the ferricyanide, the value of the constant increasing in such a manner with the initial concentration of iodide as to suggest that the term $[I^-]^3$ is involved. In view of the knowledge which we now possess, but which was not

* *Trans. Chem. Soc.*, **83**, 703, (1903).

available at the time of the investigations, it seems that this change may be due to the increased concentration of electrolyte. The presence of thiocyanate and tetrathionate ions further complicates matters, especially at the high concentrations employed. Even with the simpler reaction between thiosulphate and bromacetate ions, at low concentrations, the limiting law of Debye and Hückel holds only when uni-univalent electrolytes are added. Deviations amounting to 40 per cent. for bivalent ions and 440 per cent. for tervalent ions have been found.* It now appears that the iodide-ferricyanide reaction is termolecular.†

Noyes and subsequent workers (see p. 37) have concluded that the following reaction is termolecular,

$$Sn^{++}+2Fe^{+++} \rightarrow Sn^{++++}+2Fe^{++}$$

since the velocity constant equation for a third order reaction is approximately obeyed. Actually, however, the agreement is frequently not good; and in the presence of hydrochloric acid the reaction is apparently bimolecular. Theory predicts for this reaction a positive and very large electrolyte effect. Examination of the original results of Noyes shows this to be so, for in the presence of hydrochloric acid, k increases (almost linearly) by about 450 per cent. from $\mu = 0{\cdot}250$ to $\mu = 0{\cdot}475$. van 't Hoff, using the same results, has calculated in various ways the order of reaction.‡ His figures are given in Table 20, along with the two initial concentrations used in determining each figure. By a slight though somewhat uncertain extrapolation, the value of n corresponding

Table 20

Initial concentrations	Average concentration	n
0·1000–0·0625	0·08125	3·22
0·1000–0·0500	0·0750	3·20
0·0625–0·0250	0·04375	2·56
0·0500–0·0250	0·0375	2·37

* La Mer and Fessenden, *J. Amer. Chem. Soc.*, **54**, 2351, (1932).
† von Kiss, *Rec. trav. chim. Pays-bas*, **52**, 289, (1933).
‡ *Studies in Chemical Dynamics*, p. 113.

to $\mu = 0$ is 1·8. In all probability, therefore, the reaction is bimolecular.

This method may be generally applied to determine the order of ionic reactions; provided it is possible to work with very dilute solutions, the extrapolated value will undoubtedly turn out to be the requisite whole number. The number of true termolecular reactions known is very small; no authentic cases of reactions of higher order have been found. Among those seemingly very complicated reactions of inorganic chemistry which have proved to be kinetically simple, the following deserves mention, if only on account of the thoroughness and accuracy with which Hood* amassed and interpreted his results.

$$KClO_3+6FeSO_4+3H_2SO_4 \rightarrow KCl+3Fe_2(SO_4)_3+3H_2O.$$

After definitely establishing its bimolecular character, he cautiously concluded that the influence of temperature 'upon this reaction at least' was of an exponential form. A few years later, Arrhenius generalized the same conclusion.

Ionic Reactions in Non-Aqueous Solvents.

The subject of the kinetics of ionic reactions in non-aqueous solvents has not yet developed to that stage where discussion at any length becomes profitable. Of the few reactions which have been investigated up to the present,† there has not been discovered one which is very suitable for the purpose in hand. Nevertheless, there are indications of conformity with the theory of Brönsted in a general way, e.g. the magnitude of the electrolyte effect varies inversely with the dielectric capacity of the solvent.

The absolute values of the velocities in methyl alcoholic and in acetone solutions are of the same order of magnitude

* *Phil. Mag.*, **6**, 371, (1878); *ibid.*, **20**, 323, (1885).

† See, for example, Brönsted and Bell, *J. Amer. Chem. Soc.*, **53**, 2478, (1931); Weissberger and Högen, *Z. physikal. Chem.*, **A**, **156**, 321, (1931); Weissberger, Dörken, and Schwarze, *Berichte*, **64**, 1200, (1931); Kailan and Irresberger, *Monatsh.*, **56**, 428, (1930).

as those for comparable reactions in water.* This, of course, is to be expected, for, compared with the term $e^{-E/RT}$, the electrolyte effect, even intensified by a solvent of low dielectric capacity, is of quite subordinate importance.

* See, for example, *Phil. Mag.*, **14**, 112, (1932); Walden and Centnerszwer, *Z. Elektrochem.*, **15**, 310, (1909); Kirner and Richter, *J. Amer. Chem. Soc.*, **51**, 3409, (1929).

VIII

CATALYSED REACTIONS

ANY substance which hastens a chemical reaction is termed a catalyst. It performs its work in a variety of ways, for example, by initiating reaction chains or lengthening previously existing ones, by increasing the concentration of molecules of one reactant in the locality of a molecule of the other, and by lowering the energy of activation. The last of these mechanisms is by far the commonest, although a few chain reactions are known in solution, and will be discussed later. The way in which ions of one sign cluster round those of opposite sign, and the manner in which this clustering is altered by the addition of electrolytes and non-electrolytes have been described in the preceding chapter. We are thus left with the task of discovering to what extent, and why, the energy of activation of any reaction is lowered by the presence of a catalyst. Experiment gives a direct answer to the first of these questions, and shows that the fall in the critical increment of any reaction is characteristic of the catalyst but independent of its amount. The second query goes to the root of the matter but finds no ready answer although shrewd guesses are being made. In a sense it is still true to say that the term catalysis is synonymous with unsolved mechanism.

In the presence of the catalyst, the uncatalysed and the catalysed reactions proceed simultaneously, so that $k_{\text{observed}} = k_0 + k_c[\text{Catalyst}]^n$. If successive additions of the catalyst bring about proportionate increases in the observed velocity, n is unity, and k_c becomes a bimolecular constant or catalytic coefficient. By plotting $\ln k_c$ against $1/T$ in the usual way, we can evaluate the critical increment of the catalytic reaction. It has already been stressed, and must be repeated here, that the value of E obtained from the equation $E = RT^2 \frac{d \ln k_{\text{obs}}}{dT}$ is often meaningless. If, as not

infrequently it happens, even small amounts of catalyst produce a large effect on the velocity, k_0 may be ignored in comparison with k_c. This is the case with the decomposition of hydrogen peroxide; in the presence of minute quantities of certain catalysts the unimolecular velocity constant is millions of times greater than the constant for the uncatalysed decomposition. Occasionally, as with the hydrolysis of casein, the spontaneous reaction has never been detected under any conditions, and k_0 accordingly does not enter. On the other hand, the two constants of the reaction may be commensurate: when this is so, a careful analysis of the influence of varying amounts of the catalysts is essential at all temperatures. A case in point is the decomposition of acetonedicarboxylic acid; k_0 at 60° C. is $5{\cdot}48 \times 10^{-2}$ seconds^{-1}; the addition of 0·0165 gram molecule of aniline per litre gives $k_{obs} = 11{\cdot}9 \times 10^{-2}$. k_c thus becomes 3·89 litres/gram molecule-second, and E_c has the approximate value given in Table 1. E_{obs} is 19,500 calories, but has no real significance. The results in this table are self-explanatory. The catalysts themselves are as varied as the reactions which they facilitate and the media in which the chemical changes take place. The extent to which a catalyst accelerates a reaction is dependent on the solvent.

There is a close parallelism between catalysis in solution and in the homogeneous gas phase. Hinshelwood and his collaborators have investigated the uncatalysed decomposition of various substances as well as their decomposition in the presence of halogens. Iodine was found to be the best catalyst. Some of their results are given in Table 2, concerning which Clusius and Hinshelwood* remark: 'in one case there is a general break up of the molecule caused by collision between two ether molecules, for example, with a large amount of energy. In the other case the catalyst brings a smaller amount of energy to a point in the molecule where it is more effectively and economically utilized.' This is a

* *Proc. Roy. Soc.*, **A, 128,** 82, (1930).

Table 1

Reference	Reaction	Catalyst	E
(1)	The decomposition of hydrogen peroxide in aqueous solution	None	18,000
(2)		Iodide ion	13,500
(3)		Colloidal platinum	11,700
(4)		Liver catalase	5,500
(5)	The decomposition of acetone-dicarboxylic acid in aqueous solution	None	23,200
		Aniline	13,900
(6)	The hydrolysis of sucrose in aqueous solution	Hydrogen ion	25,560
(7)		Saccharase	8,700
(8)	The hydrolysis of casein in aqueous solution	Hydrochloric acid	20,600
(9)		Trypsin-kinase	14,400
(10)	The decomposition of triethyl-sulphonium bromide in acetone solution	None	33,500
		4 per cent. water	30,700
(11)	The decomposition of trinitro-benzoic acid in nitrobenzene solution	None	35,000
		Adventitious impurity, probably water	21,700

(1) Possibly some decomposition upon dust particles. Pana, *Trans. Faraday Soc.*, **24**, 486, (1928).
(2) Walton, *Z. physikal. Chem.*, **47**, 185, (1904).
(3) Bredig and von Berneck, *ibid.*, **31**, 258, (1899).
(4) Williams, *J. General Physiol.*, **11**, 309, (1928).
(5) Wiig, *J. Physical Chem.*, **32**, 961, (1928).
(6) Lamble and Lewis, *Trans. Chem. Soc.*, **105**, 2330, (1914).
(7) Nelson and Bloomfield, *J. Amer. Chem. Soc.*, **46**, 1025, (1924).
(8) Nasset and Greenberg, *ibid.*, **51**, 836, (1929).
(9) Moelwyn-Hughes, Pace, and Lewis, *J. General Physiol.*, **13**, 323, (1930).
(10) von Halban, *Z. physikal. Chem.*, **67**, 129, (1909).
(11) Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, **A, 131**, 186, (1931).
(4, 7, 9) These figures refer to the optimum *p*H.

concise interpretation of the two significant facts concerning the energy of activation, which are (*a*) E is large for the uncatalysed reaction, and is shared among a number of square terms, and (*b*) E is smaller for the catalysed decomposition, and is shared between two terms only. The theory of Kassel* and of Rice and Ramsperger† supposes that a

* *J. Physical Chem.*, **32**, 225, (1928). † *J. Amer. Chem. Soc.*, **49**, 1617, (1927).

Table 2

Decomposition of	E for uncatalysed reaction	E for reaction catalysed by iodine
Di-isopropyl ether	60,500	28,500
Diethyl ether	53,500	34,300
Acetaldehyde	45,500	32,500

critical amount of energy must be acquired by one valency-bond or by one degree of freedom. Let us examine in a qualitative way the kinetics of the decomposition of diethyl ether, assuming that the energy required to activate the necessary link is 34,300 calories. Iodine can supply this energy directly, but before an ethyl ether molecule can do so the molecule as a whole must be activated to the extent of 53,500 calories. When this limit is reached, the appropriate fraction of the total energy can flow into the crucial bond. If each vibration in the molecule is simple harmonic, there will be associated with it an energy of RT calories. On the assumption that the difference between E_0 and E_c can be accounted for in this way, the number of internal degrees of freedom concerned is 7, which, although higher than the value of 3 found as the minimum number from the velocity at low pressures, is quite a reasonable figure. The precise development of the theory is, of course, much more complicated than this and has been fully discussed elsewhere.* The important circumstance for us to note is that current ideas of catalysis are definitely forming themselves into a coherent system which is as formal from the mathematical point of view as it is satisfactory from the chemical. As in the general treatment followed in this book, the claim may be made here also that the theory of catalysis now evolving from the study of gaseous reactions must be adequate, when properly applied, to the study of reactions in solution. Before proceeding to a more detailed examination of particular instances, the general analogy between catalytic

* Kassel, *The Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Company, (1932).

phenomena in the two systems may be revealed in numerous ways.

The total catalytic effect in the simplest conceivable case is denoted by the quantity $(E_0-E_c)/RT$, in which T is the temperature of investigation, and E_0 and E_c are the critical increments of the uncatalysed and catalysed reactions respectively. The total catalytic effect for homogeneous reactions in solution and in the gas phase are usually of similar magnitudes. In the case of the decomposition of diethyl ether by molecular* iodine, the factor is 4×10^3, which is almost exactly equal to the catalytic effect of the decomposition of hydrogen peroxide by the iodide ion. The interpretation of this factor is that it gives directly a comparison of the velocity of the uncatalysed reaction with that which would be observed in the presence of the catalyst at a concentration of one gram molecule per litre. When the two reactions are not bimolecular, the total catalytic effect is still proportional to $(E_0-E_c)/RT$, although not equal to it.

At least four internal degrees of freedom contribute to the energy of activation when acetonedicarboxylic acid decomposes without a catalyst in aqueous solution (Table 4, Chap. VI). With aniline present, the velocity of reaction can be fully accounted for on a simple collisional basis, involving energy in two square terms. Here, again, the similarity with gaseous systems is manifest.

The necessity for postulating the existence of an intermediate complex has repeatedly been stressed in the study of reactions in solution. The same necessity has not arisen in respect to gaseous reactions until quite recently, due, there is little doubt, to the smaller number of homogeneous gas reactions which have been investigated. The decomposition of nitrogen peroxide (see Table 1, Chap. IV), contrary to earlier conclusions,† has a bimolecular velocity constant which is about 34 times lower than that calculated by the

* The percentage dissociation into atoms is small at 800° abs. (see Table 1, Chap. V).

† Norrish, *Nature*, **122**, 923, (1928).

equation of Lewis.* The discrepancy can be fully accounted for if the formation of an intermediate oxide N_2O_2 is associated with the evolution of 4,900 calories.

$$2NO \rightleftarrows N_2O_2 + 4{,}900 \text{ cal.}$$

Hinshelwood has pointed out that the same supposition explains in a satisfactory manner the 'negative critical increment' observed by Bodenstein† for the reverse reaction.

The relative catalytic efficiencies of the halogens in the gaseous decomposition of ethers‡ are, in the familiar order (I > Br > Cl), found to hold for reactions in solution by Menschutkin,§ Conrad and Brückner,|| Griffith and McKeown,** and others whose work has been described in preceding chapters.

In a general way, therefore, experiments on catalysis in gases and dilute solutions reveal the similarity which is to be expected. Following the arguments which were outlined in Chapter III, the logical approach to the study of catalysis in solution would lead to investigations in inert solvents such as hexane and carbon tetrachloride. Unfortunately, the amount of work of this kind which has been attempted, particularly in connexion with the temperature effect, is very small. Almost all the work has been directed to the study of catalysis in aqueous solution. Furthermore, the catalyst usually employed has been an acid or a base, such catalysts as the halogen ions and the cyanide ion having been found either inefficient or uninteresting. In the hands of Lowry, Dawson, and Brönsted, the study of acidic and basic catalysis in aqueous solutions has afforded important new knowledge on the mechanism of such chemical changes, and has indeed necessitated a revision of our views about acids and bases in general. It is, nevertheless, appreciated that reactions which are hastened by hydrogen ion or hydroxyl

* Kassel, *loc. cit.*, p. 156, (1932). † *Z. physikal. Chem.*, **100**, 68, (1922).
‡ Clusius and Hinshelwood, *Proc. Roy. Soc.*, **A, 128**, 75, (1930).
§ *Z. physikal. Chem.*, **5**, 589, (1890). || *Ibid.*, **4**, 631, (1889).
** *Trans. Faraday Soc.*, **28**, 752, (1932).

ion in aqueous solution must constitute a highly specialized type of catalysis, since the solvent, being amphoteric, can supply both ions. Moreover, in hydrolytic changes, the solvent participates stoichiometrically in the reaction. A cautious attitude must accordingly be maintained towards conclusions based upon the study of these reactions if and whenever they are made the grounds of a theory which claims to be true for catalysis in general.

The literature upon catalysis in solution has attained such alarming proportions that only a very brief sketch can be given here. A few of the most important reactions may be dealt with in some detail.

The Mutarotation of Beryllium Benzoylcamphor in Non-Aqueous Solvents.

Lowry and Traill* have determined polarimetrically the velocity of the mutarotation of beryllium benzoylcamphor under the influence of various catalysts in carbon tetrachloride solution and in chloroform solution. A relatively slow unimolecular change is observed in pure carbon tetrachloride, k being $6{\cdot}66\times10^{-6}$ seconds^{-1} at 25° C. In pure chloroform also there is some change, but its velocity is not accurately reproducible. Sometimes the reaction is completely arrested for a period of 1·2 hours. The authors interpret this as showing that mutarotation is not spontaneous, but must be aided by a catalyst, which is possibly a trace of impurity in the solvent. There is, however, no necessity to doubt the existence of a genuinely uncatalysed reaction. In carbon tetrachloride solution, a unimolecular constant of this magnitude would be quite a reasonable one to expect for a reaction having a critical increment of some 26,500 calories. The results themselves are in fact more consistent with the view that the slow reaction in CCl_4 is uncatalysed, for, as will be shown presently, Lowry and Traill have established that most organic catalysts influence

* *Proc. Roy. Soc.*, **A, 132,** 398, (1931).

the velocity of this reaction to about the same extent. Taking an average of many values of the catalytic coefficient, it can be shown that a unimolecular constant equal to $6{\cdot}66\times10^{-6}$ seconds^{-1} at 25° C. in this solvent would necessitate the presence of organic impurity to an extent corresponding to more than 0·001 gram molecules per litre. This is unlikely.

Turning to the influence of catalysts on the velocity of mutarotation, pyridine, alcohol, and *p*-cresol exert very similar effects. The unimolecular constant is found to be linearly related to the concentration of pyridine, but with the other catalysts the same relation only holds in very dilute solutions. Consequently, the catalytic coefficients have in these cases been obtained by a slight extrapolation (Table 3, which is taken from Lowry and Traill's paper).

Table 3

Catalytic Coefficients (Litres/gram molecule-minute).

(*a*) Mutarotation of glucose in water at 20°	(*b*) Mutarotation of beryllium benzoylcamphor	
$[\bar{O}H]$ = 8000	Pyridine in CCl_4 at 20° . .	0·132
	Pyridine in CCl_4 at 25° . .	0·227
$[OH_2]$ = 0·00026	Pyridine in CCl_4 at 30° . .	0·385
	Pyridine in $CHCl_3$ at 25° . .	0·100
$[\dot{O}H_3]$ = 0·36	Alcohol in CCl_4 at 20° . .	0·231*
	Alcohol in CCl_4 at 25° . .	0·370*
[HCl] = about 0·5	Alcohol in CCl_4 at 30° . .	0·658*
	Alcohol in $CHCl_3$ at 25° . .	0·204*
[HAc] = 0·0065	*p*-Cresol in CCl_4 at 25° . .	0·318*
	p-Cresol in $CHCl_3$ at 25° . .	0·103*
$[\bar{A}c]$ = 0·069	Acetone in CCl_4 at 25° . .	0·015*
$[\dot{N}H_4]$ = 0·0012	CCl_4 and $CHCl_3$ at 25° . .	Negligible in comparison

* Extrapolated to infinite dilution.

As the authors point out, the most interesting feature of this table is the uniformity of the catalytic efficiency of pyridine, cresol, and ethyl alcohol, representing a weak base, a weak acid, and a simple organic molecule. This is in striking

contrast with the highly specific action of acids and bases upon the mutarotation of glucose in water.

Reference has already been made (p. 149) to the isolation of a compound of beryllium benzoylcamphor and chloroform, and its bearing upon the kinetics of mutarotation in this solvent.

An analysis of these results in terms of the kinetic theory has been given by Traill,* who finds that the equation of Lewis gives values of the catalytic coefficients which are equal to the experimental values to within a factor of about 2·7. A somewhat closer agreement results from independent and slightly different calculations.† The results refer to CCl_4 and are given in Table 4. The calculated values of the energy of activation are obtained from the equation

$$\frac{\text{number of molecules reacting}}{\text{total number of collisions}} = e^{-E/RT}. \qquad (1)$$

Table 4

Catalyst	$E_{observed}$	$E_{calculated}$
Pyridine	18,850	18,840
Alcohol	18,410	18,690

The disparity in the results of the two calculations, although small, is worth examining, since the choice of reactants, solvent, and catalysts made by Lowry and Traill offer an unusually favourable test of the applicability of the gas-collision formula to calculate the frequency of encounters in dilute solution. For catalysis by alcohol a critical increment of 18,500 calories may be accepted‡ in preference to the value of 20,200 calories previously published. The other sources of the discrepancy may be traced to the use of a form of the collision equation which gives values that are 10 per cent. higher than those given by equation (6) of Chapter I, and finally to the small correction of $\frac{1}{2}RT$. When all these factors

* *Phil. Mag.*, **13**, 225, (1932).

† Moelwyn-Hughes, *Nature*, **129**, 316, (1932).

‡ Dr. R. C. Traill, private communication.

are taken into account, the results of Lowry and Traill give an agreement with theory which is as absolute as the uncertainty in estimating the molecular diameters will allow.

Although incidental to the main argument, it may be noted that aluminium benzoylcamphor mutarotates in carbon tetrachloride solution in such a manner as to indicate two consecutive unimolecular reactions, the first one being the faster. The rotation at time t, is given by the equation*

$$[\alpha]_t = Ae^{-m_1 t} + Be^{-m_2 t} + C.$$

The general equation in such cases is

$$(x+y) = (a-z) = a\left\{\frac{k_2}{k_1-k_2}e^{-k_1 t} + \frac{k_1}{k_2-k_1}e^{-k_2 t}\right\},$$

where a is the initial concentration of the reactant, and x, y, and z give the concentrations at time t of the reactant, the intermediate compound, and the resultant respectively. The velocity of oxidation of oxalic acid by an acidic solution of potassium permanganate,† and of the mutarotation of α- and β-galactose‡ are expressible by an equation of this form.

A second example of a catalysed reaction in a non-aqueous solvent is the conversion of diazoaminobenzene into p-aminoazobenzene in aniline solution, under the catalytic influence of aniline hydrochloride.§ The unimolecular constant is linearly related to the concentration of catalyst, E being 24,020 calories.

$$C_6H_5N_2.NH.C_6H_5 \rightarrow C_6H_5N_2.C_6H_4NH_2.$$

The calculated critical increment is 22,000 calories by equation (1), which cannot, however, be strictly applicable to a reaction so complicated.

The Mutarotation of Glucose in Water.

Reference has already been made to the earlier work carried out upon this reaction (p. 44). By methods which

* Lowry and Traill, *Proc. Roy. Soc.*, **A, 132**, 416, (1931).
† Harcourt and Esson, *Phil. Trans.*, **156**, 193, (1866).
‡ Smith and Lowry, *Trans. Chem. Soc.*, 666, (1928).
§ Goldschmidt and Reinders, *Berichte*, **29**, 1369, (1896).

will now be familiar to the reader, Brönsted and Guggenheim* have measured the catalytic coefficients of hydrogen ion, pyridine, and acetate ion towards this reaction, and have obtained by difference the component of the velocity which is due to the water molecules. Their results were obtained at 18° C.; converted from minutes^{-1} and $\log_{10}$ to seconds^{-1} and $\ln_e$, they have the values given in Table 5.

Table 5

Catalyst	$k_{18°C.}$	$E_{observed}$		$E_{calculated}$
Hydrogen ion	$1{\cdot}27\times10^{-2}$		19,300	20,860
Pyridine	$7{\cdot}37\times10^{-3}$		18,000	17,980
Acetate ion	$2{\cdot}61\times10^{-3}$		19,100	19,570
Water	$4{\cdot}68\times10^{-4}$	(By Arrhenius)	17,600	..
		(Corrected)	22,000	22,120

The critical increments of the individual processes, as determined by Kilpatrick,† are also given. It is to be observed that the first three constants are really bimolecular, whereas that referring to water is unimolecular. In order to make k_{H_2O} roughly comparable with the others, we may divide by $[H_2O]$ and obtain the value of $8{\cdot}43\times10^{-6}$. The most significant result, therefore, is that the slowest velocity should be connected with the lowest critical increment. The reason for this is that the frequency of activating collisions between glucose and water molecules decreases rapidly with temperature, whereas the frequency of collisions in the other cases (which involve two solute molecules) is fairly constant. The correction to be applied in the temperature range (0–25°) to which E refers is 4,400 calories. This gives a corrected E of 22,000 calories for the reaction in pure water. We may now calculate the energies of activation, using the equation of Lewis as before,

$$\frac{\text{number of molecules reacting}}{\text{total number of collisions}} = e^{-E/RT}.$$

In the first three examples, the gas-collision formula may

* *J. Amer. Chem. Soc.*, **49**, 2554, (1927). † *Ibid.*, **53**, 3698, (1930).

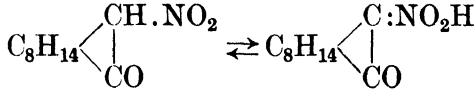
be used. The theoretical values of E are in excellent agreement with observation in the case of pyridine and acetate ion. The higher value obtained for hydrogen-ion catalysis may be fully explained if one internal degree of freedom is called in. The equation used to calculate the total number of collisions between glucose and water is $Z = 3\pi\eta\sigma/2m$. It will be recalled that each observed velocity coefficient is a composite term, which may be resolved in the manner described on p. 45. We finally arrive at the following expressions for the velocity of the uncatalysed mutarotation of glucose in water, at 18° C., accepting the value of E as 22,000 calories:

$$\text{observed rate for } \alpha\text{-glucose} = 11{\cdot}4\times10^{12}e^{-E/RT}$$
$$\text{observed rate for } \beta\text{-glucose} = 6{\cdot}35\times10^{12}e^{-E/RT}$$
$$\text{calculated rate for either} = 10{\cdot}9\times10^{12}e^{-E/RT}.$$

Apart from a discrepancy factor of 16 between the observed and theoretical velocities in the case of hydrogen-ion catalysis, there is no reason to seek farther for an interpretation of the results upon the mutarotation of glucose in water. Similar changes in other solvents are often not so easy to understand. They have been studied extensively by Lowry and his collaborators, and have been made the basis of a theory which must now be discussed.

Lowry's Theory of Prototropic and Hydrolytic Changes.

The mutarotation of nitrocamphor can be attributed to the partial conversion of the nitrocompound into an isomer.* The change is seen to involve the migration of a hydrogen atom, and a rearrangement of bonds.



Reducing and oxidizing agents, however, which can furnish or remove hydrogen atoms, have no influence on the

* Lowry, *Trans. Chem. Soc.*, **75**, 213, (1899).

change, hence the real migratory unit must be the proton. It is with such changes that the theory of Lowry has to deal. To the mutarotation of sugars, the enolization of ketones, and other chemical transformations which can be represented by the migration of a proton, Lowry has given the name of prototropy.* The study of these reactions has led to the development of an electrolytic theory of catalysis which has a bearing on chemical changes other than those for the interpretation of which it was invented. The presentation of the theory has been given in detail by its author.†

Nitrocamphor undergoes mutarotation more slowly in hydrocarbon solvents than in hydroxylic solvents and esters (cf. Menschutkin's results on the formation of tetraethylammonium iodide). The change is not conditioned, however, by the presence of an oxygen atom in the solvent molecule‡ nor by the dissociating power (high dielectric constant) of the solvent. Two discoveries have indicated the true conditions. (1) The mutarotation of several compounds can be suspended entirely in certain pure non-aqueous solvents. Tetramethylglucose does not undergo change in dry pyridine, nor in dry cresol.§ With specially cleaned silica vessels, and solvents stringently purified, tetramethylglucose and tetracetylglucose may be kept unchanged for several hours in chloroform, benzene, methyl acetate, and other solvents.‖ (2) Although pure pyridine and pure cresol separately do not catalyse mutarotation, a mixture of the two acts as an even more effective catalyst than water. The results show that the change is not spontaneous: the condition for its inception is the presence of an amphoteric medium. The facility of prototropic changes in water thus becomes readily intelligible. Since the solvent is amphoteric, it can furnish

* Lowry, *ibid.*, **123**, 828, (1923).
† Lowry, *Réunion internationale de chimie physique*, p. 219, (1928).
‡ Lowry and Magson, *Trans. Chem. Soc.*, **93**, 119, (1908).
§ Lowry and Faulkner, *ibid.*, **127**, 2884, (1925).
‖ Lowry and Owen, *Proc. Roy. Soc.*, **A**, **119**, 505, (1928).

the substrate molecule with a proton at one position and remove a proton from another position. The intramolecular change is then formulated as a transmission of an electron through the molecule, attended by the passage of a proton through the amphoteric solvent. The process accordingly resembles electrolysis, in which the substrate molecule is the electrolyte. For the general application of this idea, the original papers of Lowry must be consulted. The aspect of the theory which is of immediate importance to us is that prototropic and hydrolytic changes proceed by consecutive stages. When, for example, they are catalysed by acids in aqueous solution, the following steps are involved: (1) the reactant molecule collides with a proton-donor, giving rise to an acid complex; (2) this complex collides with a molecule of water; whereby (3) internal electrolysis of the reactant molecule results, the water acting as a proton-acceptor in the case of prototropy and as a hydroxyl-donor in the case of hydrolysis. Since stage (3) may be regarded as instantaneous, there are left two stages either of which may determine the velocity. The study of the kinetics of hydrolytic reactions in the light of these views is taken up at a later stage.

The crucial experiment upon which the present theory rests is that of mutarotation in pyridine-cresol mixtures. The study of other types of chemical changes in 'synthetic' amphoteric solvents would be of great interest.

It is significant that esterification* and the saponification† of esters take place much more rapidly in alcoholic solution than in water, and that the addition of water to organic solvents frequently has a marked inhibitive action.‡

Dawson's Theory of Multiple Catalysis.

That undissociated molecules of acid as well as hydrogen ions possess definite catalytic properties has been shown

* Goldschmidt and Udly, *Z. physikal. Chem.*, **60**, 728, (1907).

† Gilby and Waters, *Trans. Chem. Soc.*, 2643, (1932).

‡ Goldschmidt, *Berichte*, **29**, 2208, (1896); Lapworth and Fitzgerald, *Trans. Chem. Soc.*, **93**, 2167, (1908).

beyond doubt by the work of Goldschmidt,* Bredig,† Snethlage,‡ and Dawson.§ Dawson's researches, however, proved that the hypothesis of dual catalysis in solution was insufficient to explain any but a limited number of results, and the hypothesis was extended by ascribing catalytic effects to all the molecular and ionic species present. Dawson's work may therefore be described as a test of the theory of multiple catalysis. It finds its theoretical counterpart in the modern electronic definition of acids and bases as proton-donors and proton-acceptors.||

Numerous papers have been published dealing in particular with two catalytic reactions which have been measured very thoroughly in aqueous solution at 25° C. By analysis of the results, Dawson and his collaborators have brought to light some interesting facts and have obtained quantitative confirmation of many others which have previously or subsequently been revealed by independent inquiry along other lines. For complete information the reader must be referred to the original memoirs,** as it is impossible in a book of this scope to examine the results at all fully. The general method of analysis, however, may be described, along with a few of the more important deductions which it has yielded.

The reactions studied are the enolization of acetone and kindred ketones (followed by the rapid substitution of iodine)

$$CH_3.CO.CH_3 \rightarrow CH_3.C(OH):CH_2$$

and the hydrolysis of ethyl acetate

$$CH_3.COOC_2H_5+H_2O \rightarrow CH_3.COOH+C_2H_5OH.$$

Both are catalysed not only by hydrogen ion and hydroxyl ion, but by acids and bases in the widest sense. Although

* *Z. physikal. Chem.*, **70**, 627, (1910).
† *Z. Elektrochem.*, **18**, 535, (1912). ‡ *Ibid.*, p. 539.
§ *Trans. Chem. Soc.*, **103**, 2135, (1913).
|| Lowry, *ibid.*, 2554, (1927); Brönsted, *J. Physical Chem.*, **30**, 777, (1926).
** *Trans. Chem. Soc.*, 1926 onwards.

occasionally the complete course of the autocatalytic reactions has been followed, the initial velocity of reaction (dx/dt) alone is usually measured.* According to the basic postulate of the theory, the catalysts in an aqueous solution containing any substrate with an acid and its salt will be hydrogen ion, hydroxyl ion, the acid anion, the metallic cation, the undissociated acid molecule, and the water molecule. Experiment shows that low concentrations of metallic cations have no influence on the rate, hence, if we denote the substrate by S and the acid by HA, the instantaneous velocity is

$$-\frac{dS}{dt} = k_{\mathrm{H}}[S][\mathrm{H}^+]+k_{\mathrm{OH}}[S][\mathrm{OH}^-]+ \\ +k_M[S][HA]+k_A[S][A^-]+k_W[S][\mathrm{H_2O}].$$

The velocity is unimolecular with respect to the concentration of substrate. Dawson denotes the unimolecular constant by v (the unit being minutes^{-1}), hence

$$v = -\frac{dS}{dt}\frac{1}{S} = k_{\mathrm{H}}[\mathrm{H}^+]+k_{\mathrm{OH}}[\mathrm{OH}^-]+ \\ +k_M[HA]+k_A[A^-]+k_W[\mathrm{H_2O}]. \qquad (2)$$

The manner in which the various catalytic coefficients are evaluated may be demonstrated by referring to the acetone-iodine reaction.† Since the reaction in water is very slow, k_W can be neglected in comparison with the other constants. It is a definite though small quantity which can be determined indirectly. k_{H} is found by measuring the velocity in the presence of a strong acid (such as HCl) whose anion is devoid of catalytic properties. Under these conditions $[\mathrm{OH}^-]$ and $[HA]$ are negligibly small, and k_A is zero, so that v is linearly related to $[\mathrm{H}^+]$. Consider the reaction to be catalysed by mixtures of a weak acid (e.g. acetic acid) and its sodium salt, which may be regarded as completely

* This procedure has the advantage of being expeditious and of giving results which refer to a fairly constant ionic environment.

† Dawson and Carter, *Trans. Chem. Soc.*, 2282, (1926).

dissociated. Making use of the equilibrium relations, $K_A = \frac{[H^+][A^-]}{[HA]}$ and $K_W = [OH^-][H^+]$, the above equation becomes

$$v = k_H[H^+] + \frac{k_{OH}K_W}{[H^+]} + k_M[HA] + \frac{k_A K_A[HA]}{[H^+]}. \qquad (3)$$

With moderate concentrations of acid, the second term can be omitted. The concentration of hydrogen ion is determined electrometrically, so that by varying the concentrations of acid and salt, the three catalytic coefficients can readily be found. At 25° C., using acetic acid, they are $k_H = 4{\cdot}42\times10^{-4}$, $k_M = 1{\cdot}5\times10^{-6}$, $k_A = 4{\cdot}5\times10^{-6}$ minutes^{-1}. With monochloracetic acid, $k_M = 2{\cdot}4\times10^{-5}$ and $k_A = 1{\cdot}2\times10^{-7}$ minutes^{-1}. The inversion in the relative catalytic coefficient of anion and undissociated acid is somewhat surprising. k_{OH} is found in the following way. In dilute solutions of acetic acid, the observed velocity v_{obs} is compared with the calculated value found by employing these catalytic coefficients, and the difference is attributed to the term $k_{OH}[OH^-]$. The method is liable to considerable error, but gives values of k_{OH} of the correct order of magnitude ($k_{OH} = 10$ minutes^{-1}). In Table 6 are given the observed velocities alongside of those calculated by the relation

$$v = k_H[H^+] + k_M[HA] + k_A[A^-] + k_{OH}[OH^-]$$

$$4{\cdot}42\times10^{-4} \quad 1{\cdot}5\times10^{-6} \quad 4{\cdot}5\times10^{-6} \quad 10$$

x is the number of gram molecules of sodium acetate present per litre, with $(0{\cdot}2-x)$ molecules of acetic acid. The equation expresses the facts accurately, giving the minimum velocity at the right pH. The minimum velocity (v_i) and the concentration of hydrogen ion (H_i) corresponding to it are two important items in Dawson's theory. Before dealing with them more fully, it is necessary to give briefly some of the results which similar analytical methods have afforded.

Table 6

x	$[H^+]\times10^4$	$v\times10^6$ (obs.)	$v\times10^6$ (calc.)
0	19·2	1·16	1·15
0·015	2·51	0·46	0·455
0·024	1·58	0·44	0·445
0·036	1·00	0·46	0·45
0·053	0·63	0·495	0·49
0·074	0·40	0·54	0·54
0·098	0·25	0·59	0·61
0·141	0·11	0·74	0·74
0·158	0·063	0·80	0·795
0·171	0·041	0·835	0·84
0·181	0·025	0·88	0·885
0·190*	0·013	0·94	0·945
0·195*	0·0062	1·07	1·045
0·198*	0·0025	1·26	1·295

* Some side reaction, giving iodoform.

The different catalytic coefficients show wide variations in magnitude, e.g. k_{OH}/k_W for the acetone-iodine reaction is about 5×10^{10}.* Constants of similar order have been found for the intramolecular transformations of phorone† and of mesityl oxide.‡ The ionic product of water§ and the dissociation constants of other acids‖ have been found from catalytic data to have values almost identical with those derived from conductivity measurements (see Table 7). The dissociation constants, moreover, vary with the ionic

Table 7

Acid	$k_M\times10^6$	$K_A\times10^5$ (From catalytic data)	$K_A\times10^5$ (From conductivity data)
Propionic	1·1	1·38	1·40
Acetic	1·35	1·85	1·85
Succinic	4·3	6·30	6·55
β-chloropropionic	3·7	10·1	10·4
Glycollic	5·7	15·0	15·2
Chloracetic	22·3	151	155

* Dawson and Key, *Trans. Chem. Soc.*, 543, (1928).
† Dawson and Spivey, *ibid.*, 2658, (1931).
‡ Dawson and Key, *ibid.*, 2154, (1928). § Dawson, *ibid.*, 1290, (1927).
‖ Dawson, Hall, and Key, *ibid.*, 2844, (1928).

strength according to the predictions of the Debye-Hückel theory for univalent electrolytes ($\log K_\mu = \log K_0 + A\sqrt{\mu} - \beta\mu$),* although the absolute value of A found by experiment is usually only about one-half the theoretical value. Catalytic data thus reinforce the argument raised by conductivity measurements concerning the inadequacy of the interionic theory to cope with all the facts.† Brönsted's equation (*vide infra*) connecting the catalytic coefficient (k_M) of the undissociated acid with its equilibrium constant (K_A) is also satisfied, the numerical factors for the acetone-iodine reaction being $k_M = 3{\cdot}0\, k_H\, K_A^{0.64}$.‡

The earlier applications of the theory of multiple catalysis were marred by an insistence that the various catalytic coefficients were independent of the ionic environment. Accurate measurements of the initial velocity of hydrolysis of ethyl acetate by hydrochloric acid certainly showed k_H to be constant over a concentration range of HCl from 0·0002 M to 0·02 M.§ Addition of inert salts (such as sodium chloride), however, causes k_H to increase.|| Catalytic coefficients like other bimolecular constants must in general be sensitive to salt effects. The acceptance of this principle, as is now realized, in no way detracts from the value of the multiple theory. Experiment shows the salt effect to be linear** and specific.††

The Catalytic Catenary.

An equation has been deduced by Dawson‡‡ connecting the minimum velocity of a hydrolytic reaction in water with the corresponding *p*H. Ignoring the contributions due to

* This equation results from combining the mass-action equation with equations (5) and (13) of Chapter VII.

† Dawson and Smith, *ibid.*, 2530, (1929); 79, (1930).

‡ Dawson, Hoskins, and Smith, *ibid.*, 1884, (1929); Dawson and Lowson, *ibid.*, 1217, (1929).

§ Dawson and Lowson, *ibid.*, 2146, (1928).

|| Dawson and Key, *ibid.*, 1239, (1928).

** Dawson and Key, *ibid.*, 1249, (1928).

†† Dawson and Lowson, *ibid.*, 393, (1929).

‡‡ *Ibid.*, 213, (1927).

hydroxyl ions and to water molecules, we have

$$v = k_{\mathrm{H}}[\mathrm{H}^+]+k_A[A^-]+k_M[HA]. \tag{4}$$

If the total concentration of acid be C, $[A^-] = C-[\mathrm{H}^+]$.

Also, since $K_A = \dfrac{[\mathrm{H}^+][A^-]}{[HA]}$,

$$v = k_{\mathrm{H}}[\mathrm{H}^+]+\frac{k_A K_A(C-[\mathrm{H}^+])}{[\mathrm{H}^+]}+k_M(C-[\mathrm{H}^+])$$

$$= (k_{\mathrm{H}}-k_M)[\mathrm{H}^+]+\frac{k_A K_A C}{[\mathrm{H}^+]}-k_A K_A+k_M C. \tag{5}$$

$k_A K_A$ is negligibly small. $k_M C$ denotes the effect due to undissociated acid molecules. Hence the component of the velocity due to the ions only is

$$u = (k_{\mathrm{H}}-k_M)[\mathrm{H}^+]+\frac{k_A K_A C}{[\mathrm{H}^+]}. \tag{6}$$

At the optimum stability of the substrate, $\dfrac{du}{d[\mathrm{H}^+]} = 0$;

$$\frac{du}{d[\mathrm{H}^+]} = (k_{\mathrm{H}}-k_M)-\frac{k_A K_A C}{[\mathrm{H}^+]_i^2} = 0.$$

The concentration of hydrogen ion corresponding to this minimum ionic velocity is accordingly

$$[\mathrm{H}^+]_i = \sqrt{\frac{k_A K_A C}{k_{\mathrm{H}}-K_M}}. \tag{7}$$

By substituting in equation (6), the minimum ionic velocity is

$$u_i = (k_{\mathrm{H}}-k_M)\sqrt{\frac{k_A K_A C}{k_{\mathrm{H}}-k_M}}+k_A K_A C\sqrt{\frac{k_{\mathrm{H}}-k_M}{k_A K_A C}}$$

$$= 2\sqrt{\{(k_{\mathrm{H}}-k_M)k_A K_A C\}}. \tag{8}$$

Now let us express the velocity generally in terms of that at the minimum point, and the hydrogen-ion concentration in terms of the hydrogen-ion concentration at the minimum, i.e.

$$u = ru_i \quad \text{and} \quad [\mathrm{H}^+] = n[\mathrm{H}^+]_i. \tag{9}$$

r is termed the reduced ionic velocity, and n the reduced

hydrogen-ion concentration. By equation (6)

$$u = (k_{\mathrm{H}}-k_M)n[\mathrm{H}^+]_i+\frac{k_A K_A C}{n[\mathrm{H}^+]_i}$$

$$= n\sqrt{\{(k_{\mathrm{H}}-k_M)k_A K_A C\}}+\frac{1}{n}\sqrt{\{(k_{\mathrm{H}}-k_M)k_A K_A C\}}$$

$$= \frac{nu_i}{2}+\frac{u_i}{2n}. \qquad (10)$$

$$\therefore \quad r = \tfrac{1}{2}\left(n+\frac{1}{n}\right).$$

Calling $\ln n = h$,

$$r = \tfrac{1}{2}\,(e^h+e^{-h}), \qquad (11)$$

or

$$r = \cosh h. \qquad (12)$$

This is the equation of a catenary, and indicates that the reduced ionic velocity is equal to the hyperbolic cosine of the logarithm of the reduced hydrogen-ion concentration.

The simplest way of testing this relation is by plotting experimental values of r against $\Delta p\mathrm{H}$, where

$$\Delta p\mathrm{H} = \log_{10} n = (p\mathrm{H})_i - p\mathrm{H}.$$

Dawson has done this using his own data, supplemented by those of Karlsson* upon the reactions in question, examined under the influence of various catalysts at different temperatures. A general catalytic catenary is found, which seems to be independent of the reaction, the catalyst, and the temperature.

The translation of this conclusion into physical terms is a difficult matter. It will be appreciated that, from its nature, it can tell us nothing of the absolute velocity of any reaction or of the catalytic coefficient of the undissociated acid or base. $p\mathrm{H}_i$ and u_i, which are the real specifics of the systems, have been eliminated by the use of the ratios n and r, and k_M has been subtracted from the total velocity. The catenary therefore shows how the velocity of ionic reaction varies relatively to the velocity at the minimum

* *Z. anorg. Chem.*, **119**, 69, (1921).

point by displacing the pH to the right or to the left of the minimum pH. It implies that positive and negative ions have a similar effect, which in both cases is exponential.

The derivation of Dawson's equation is not free from criticism. In the first place, the term $k_{H,O}$ is neglected. Although this is a small figure,* it attains maximum importance at the minimum pH, where ionic effects are at their lowest. Secondly, the term k_{OH} is omitted, presumably because $(p\text{H})_i$ is always less than 7. An examination of Dawson's curve shows that in one set of conditions $(p\text{H})_i$ is 5·05. This corresponds to $\frac{[H^+]}{[OH^-]} = 6{,}800$, but generally $\frac{k_{OH}}{k_H}$ is about 2×10^4, hence the contribution $(k_{OH}[OH^-])$ due to hydroxyl ions is actually about 300 times as great as that due to hydrogen ions $(k_H[H^+])$. The inclusion of this term would destroy the symmetry of the catenary, and lead to a $(v, p\text{H})$ curve which is steeper on the alkaline side of the optimum, as in the earlier work of Wijs.†

The theory of buffer solutions has been examined in the light of these considerations.‡ Dawson's analytical method has been adopted by Ingold and his collaborators in applications of the electronic theory to determine the course of chemical reactions.§

The Order of Magnitude of the Catalytic Coefficients.

Nearly all the work which has been done upon the kinetics of catalysed reactions has been directed to a study of the factors which modify the velocity of reaction at a given temperature, or to the influence of temperature under otherwise constant catalytic conditions. Table 8 gives the

* Skrabal and Zahorka (*Monatsh.*, **54**, 562, (1929)) state that 36 per cent. of the rate of hydrolysis of ethyl acetate at the minimum point is due to water, but the effect is not as great as this if the buffer correction is applied (Groocock, Ingold, and Jackson, *Trans. Chem. Soc.*, 1039, (1930)).

† *Z. physikal. Chem.*, **12**, 514, (1893). ‡ Dawson, *ibid.*, 1146, (1927).

§ Burton and Ingold, *ibid.*, 904, (1928).

Table 8

Reference	Reaction catalysed by H^+	$E_{observed}$	$Z_{observed}$
(1)	Hydrolysis of methyl acetate	16,920	$3{\cdot}86 \times 10^8$
(2)	Hydrolysis of ethyl acetate	16,830	$1{\cdot}66 \times 10^8$
(3)	Hydrolysis of acetamide	18,780	$9{\cdot}43 \times 10^9$
(4)	Conversion of creatine into creatinine	19,690	$4{\cdot}35 \times 10^8$
(5)	Hydrolysis of benzoyl glycine	22,100	$1{\cdot}72 \times 10^9$
(5)	Hydrolysis of acetyl glycine	22,100	$7{\cdot}41 \times 10^9$
(6)	Conversion of γ-hydroxyvaleric acid into lactone	16,630	$4{\cdot}55 \times 10^9$
(7)	Enolization of acetone	20,580	$3{\cdot}94 \times 10^{10}$
(8)	Decomposition of nitrosotriacetonamine (catalysed by OH^-)	16,040	$4{\cdot}69 \times 10^9$
(9)	Decomposition of diazoacetic ester	17,480	$4{\cdot}64 \times 10^{12}$
(10)	Hydrolysis of lactose	24,680	$3{\cdot}21 \times 10^{11}$
(11)	Hydrolysis of sucrose	25,560	$8{\cdot}89 \times 10^{14}$
(12)	Hydrolysis of maltose	30,970	$1{\cdot}86 \times 10^{15}$
(12)	Hydrolysis of cellobiose	30,710	$9{\cdot}78 \times 10^{14}$

(1) Lamble and Lewis, *Trans. Chem. Soc.*, **105**, 2330, (1914).
(2) Taylor, *J. Amer. Chem. Soc.*, **37**, 551, (1915).
(3) Meehan, *Thesis*, Liverpool, (1923); Euler and Rudberg, *Z. anorg. Chem.*, **127**, 244, (1923); von Peskoff and Meyer, *Z. physikal. Chem.*, **82**, 129, (1913); Crocker, *Trans. Chem. Soc.*, **91**, 573, (1907).
(4) Edgar and Wakefield, *J. Amer. Chem. Soc.*, **45**, 2242, (1923).
(5) Escolme and Lewis, *Trans. Faraday Soc.*, **23**, 651, (1927).
(6) Garrett and Lewis, *J. Amer. Chem. Soc.*, **45**, 1091, (1923); Taylor and Close, *J. Physical Chem.*, **29**, 1085, (1925).
(7) Rice, Fryling, and Wesolewski, *J. Amer. Chem. Soc.*, **46**, 2405, (1924); Rice and Kilpatrick, *ibid.*, **45**, 1401, (1923); Dawson and Powis, *Trans. Chem. Soc.*, **101**, 1502, (1912); see also Dawson and co-workers in subsequent issues of this journal.
(8) Clibbens and Francis, *ibid.*, **101**, 101, (1912); Colvin, *Trans. Faraday Soc.*, **22**, 241, (1926).
(9) Fraenkel, *Z. physikal. Chem.*, **60**, 202, (1907).
(10) Bleyer and Schmidt, *Biochem. Z.*, **135**, 546, (1923); Moelwyn-Hughes, *Trans. Faraday Soc.*, **24**, 309, (1928).
(11) Urech, *Berichte*, **17**, 2175, (1884); Spohr, *Z. physikal. Chem.*, **2**, 195, (1888); Arrhenius, *ibid.*, **4**, 226, (1889); Lamble and Lewis, *Trans. Chem. Soc.*, **107**, 233, (1915); Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 81, (1929).
(12) Moelwyn-Hughes, *ibid.*, **25**, 503, (1929).

results of an attempt which has been made at calculating the catalytic coefficient in terms of independently measurable physical properties, accepting the Arrhenius critical increment

as a true value of the energy of activation.* How far this assumption can be regarded as acceptable will become clear from the following discussion, which seeks to compare the experimental results with those predicted by the collision theory in various forms. The reactions referred to in Table 8 are catalysed by hydrogen ion, with the exception of the decomposition of nitrosotriacetonamine, which is catalysed by hydroxyl ion. The true bimolecular constant or catalytic coefficient is obtained by dividing the observed unimolecular constant by the concentration of the catalyst. This is a simple matter where k_{uni} is proportional to $[H^+]$, as, for example, in the case of the decomposition of diazoacetic ester (9) and the conversion of creatine into creatinine (4); similarly, k_{uni} for the decomposition of nitrosotriacetonamine (8) is proportional to $[OH^-]$. In certain other cases, however, this linear relation does not hold, the observed unimolecular constant being more closely proportional to the activity of the hydrogen ion: this is true for the hydrolysis of lactose (10) and the substituted glycines (5). The true bimolecular constant in these instances is k_{uni}/a_{H^+}, since the activity of hydrogen ion becomes equal to its concentration at great dilutions. Wherever it has been possible to compare values of k_{uni}/a_{H^+} determined at fairly high concentrations of acids with values of $k/[H^+]$ measured in dilute solutions the agreement is quite good. Thus, for the conversion of γ-hydroxyvaleric acid into valerolactone at 30° C., Garrett and Lewis give $k_{\text{uni}}/a_{H^+} = 4{\cdot}45\times10^{-3}$, while Taylor and Close find $k_{\text{uni}}/[H^+]$ to be $4{\cdot}31\times10^{-3}$ litres/gram molecule-second (6). Similarly, for the hydrolysis of sucrose at 25° C. the bimolecular constant given by Moelwyn-Hughes from the activity of hydrogen ion is $1{\cdot}47\times10^{-4}$; $k_{\text{uni}}/[H^+]$ in very dilute solutions is found by Lamble and Lewis to be $1{\cdot}35\times10^{-4}$ litres/gram molecule-second (11). The experimental velocity constants have been corrected for the attainment of an equilibrium stage in certain instances (e.g. the hydrolysis of

* *Phil. Mag.*, **14**, 112, (1932).

methyl acetate (1), and the formation of valerolactone) and for auto-catalysis in the case of the enolization of acetone.

Results as numerous as possible have been used in the graphical evaluation of the critical increment. E for the hydrolysis of sucrose (11) by acids is the average of 36 values in very close agreement; E for the enolization of acetone (7) is the average of 25 values. These are among the most accurately determined critical increments for reactions in solution. The constants obtained by Meehan, by Euler and Rudberg, and by von Peskoff and Meyer for the hydrolysis of acetamide (3), taken jointly, give $E = 18{,}780$ calories, which is in fair agreement with Crocker's value of 18,320. The present value of the critical increment for the hydrolysis of lactose (10) was obtained from the data of Bleyer and Schmidt at six temperatures, and is a more reliable value than that previously quoted by Moelwyn-Hughes.

If these chemical changes were due to collisional activation of the simple kind, E being equal to the Arrhenius value, Z should in all cases be about $2{\cdot}8 \times 10^{11}$. As shown in the Table, only in the hydrolysis of lactose does it approximate to this figure. There are a few other examples where the agreement is good (e.g. the mutarotation of glucose (Table 5) and the hydrolysis of phloridzin),* but their number is insignificant. General theoretical explanations for the discrepancy have been given in Chapter IV. The most natural explanation of the fast reactions is that the activation involves a number of internal degrees of freedom—a view which is consistent with the greater complexity of the substrate molecules in those instances where large values of Z are found. A more serious difficulty arises in attempting to understand why the rate of hydrolysis of esters, for example, is about 1,000 times slower than the normal value. The failure of other experiments to support the view that deactivations by solvent molecules is a prominent factor in dealing with reactions in solution lessens our faith in the

* Moelwyn-Hughes, *Trans. Faraday Soc.*, **24**, 309, (1928).

belief that the explanation is the correct one in this case. The real objection to the deactivation view is that it aggravates the already great disparity, rather than removes it. The simple assumption that only one out of a thousand activated molecules undergoes chemical reaction would supply no real answer to the problem.

In order to maintain the Maxwellian distribution, it must also be assumed that water molecules can activate the solute molecules. This is in general true, but under the conditions which we are imagining, the part played by the solvent molecules alone is known to be of subordinate importance, since the velocity of reaction in water is relatively slow. The problem may be approached by a method analogous to that used by Hinshelwood* to show the kinetic connexion between reactions of the first and second orders.

Let n_S = number of substrate molecules per c.c.

n_{H} = ,, hydrogen ions ,,

n_W = ,, water molecules ,,

and n_A = number of activated molecules produced per second by collisions between substrate molecules and hydrogen ions, and by collisions between substrate molecules and water molecules.

Then rate of activation $= k_1 n_S n_{\mathrm{H}} + k_2 n_S n_W$

rate of deactivation $= k_3 n_A n_W$

rate of reaction $= k_4 n_A$.

The condition for a stationary concentration of active molecules is

$$k_1 n_S n_{\mathrm{H}} + k_2 n_S n_W = k_3 n_A n_W + k_4 n_A. \qquad (13)$$

Hence

$$n_A = \frac{k_1 n_S n_{\mathrm{H}} + k_2 n_S n_W}{k_4 + k_3 n_W},$$

and

$$\text{rate of reaction} = k_4 n_A = \frac{k_1 n_S n_{\mathrm{H}} + k_2 n_S n_W}{1 + \frac{k_3}{k_4} n_W}. \qquad (14)$$

* *Annual Reports of the Chemical Society*, p. 42, (1932); cf. p. 152 of this book.

When the part played by the water molecules is small, the equation reduces to the ordinary expression for the catalytic coefficient, but with considerable activation and deactivation due to water molecules the observed velocity would not be bimolecular, which is contrary to experience. If the idea of considerable deactivation by water molecules is retained, while admitting the first term in the numerator of equation (14) to be the important one, it follows that since the temperature coefficient of k_3 is negative, the true energy of activation upon this mechanism would be actually lower than the already low value which is found.

It is possible that activating collisions in these reactions occur not between substrate and hydrogen ions but between complex molecules and water. If this were so it would invalidate the use of the gas-collision formula completely, and would necessitate a correction in the Arrhenius critical increment. The idea has been applied to numerous examples.*

In principle the calculations may be made by using the formula

$$_1Z_W = \frac{3\pi N_0 \eta \sigma}{2M} \qquad (15)$$

to determine the total number of water molecules which collide per c.c. per second against one molecule of complex of molecular weight M, but the difficulties of estimating the number of complexes present and of finding the probability that when activated they will react are at present insurmountable.† The simplest assumption to make is that complex formation is complete, i.e. one hydrogen ion instantly attaches itself to one molecule of substrate, the complex being stable enough to await the necessary activation. This would mean, however, that addition of acid in quantities greater than the concentration of the substrate would

* *Phil. Mag.*, **14**, 112, (1932).

† The number of complexes at a given temperature can occasionally be computed (e.g. from the dissociation constant of glucose, Britton, *Trans. Chem. Soc.*, 1896, (1924)), but the temperature coefficient of the equilibrium which governs complex formation is not known.

produce no further increase in the velocity, which again is contrary to experience.

The problem may be approached so as to circumvent our ignorance concerning the nature or number of complex molecules. It may be assumed that reaction takes place whenever a water molecule collides with sufficient violence against a substrate molecule, a hydrogen ion being in the collision zone. This is equivalent to making the rate of change dependent upon ternary collisions with unit probability that the activated ternary complex will undergo transformation. Adhering to the nomenclature given above, we have for the total number of collisions occurring per c.c. per second between molecules of substrate and molecules of water

$$Z_{S,W} = \frac{3\pi N_0 \sigma \eta n_S}{2M_S}. \tag{16}$$

The probability that hydrogen ion shall be present at such collision is

$$\frac{n_H}{n_H + n_S + n_W},*$$

which in dilute solution is nearly equal to n_H/n_W. The frequency of ternary collisions is therefore

$$Z_{S,W,H} = \frac{3\pi N_0 \sigma \eta n_S n_H}{2M_S n_W}, \tag{17}$$

and the expression for the velocity becomes

$$\frac{dn}{dt} = \frac{3\pi N_0 \sigma \eta}{2M_S n_W} n_S n_H e^{-E'/RT}. \tag{18}$$

The energy of activation according to this mechanism is equal to the Arrhenius value plus the correction for the variation of collision frequency with temperature. The results of applying this equation to a few instances are given in Table 9.

* A more accurate, but still approximate, expression for the probability is $\frac{v_H}{v_H + v_S + v_W}$, where v is the fraction of the total volume which is occupied by each molecular species. The simpler form ignores the differences in molecular dimensions.

Table 9

Reaction catalysed by hydrogen ion	E'	$t°$C.	$k = k_1/[\text{catalyst}]$ Observed	Calculated	F
Hydrolysis of methyl acetate	20,790	30	$2{\cdot}16\times10^{-4}$	$2{\cdot}55\times10^{-4}$	—
Hydrolysis of ethyl acetate	20,840	25	$9{\cdot}38\times10^{-5}$	$1{\cdot}23\times10^{-4}$	—
Hydrolysis of acetamide	22,790	25	$6{\cdot}60\times10^{-6}$	$6{\cdot}79\times10^{-6}$	—
Conversion of creatine into creatinine	22,810	78	$2{\cdot}18\times10^{-4}$	$4{\cdot}08\times10^{-4}$	—
Hydrolysis of benzoyl glycine	25,210	80	$5{\cdot}05\times10^{-6}$	$1{\cdot}13\times10^{-5}$	—
Hydrolysis of acetyl glycine	25,430	60	$2{\cdot}05\times10^{-5}$	$2{\cdot}77\times10^{-5}$	1
Conversion of hydroxyvaleric acid into lactone	20,500	30	$4{\cdot}38\times10^{-3}$	$3{\cdot}38\times10^{-3}$	1
Enolization of acetone	24,620	24	$2{\cdot}53\times10^{-5}$	$3{\cdot}63\times10^{-5}$	2
Decomposition of nitrosotriacetonamine (catalysed by hydroxyl ion)	19,910	30	$3{\cdot}04\times10^{-2}$	$4{\cdot}09\times10^{-2}$	2
Decomposition of diazoacetic ester	21,490	25	$6{\cdot}42\times10^{-1}$	$1{\cdot}63\times10^{-1}$	4
Hydrolysis of lactose	28,690	25	$3{\cdot}24\times10^{-7}$	$3{\cdot}12\times10^{-7}$	4
Hydrolysis of sucrose	29,570	25	$1{\cdot}41\times10^{-4}$	$9{\cdot}82\times10^{-5}$	10
Hydrolysis of maltose	34,300	60	$1{\cdot}68\times10^{-5}$	$2{\cdot}00\times10^{-5}$	9
Hydrolysis of cellobiose	34,040	60	$5{\cdot}89\times10^{-6}$	$5{\cdot}47\times10^{-6}$	9

Referring to the three stages which according to Lowry constitute all hydrolytic and prototropic changes, it is known that the third stage, being almost instantaneous, does not determine the velocity. From the purely kinetic considerations advanced here, and illustrated by Tables 5 and 9, it seems likely that either stage (i) or stage (ii) may be responsible for the velocity. Up to this point, therefore, there is considerable harmony between the electronic theory of hydrolytic reactions and the kinetic theory of reaction velocity. The elementary treatment of the problem given here is admittedly inadequate, but even in its present form it has been made possible only by imposing an artificial simplicity implied in the purposeful omission of such factors as orientation during collision and persistence of velocity after collision. It is becoming increasingly clear that no single theory can account for all chemical rates, and that reactions must be studied from the kinetic standpoint in groups wherein certain factors predominate and others are

sufficiently suppressed to be of no serious consequence. The conclusion which the foregoing calculations entitle us to draw must be accepted hand in hand with its limitations. It is that many examples of hydrolytic and prototropic changes are known with velocities lying near to those predicted by theoretical equations based on the assumption that the postulated mechanism holds good.

The values of F given in the table have been determined by applying the equation of Hinshelwood in the usual way, E being now taken as $(E'+FRT)$. They reveal in an interesting manner the relative complexity of the activation process. The decomposition of diazoacetic ester, for example,

$$-\mathrm{CH}\begin{matrix}\diagup\!\!\diagdown\mathrm{N}\\ \|\\ \diagdown\!\!\diagup\mathrm{N}\end{matrix}+\mathrm{H_3O^+}\rightarrow -\mathrm{CH_2OH}+\mathrm{N_2}+\mathrm{H^+},$$

requires energy drawn from four internal degrees of freedom. The hydrolysis of sucrose, entailing the opening of a five-membered γ-fructoside link, involves ten internal degrees of freedom, while the mutarotation of glucose, which is concerned with the relative positions of the hydrogen atom and hydroxyl group attached to a terminal carbon atom, involves not more than one (p. 234). The value of these conclusions naturally depends upon how close to the truth are the assumptions underlying the calculations.

Application of the same principles to the reaction between esters and alkalis reduces the ratio of $k_{\text{calculated}}/k_{\text{observed}}$ from about 25,000 to 14.

A Comparison between Catalysis by Hydrogen Ion and by Hydroxyl Ion.

It has long been known that hydroxyl ions are more efficient catalysts for many reactions than are hydrogen ions. According to the mechanism of catalysis which was shown in the preceding sections to be most commonly at work in solutions, we should anticipate a lower critical increment for the basic catalysis. The anticipation is fully justified, as the results in Table 10 indicate. All the data

Table 10

Reaction	E		Difference
	Catalysed by hydrogen ion	Catalysed by hydroxyl ion	
Decomposition of nitrosotriacetonamine	22,100	16,210	5,890
Hydrolysis of methyl acetate	16,920	11,220	5,700
Hydrolysis of ethyl acetate	16,830	11,210	5,620
Conversion of hexamethylpararosaniline hydrochloride from carbinol to quinonoid form*	17,770 18,910 19,460	11,260 12,950 13,750	6,510 5,960 5,710
Hydrolysis of acetamide	19,210	13,320	5,890
Hydrolysis of propionamide	19,490	12,930	6,560
Hydrolysis of butyramide†	18,890	13,870	5,020

refer to aqueous solutions, and point to an approximately fixed value of 5,900 calories for $(E_{\text{H}}-E_{\text{OH}})$ in the case of all these reactions. At 25° C., the ratio $k_{\text{OH}}/k_{\text{H}}$ of the catalytic coefficients in the case of the mutarotation of glucose (Table 3) is $2{\cdot}22\times10^4$ and in the case of the enolization of acetone‡ $4{\cdot}3\times10^4$. Assuming the collision frequency to be the same for basic and acidic catalysis, we have $\Delta E = RT\ln(k_{\text{OH}}/k_{\text{H}})$. For mutarotation $(E_{\text{H}}-E_{\text{OH}})$ thus becomes 5,910 calories, and for the acetone-iodine reaction, 6,310 calories. Although the temperature coefficients of these reactions, catalysed by hydroxyl ion, have not been measured experimentally, we can with some confidence predict the values of E_{OH} to be 13,400 and 14,300 calories respectively.

Why E_{OH} should be lower than E_{H} remains unexplained, just as the greater catalytic efficiency of iodine over the other halogens is not understood, but an interesting implication

* This reaction is probably not simple, the critical increments falling with rise in temperature. Nevertheless $(E_{\text{H}}-E_{\text{OH}})$ remains roughly constant at all temperatures. The reaction was measured by Biddle and Porter (*J. Amer. Chem. Soc.*, **37**, 1571, (1915)).

† Crocker (*loc. cit.*) whose results with alkalis are probably liable to considerable error. References to the other sources of information have already been given.

‡ Dawson, *Trans. Chem. Soc.*, 458, 2449, (1927).

may be pointed out. Consider a reaction to be catalysed in aqueous solution by water molecules and by hydrogen and hydroxyl ions. The experimental conditions may be realized by measuring the velocity of the reaction in pure water, and in the presence of small amounts of a strong acid (e.g. HCl) and a strong base (e.g. NaOH), whose anions and cations respectively have no catalytic properties. Under these conditions

$$k = k_{H,O} + k_H[H^+] + k_{OH}[OH^-] \quad (19)$$

$$= k_{H,O} + k_H[H^+] + \frac{k_{OH}K_W}{[H^+]}. \quad (20)$$

The minimum velocity corresponds to

$$\frac{dk}{d[H^+]} = k_H - \frac{k_{OH}K_W}{[H^+]^2} = 0,$$

and the pH to $$[H^+]_i = \sqrt{\frac{k_{OH}K_W}{k_H}}, \quad (21)$$

whence $$\frac{d(pH)_i}{dT} = \frac{E_H - E_{OH} - Q_W}{2 \times 2{\cdot}303 \times RT^2}. \quad (22)$$

Q_W is the heat of ionization of water (13,700 calories), hence the numerator becomes $5{,}900 - 13{,}700 = -7{,}800$ calories. This means that the pH corresponding to the minimum velocity has a negative temperature coefficient, which is nearly the same for all hydrolytic reactions. A rise in temperature from 20 to 30° C. should reduce $(pH)_i$ by nearly 0·1. This relation has not been verified.*

The Relation between Catalytic Coefficient and Dissociation Constant.

The work of Lowry, Dawson, and Brönsted has jointly led to the new definitions of acids and bases. An acid is a proton-donor: a base is a proton-acceptor. It is not unreasonable to expect some kind of parallelism between two of the more characteristic properties of acids, viz. their

* Professor H. M. Dawson, private communication.

catalytic activity and their ability to yield protons. The first of these properties may be estimated by measuring the velocity of reaction, and the second by the dissociation constant determined from conductivity measurements. Brönsted* has shown that the catalytic coefficient k_A of an acid is empirically related to the dissociation constant K_A by the equation

$$k_A = GK_A^x, \tag{23}$$

where G and x are constant for a whole series of acids. The hydrolysis of ethylorthoacetate, the mutarotation of glucose,† and the enolization of acetone,‡ obey the rule, although the agreement in the last instance is approximate only. Similarly, the catalytic coefficient of bases might be expected to run parallel with some function of the dissociation constant of the base, or, more strictly, of the equilibrium constant of the base, its conjugated acid, and hydrogen ion. This has been tested in the case of the decomposition of nitramide, catalysed by a wide variety of weak bases, such as the orthophosphate ion

$$PO_4^{---} + H^+ \rightleftarrows HPO_4^{--},$$

and the acetate ion

$$CH_3.COO^- + H^+ \rightleftarrows CH_3.COOH.$$

Considering the second example, we see that the power of the base $CH_3.COO^-$ to accept hydrogen ions is measured by the constant $K_B = \dfrac{[CH_3.COOH]}{[CH_3.COO^-][H^+]}$. The ability of the base to accept a proton from the substrate is estimated by the velocity of the reaction

$$H_2N_2O_2 \rightarrow H_2O + N_2O$$

referred to unit concentration of the basic catalyst, i.e. $k_B = k_{\text{observed}}/[CH_3.COO^-]$. Using a number of different bases,

* *Trans. Faraday Soc.*, **24**, 630, (1928).

† Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, **49**, 2554, (1927).

‡ Dawson, *Trans. Chem. Soc.*, 2844, (1928).

Brönsted and Pedersen* found the following relation to hold:

$$k_B = G(nK_B)^x .$$

At 25° C., G is $6{\cdot}2\times10^{-5}$, the velocities being in minutes^{-1} and $\log_{10}$. x is 0·83 (see Fig. 1). The factor n is a statistical ratio, calculated to allow for the comparative probabilities of the transference of the proton in dissociation and in catalysis.

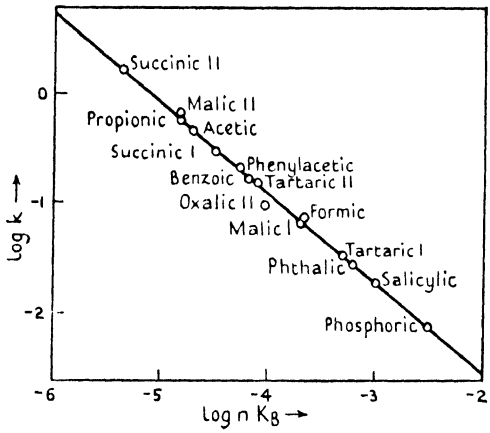


FIG. 1.

n = the chance that a proton will be accepted by the base / the chance that a proton will be accepted by the substrate

= number of missing protons in the base / total number of protons in the base.

Brönsted's relation is a semi-empirical one, which can be interpreted but not deduced theoretically.

The Velocity of Reaction under great External Pressures.

If the rate (in aqueous solution) of reactions which are catalysed by hydrogen ions and hydroxyl ions depends on collisions between solute and solvent molecules, we should expect an increase in pressure to bring about an increase in the velocity, corresponding to the diminished free space and

* *Z. physikal. Chem.*, **108**, 185, (1924).

mean free path. It has, in fact, been found that the rate of hydrolysis of sucrose by acetic acid* and the rate of hydrolysis of esters by acids† and alkalis‡ are increased about 25 per cent. when an external pressure of 1,000 atmospheres is applied. The catalytic effect of strong acids upon the velocity of inversion is diminished by an increase in pressure.§ The evidence is therefore not conclusive. Other factors besides the collision frequency enter into the problem, such, for example, as the deformability of the molecules, and appear to be a more probable explanation since the influence of the pressure is independent of temperature.‖

Termolecular Reactions.

Few reactions are known which are definitely of the third kinetic order. The polymerization of benzaldehyde into benzoin in alcoholic solution

$$2C_6H_5.CHO \rightarrow C_6H_5.CH(OH).CO.C_6H_5$$

is bimolecular with respect to the aldehyde, but the reaction is powerfully catalysed by cyanide ion, k_{bi} being directly proportional to the concentration of this catalyst. The reaction has been examined by Stern,** and appears to be singularly free from complications. The relation

$$-\frac{dx}{dt} = k_3[\text{aldehyde}]^2[\text{cyanide}]$$

holds over a fairly wide range of conditions, at temperatures of from 25° to 60° C. Stern's results may be summarized in the form

$$k_3 = 5{\cdot}27 \times 10^5 e^{-13{,}000/RT},$$

the termolecular constant being in (litres/gram molecule)^2

* Stern, *Ann. Phys. Chem.*, **59**, 657, (1896); Cohen and Valeton, *Z. physikal. Chem.*, **92**, 433, (1917).

† Rothmund, *ibid.*, **20**, 168, (1896).

‡ Cohen and Kaiser, *ibid.*, **89**, 338, (1915); Walker, *Proc. Roy. Soc.*, **78**, 157, (1907).

§ Cohen and de Boer, *Z. physikal. Chem.*, **84**, 41, (1913).

‖ Moesveld, *ibid.*, **103**, 486, (1923).

** *Z. physikal. Chem.*, **50**, 513, (1904).

per second. A bimolecular reaction with this energy of activation we should expect to go about 500,000 times as fast. The disparity is clearly due, in part at least, to the much smaller probability of ternary collisions.

Among other reactions which appear to be termolecular are the oxidation of ferrous sulphate in water,* the action of ammonia on ethyl malonate in ethyl-alcoholic solution,† the reaction between iodide and ferric ions in water,‡ and that between benzoyl chloride and alcohols in etheric solution.§ The order in some of these examples has been assessed by the method of trial and error, which is known to yield insecure conclusions.

Negative Catalysis.

Just as a positive catalyst can accelerate a reaction in many ways, a negative catalyst can retard it in many ways. Since small amounts of a catalyst can produce a marked increase in the rate, a small amount of any substance which will destroy or incapacitate the catalyst can produce a marked decrease in the velocity. Examples will be cited in Chapter IX, when dealing with catalytic poisons. The retarding influence of a negative catalyst upon the rate of an uncatalysed reaction cannot be understood in this way, and other hypotheses are necessary. Two of these may be mentioned here. When a reaction proceeds by a chain mechanism, any substance which interrupts a single process in the chain can produce a considerable damping of the velocity by prematurely terminating a chain which would otherwise have involved many cycles. Secondly, a negative catalyst may function by combining with the reactant to form a complex which is more resistant to chemical change than is the uncombined reactant. Instances of both types of negative catalysis are known.

* Lamb and Elder, *J. Amer. Chem. Soc.*, **53**, 137, (1931).
† Bailey, *Proc. Roy. Irish Acad.*, **B, 39**, 567, (1930).
‡ von Kiss, *Z. anorg. Chem.*, **198**, 102, (1931).
§ Ashdown, *J. Amer. Chem. Soc.*, **52**, 268, (1930).

The chain theory of negative catalysis has been given by Christiansen* as a corollary to the more general theory of chain reactions previously developed by Christiansen and Kramers.† The theory can be dealt with but briefly in this place, giving no more of it than is necessary to understand the interesting results obtained by Bäckström‡ and others upon chain reactions in solution. The problem has been reviewed by Hinshelwood,§ whose version we here follow.

Consider the thermal decomposition of a single gas. The molecules are initially activated by collision, but the product of reaction is able to activate fresh molecules of the initial substance by giving up its excess energy to it. Each molecule of the product is supposed to activate α molecules in the process of relapsing into the normal condition. Let n be the concentration of normal, unactivated molecules of the gas, a that of activated molecules of reactant, and a' that of activated molecules of product. The condition for a stable chain is that

$$\frac{da}{dt} = 0 \quad \text{and} \quad \frac{da'}{dt} = 0. \tag{24}$$

Now

$$\frac{da'}{dt} = Aa - Z_1 n a' = 0; \tag{25}$$

i.e. the rate at which activated molecules of products are produced is equal to the rate (Aa) at which activated reactant molecules spontaneously pass over, minus the rate ($Z_1 n a'$) at which activated product molecules become deactivated by collision with normal molecules. Similarly,

$$\frac{da}{dt} = Kn^2 + \alpha Z_1 n a' - Aa - Z_2 n a = 0. \tag{26}$$

The four processes here are: (1) formation of active reactants

* *J. Physical Chem.*, **28**, 145, (1928).

† *Z. physikal. Chem.*, **104**, 451, (1923).

‡ *J. Amer. Chem. Soc.*, **49**, 1460, (1927); *Medd. K. Wetenskapsakad. Nobel-Inst.*, **6**, 15 and 16, (1917); *Trans. Faraday Soc.*, **24**, 601, (1928).

§ *The Kinetics of Chemical Change in Gaseous Systems*, 3rd ed., Chapter VII, (1933).

by collisions among normal molecules; (2) formation of active reactants by collisions between normal molecules and a certain fraction of active products; (3) spontaneous conversion of active reactants to active products; and (4) deactivation of active reactants by collisions with normal molecules. Z_1 and Z_2 are collision frequencies determined by the temperature and size of the molecules. K and A are more specific constants of the reaction itself. Substituting the value of a' ($a' = Aa/Z_1 n$) given by equation (25) into equation (26) and rearranging, we have

$$a = \frac{Kn^2}{Z_2 n + A(1-\alpha)}. \tag{27}$$

$$\text{rate of reaction} = Aa = \frac{AKn^2}{Z_2 n + A(1-\alpha)}. \tag{28}$$

When each activated molecule of product activates one molecule of reactant, i.e. when $\alpha = 1$, the rate reduces to $\frac{AK}{Z_2} n$, and the reaction becomes unimolecular. As pointed out by Christiansen, this gives an alternative theory of unimolecularity. In principle, a first order reaction would also result if α were less than unity, and A were negligibly small compared with $Z_2 n$. Consideration shows that this cannot be a probable condition, even if in solution the deactivations were at a maximum, every collision with solvent molecules depriving the active solute molecule of its energy. The theory in other respects also is not as helpful as the alternative one in dealing with reactions in solution. Suppose the factor α to be greater than unity, i.e. imagine one molecule of active product to be able to activate more than one molecule of the normal kind. The term $A(1-\alpha)$ thus becomes negative; and if α is so great that $A(1-\alpha)$ equals $Z_2 n$, the velocity of reaction becomes infinite. Generally, when α is greater than 1, the phenomena of branching chains appears, and explosions are possible.*

* Semenov, *Z. Physik*, **46**, 109, (1927); *ibid.*, **48**, 571, (1928).

Explosive reactions are obviously less likely to occur in solution than in the gas. There is as yet no definite evidence for the existence of explosions in solution, although the question is experimentally difficult to settle, since solutions are always examined in the presence of a vapour phase. Theory does not exclude the possibility of their existence.

The equation deduced above is the simplest of a large number which can be formulated in a similar manner for reactions of other orders and peculiarities. The significant point is that, in common with the more complicated expressions, it takes the form:

$$\left\{\begin{matrix}\text{rate of}\\ \text{reaction}\end{matrix}\right\} = \frac{\text{function of the concentration}}{\left\{\begin{matrix}\text{factor determining}\\ \text{the breaking of}\\ \text{chains by collisions}\end{matrix}\right\} + \left\{\begin{matrix}\text{factor which measures}\\ \text{the inherent reactivity}\\ \text{of the process}\end{matrix}\right\}}.$$

The experimental investigation of negative catalysis in solution was first approached in a comprehensive manner by Titoff.* Sodium sulphite in aqueous solution is oxidized by atmospheric oxygen, the velocity being unimolecular with respect to the sulphite. The most significant feature of the reaction is the marked inhibitive effect produced by the addition of minute quantities of a variety of substances such as salts of manganese and chromium, mannite, aniline, potassium cyanide, and numerous alkaloids.† That the reaction actually proceeds by a chain mechanism was proved by Bäckström,‡ who confirmed the earlier work on the inhibition by various substances, particularly alcohols, and found the rate of reaction to be given by the equation

$$\text{rate} = \frac{k_1}{kC+k_2}. \qquad (29)$$

C is the concentration of inhibitor, and k_1, k, and k_2 are constants, k depending upon the nature of the inhibitor. This equation is seen to be of the form required by Christiansen's

* *Z. physikal. Chem.*, **45**, 641, (1903).

† Young, *J. Amer. Chem. Soc.*, **24**, 297, (1902). ‡ *Loc. cit.*

theory. The relative values of k found by experiment are—mannite : methyl alcohol : ethyl alcohol : benzyl alcohol :: 1 : 0·5 : 1·3 : 60. These figures demonstrate the varying chain-breaking efficiency of the different alcohols, each of which is destroyed by the change which it inhibits.* Bäckström measured the length of the chains by assuming that, when inhibition is considerable, all the chains are broken by molecules of the inhibitor. The number of alcohol molecules which are destroyed in unit time gives the number of chains terminated in unit time, and, since the chains are stationary, the number initiated in unit time. The total number of sulphite molecules which are oxidized, when divided by the number of chains, gives the average number of links in each chain. When sodium sulphite is oxidized in aqueous solution, about 50,000 molecules are converted for each initial act. The chain is of remarkable length. Comparable figures were found also for the oxidation of benzaldehyde (10,000) and heptaldehyde (15,000).

The correctness of this interpretation is confirmed by measurements of the photochemical oxidation of these three compounds in aqueous solution. The velocity is increased by light of appropriate frequency, and is given by the relation

$$\text{rate} = \frac{k_3 k_1}{kC + k_2}. \qquad (30)$$

The constants have the same significance as in the dark reaction. The new constant k_3 is the ratio of the velocities of the photochemical and thermal reactions. The quantum efficiencies of the photochemical changes are 50,000, 10,000, and 15,000, which shows that the chain-length is not altered. In the photochemical oxidation the number of chains initiated is greater than in the thermal reaction, but otherwise the mechanism of the reaction is the same.

Further investigations† have shown that the inhibitory

* Inhibitors can break the chain without themselves undergoing chemical change.

† Alyea and Bäckström, *J. Amer. Chem. Soc.*, **51**, 90, (1929).

action is connected with the induced oxidation of the alcohols. The oxidation of benzaldehyde is inhibited also by anthracene, which during the reaction is itself converted by induced oxidation to anthraquinone.* In this case, the actual velocity of the photochemical reaction ($\lambda = 3130$ Å.) at 30° C. is about 3 times as great as that of the thermal reaction. The active agent, which is identified as a peroxide, suffers at least 1,000 collisions with benzaldehyde molecules before finally giving up its energy.

The alternative explanation of negative catalysis receives support from the large volume of work which has accumulated on the inhibitive action of water and other substances upon the velocity of decomposition of organic acids in sulphuric acid solution.† One example may be considered in detail—the quantitative conversion of malic acid into α-pyrone-β'-carboxylic acid, with water and carbon monoxide, the latter providing a suitable means for manometric estimation.‡ The reaction in pure sulphuric acid presents no novel features, k being unimolecular and given accurately by the equation $k = 1{\cdot}78 \times 10^{15} e^{-25,330/RT}$. Ten substances of widely different character inhibit the reaction, which has been measured in the presence of varying amounts of each at three temperatures. Dittmar interprets the results in terms of a reactive complex of malic acid and sulphuric acid, the existence of which is confirmed by solubility measurements. The inhibitors act by combining with malic acid and thus diminishing the concentration of the reactive complex. Dittmar's results may be examined in the following way, by a study of the observed critical increments under each set of conditions. In seven cases, the second addition of the inhibitor has caused an average increase in E of 490 calories. The factor $e^{\Delta E/RT}$ is 2·3, which accounts

* Bäckström and Beatty, *J. Physical Chem.*, **35**, 2530, (1931).

† Oxalic acid, Lichty, *ibid.*, **11**, 225, (1907); formic acid, Meyer, *Z. Elektrochem.*, **15**, 506, (1909); succinic acid, Wiig, *J. Amer. Chem. Soc.*, **52**, 4742, (1930).

‡ Dittmar, *ibid.*, **47**, 987, (1925); **52**, 2746, (1930).

Table 11

Inhibitor	*E*		
	No inhibitor	0·25 mol. of inhibitor	0·50 mol. of inhibitor
Ammonium sulphate	25,330	27,640	28,240
Phenol		27,640	29,310
p-Cresol		27,380	28,030
Coumarin		27,900	28,120
Benzophenone		26,980	27,340
Benzoic anhydride		30,400	31,060
Ethyl alcohol		26,800	26,470
Benzoic acid		27,160	27,160
Ortho-phosphoric acid		26,890	27,470
Acetophenone		26,900	26,050

almost exactly for the decrease in velocity corresponding to the second addition. The interpretation given by Dittmar seems therefore to be justified. It is a special application of the intermediate-complex theory, exhibiting a rather unusual phenomenon which is of some importance. When, as in most of the studies hitherto encountered, the intermediate complex is more reactive than the uncombined reactant, there is a fall in E, the extent of the fall being independent of the amount of catalyst. In the present case, E rises with the addition of the negative catalyst, successive additions causing a continual increase in E. The reason for this is not far to seek. With a positive catalyst, two simultaneous reactions occur side by side, but usually the catalytic coeffioient is so much greater than the uncatalysed reactivity that the latter becomes negligible in comparison. E therefore gives the heat of activation of the catalysed reaction. With a negative catalyst, also, there will be two simultaneous reactions, and since the inhibitive effect is often less marked than a catalytic effect, the velocity of the uninhibited reaction will usually be comparable with that of the inhibited one, especially with small amounts of negative catalysts. The true E for the inhibited reaction cannot be evaluated until sufficient of the negative catalyst has been added to remove nearly all of the uncombined reactant. It will be noticed

from the table that the first addition of inhibitor causes E to rise by about 2,500 calories: the second addition causes E to rise a further 500 calories only, so that the conditions are quickly approximating to those of a completely inhibited reactant. Inhibition in this case is strictly a misnomer. The slow reaction which is measured is really the decomposition of another substance. In true inhibiting effects, the chemical change which is measured is the same in the presence of all inhibitors.

Dittmar's explanation would not apply to Bäckström's results, but Christiansen's theory may be able to interpret Dittmar's. As in positive catalysis, so in negative catalysis, the variety of phenomena calls for a variety of hypotheses, all of which may find justification under special circumstances.

The Kinetics of Chain Reactions.

Hitherto we have been dealing with the initial, or instantaneous, velocity of chain reactions. The complete course of some of these reactions has been shown to be unimolecular. They are the photopolymerization of vinyl chloride, the auto-oxidation of sodium sulphite, and the photolysis of hydrogen peroxide.* Assuming that the primary step is followed by a chain of probable length $k_3/(k_2+kc)$, we have

$$\frac{dx}{dt} = k_1(a-x)\left\{1+\frac{k_3}{k_2+kc}\right\}. \qquad (31)$$

With chains of appreciable length, the initial act may be ignored, hence

$$\frac{dx}{dt} = \left\{\frac{K}{k_2+kc}\right\}(a-x), \qquad (32)$$

or

$$\frac{1}{t}\ln\frac{a}{a-x} = \frac{K}{k_2+kc}. \qquad (33)$$

By the graphical examination of the observed unimolecular

* Jen and Alyea, *J. Amer. Chem. Soc.*, **55**, 575, (1932).

constants, Jen and Alyea find the minimum number ($1/k_2$) of links in the chains to be 5,000, 900, and 540 respectively. It will be observed that when the fractional change (x/a) is small, equation (32) reduces to Bäckström's equations ((29) and (30)).

IX

HETEROGENEOUS REACTIONS

When a chemical reaction occurs in a heterogeneous system, there are superimposed on to the specific chemical effects certain interfacial factors which operate at the boundary of the phases and may influence the velocity of chemical change. A large variety of phenomena thus becomes possible theoretically, and is in fact met with in practice, although the precise information at present available is somewhat meagre.

Attention has been confined almost completely to solid-liquid systems, consisting of a solid in contact with a dilute solution. Dissolved molecules may react with the solid or undergo catalytic transformation at its surface. The study of the kinetics of these reactions is the logical prelude to the investigation of enzymic reactions. The solid may be present as a crystal, or dispersed as a suspensoid or colloid.

Since the dissolved molecules must strike the surface of the solid before reaction can occur, the change takes on the nature of a bimolecular process, with the possibility of intermediate complexes of varying natures and stability. Solute molecules may anchor on the solid surface with the tenacity denoting a polar link, or they may merely congregate in greater number about the surface than in the bulk of the solution, and be held loosely there by attractive forces not necessarily chemical in origin. In both cases, the molecules are said to be adsorbed on the surface. Since the approach of an ion or a solute molecule up to the surface, or its removal therefrom, entails the expenditure of energy, the observed critical increment of a heterogeneous reaction will usually be a composite term, consisting of the true energy of activation plus the heat of adsorption or desorption as the case may be. Surface reactions may thus be examined in the light of the intermediate-complex theory, but the heat

of formation of the complex acquires a different meaning. There are three distinct processes occurring in reactions of this kind: (1) the solute molecules approach and collide with the solid surface, where (2) chemical reaction takes place; followed by (3) the recession of the products away from the interface into the bulk of the solution. Theoretically, each of these three processes, having definite velocities, may influence the net rate of reaction, the magnitude of which is determined by the slowest process of all. Experience shows that the velocity of approach of solute molecules towards the surface is usually faster than the speed of chemical change, although the rate of approach of suitably activated molecules may be less than the usual speed of chemical reactions. The determining factor very often will be the relative magnitudes of stages (2) and (3). A sharp distinction here arises between homogeneous and heterogeneous systems, since in the latter case the rate at which molecules move away from the surface may become important. This rate has much the same value for all solutes in a given solvent at a fixed temperature, and is determined by its diffusion coefficient. When a crystal of calcite dissolves in dilute mineral acids, the chemical change is slower than the diffusion process and determines the observed velocity. Calculations given below show that a fair percentage of the hydrogen ions which strike the marble surface with the requisite energy liberate molecules of CO_2. On the other hand, when metals are attacked by aqueous acids, or cadmium by aqueous iodine, the chemical change is rapid; the observed velocity is then simply the velocity of diffusion (of cadmium ions away from the surface, or of iodine molecules towards the surface). The true kinetics of chemical change in cases like these entirely elude investigation: nothing is known of their velocity or energy of activation, except that by inference the latter must be small.

The course of a reaction between a dilute solution and a solid and its apparent kinetic order are governed by the

relative amounts of solute and solid present in the system, and by the relative adsorbability of the reactants and the resultants. When there is a large excess of solute, the surface may be perpetually saturated with adsorbed molecules of solute. The velocity, being dependent on the number of adsorbed molecules, will therefore be constant, giving a reaction of apparently zero order ($dn/dt = k$). Such behaviour is found when substrates at high concentrations are hydrolysed by small amounts of enzyme.* In general, the number n of molecules adsorbed per unit surface will be related to the number (n_s) of solute molecules per c.c. of solution by the Freundlich isotherm, $n = Kn_s^{\frac{1}{\alpha}}$. The number of molecules of solute in the bulk of the solution diminishes, and the number adsorbed by unit surface falls off continuously and proportionately as the reaction proceeds. When α is unity, the conditions for a unimolecular reaction are realized, since $-\frac{dn_s}{dt} = kn = kKn_s$. Most of the simpler reactions which are catalysed by solids or enzymes proceed unimolecularly under certain limited experimental conditions, the unimolecular constant being proportional to the amount of catalyst present. The decomposition of hydrogen peroxide is a pseudo-unimolecular reaction in the presence of massive platinized platinum,† colloidal plantinum,‡ haemase,§ and liver catalyse.|| The tryptic digestion of casein is apparently unimolecular when the enzyme concentration is maintained at a high and constant value.** Most of the glykosides and simple carbohydrates also behave in a similar manner, the general condition for unimolecular behaviour being a constancy in the enzyme concentration and a relatively low

* Lactose by emulsin, Armstrong, *Proc. Roy. Soc.*, **73**, 500, (1904); sucrose by saccharase, Hudson, *J. Amer. Chem. Soc.*, **30**, 1564, (1908); casein by trypsin, Northrop, *J. General Physiol.*, **6**, 429, (1924).

† Bredig and Teletow, *Z. Elektrochem.*, **12**, 581, (1906).

‡ Bredig, von Bernek, and Ikeda, *Z. physikal. Chem.*, **37**, 1, (1901).

§ Senter, *ibid.*, **51**, 673, (1905).

|| Zeile and Hellström, *Z. physiol. Chem.*, **192**, 171, (1930).

** Northrop, *J. General Physiol.*, **6**, 417, (1924).

concentration of substrate.* Departure from the first-order curve may result from a number of effects, among which may be noted: (1) the existence of adsorption of the Freundlich type, where α is less than unity, and dn/dt is consequently greater than dn_s/dt; (2) spontaneous or induced inactivation of the enzyme; and (3) selective adsorption of the products of reaction. In the last case, provided both reactants and resultants are highly adsorbable, but the latter more so than the former, the rate becomes inversely proportional to the concentration of products.

The problem thus becomes very complicated, and the possibility of interpreting the results is within reach only when exceptionally simple experimental conditions have been chosen. Even then a complete understanding is not possible, but the theoretical and practical approach may here be illustrated with reference to a few well-investigated reactions. A brief account of diffusion must first be given.

The Diffusion of Solutes.

The necessity arises for a knowledge not only of the translatory velocity which dissolved molecules and ions possess in virtue of their temperature but of the extent to which the velocity is modified by the superposition of directional forces. When, for example, an external electrostatic field is applied to a solution of an electrolyte, the component velocity of the ions in a direction perpendicular to the electrodes is increased. Similarly, when there is an unequal concentration of solute, and the solution is consequently not at equilibrium, there is a resultant osmotic force driving the molecules from the region of high concentration to that of low concentration, and tending to establish equilibrium by bringing about the most random distribution of solute molecules. The ions or dissolved molecules under these conditions are said to diffuse through the solution. Since

* See, for example, Kuhn and Sobotka, *Z. physikal. Chem.*, **109**, 65, (1924); Weidenhagen, *Z. deutschen Zucker-Industrie*, **82**, 503, (1932).

an adsorbed layer of molecules is formed at the surface of any solid in contact with a solution, the process of diffusion will tend to unform such a layer. If chemical change takes place very rapidly at the surface of contact, under certain conditions the observed velocity of reaction will be governed by the rate at which molecules of the product move away from the surface, or by the rate at which fresh molecules of reactant reach the surface from the bulk of the solution.

Fick* found that the quantity (ds) of solute which crosses a boundary of area A in time dt is proportional to the concentration gradient dc/dz

$$ds = DA\frac{dc}{dz}dt. \qquad (1)$$

The proportionality factor is termed the diffusion coefficient, and is seen to have the dimensions of (length)^2/time. The conventional units in which D is expressed are: area in sq. cm.; concentration gradient in gram molecules per litre per centimetre; time in days. D is thus the number of gram molecules of solute which cross a boundary of 1 sq. cm. in 1 day under unit concentration gradient, and can be determined experimentally by analysing different layers at various intervals in a tall cylinder which originally contained a concentrated layer of the solute in contact with a large volume of the solvent.

The kinetic theory of diffusion has been given by Einstein.† A cylinder of unit cross-section containing a dilute solution is imagined to be fitted with a semi-permeable membrane, through which only solvent molecules can pass. If the concentration of the solute in compartment A is greater than in B, a force F will be exerted on the piston, which is equal to the difference in osmotic pressure per unit volume.

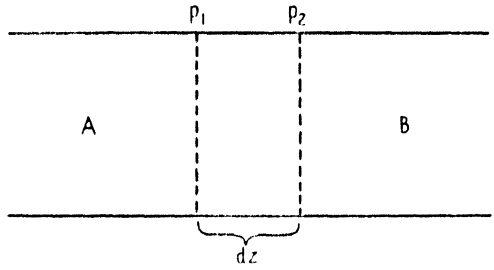
$$F = \frac{p_1 - p_2}{dz} = \frac{dp}{dz}. \qquad (2)$$

The osmotic pressure p is related to the concentration c by

* *Pogg. Annalen*, **94**, 59, (1855). † *Z. Elektrochem.*, **14**, 235, (1908).

the gas laws, $p = RTc$, provided the solution is very dilute. Hence

$$F = RT\frac{dc}{dz}. \tag{3}$$



The force exerted by one molecule is

$$\frac{F}{cN_0} = \frac{RT}{cN_0}\frac{dc}{dz}, \tag{4}$$

where N_0 is Avogadro's number. By Stokes's law, the resistance offered to the motion of each molecule is $6\pi\eta r$, hence the uniform velocity of diffusion should be

$$v = \frac{RT}{cN_0}\frac{dc}{dz}\frac{1}{6\pi\eta r}. \tag{5}$$

But $vc/(dc/dz)$ represents the number of gram molecules transported per second across unit area under unit concentration gradient, and is therefore simply the diffusion coefficient. Hence

$$D = \frac{RT}{N_0}\frac{1}{6\pi\eta r}. \tag{6}$$

This is the familiar Stokes-Einstein diffusion equation.*

The relation between the velocities of ions under unit concentration gradient and their velocities under unit electrical potential was deduced by Nernst.† Assuming a

* In applying this equation, it should be observed that, taking $R = 8{\cdot}315 \times 10^7$ ergs per degree, D becomes equal to the number of gram molecules carried across an area of 1 sq. cm. in 1 sec. when the concentration gradient is one gram molecule per c.c. per cm., and is thus 1,000 times the value of D in the units of gram mol. per litre per sec.

† *Z. physikal. Chem.*, **2**, 613, (1888).

uni-univalent electrolyte to be completely ionized in dilute solution, the diffusion coefficient is related to the ionic mobilities (U_a and U_c) of the anion and cation, and to the absolute velocities (u_a and u_c) of the ions under the influence of an electrostatic field of unit potential gradient by the equation

$$D = 2RT\left(\frac{U_a U_c}{U_a + U_c}\right). \qquad (7)$$

Numerical values have been obtained for the diffusion coefficients of numerous solutes in various solvents by the use of equations (1), (6), and (7). The three methods lead to results in close agreement, provided the radius of the solute molecule is known when equation (6) is employed. There is often some doubt about the precise value of r, since solutes, due to solvation, have greater effective diameters in solution than in the solid or liquid phase. The usual procedure is to determine D by means of Fick's law and Nernst's equation. The Stokes-Einstein relation is then often used to evaluate the diameter from a knowledge of the diffusion coefficient. Extensive experiments on diffusion have been carried out by Öholm*, and supplemented by Haskell,† and others. In a given solvent at a fixed temperature, all solutes should have diffusion coefficients of the same order of magnitude, the value of D being inversely proportional to the radius of the solute. This is known to be the case; for example, in water at 18° C., urea, hydroquinone, and sucrose have values of $1{\cdot}12\times10^{-5}$, $0{\cdot}73\times10^{-5}$, and $0{\cdot}41\times10^{-5}$ sq. cm. per second respectively. (Cf. the molecular diameters as given by equation (4) of Chapter I.) As is to be expected from equation (6), the temperature coefficient of the diffusion of all solutes in any given solvent should have the same value, which is closely related, but not exactly equal, to the temperature coefficient of the fluidity of the solvent. This also is borne out by experiment. The average value of $(D_{t+10°}/D_t)$ for most aqueous solutions at 18° C. is 1·238.

* *Z. physikal. Chem.*, **50**, 309, (1905). † *Physical Review*, **27**, 145, (1908).

For our purposes it will be most suitable to express the temperature coefficients in the form of an energy term, to which no special physical meaning need be attached except that it is defined by the equation

$$e_D = RT^2 \frac{d \ln D}{dT} \tag{8}$$

or

$$e_D = \frac{2{\cdot}303 RT_2T_1}{T_2 - T_1} \log_{10} \frac{D_2}{D_1}.$$

Similarly, from the temperature coefficient of the viscosity, which is negative, we have

$$e = RT^2 \frac{d \ln \eta}{dT}. \tag{9}$$

This is but another way of writing Andrade's equation (p. 159). From the Stokes-Einstein relation, it follows that

$$e_D = RT - e_\eta. \tag{10}$$

This equation also is accurately obeyed. As a first approximation, e_D may be taken as equal to e_η which is independent of temperature in the case of non-associated liquids, but falls with a rise in temperature in the case of water, alcohols, and other polymerized solvents.

Nernst's Theory of the Kinetics of Heterogeneous Reactions.

By rotating cylinders of benzoic acid and of lead chloride in water, and analysing the solution from time to time, Noyes and Whitney* found that the velocity of dissolution of the solids followed an apparently unimolecular law:

$$\frac{dx}{dt} = k'(a_s - x). \tag{11}$$

a_s is the solubility of the solid in water, and x the concentration of the solute in the bulk of the solution at time t. The rate of dissolution being proportional to the difference between the saturated and observed concentrations, it was

* *Z. physikal. Chem.*, **23**, 689, (1897).

suggested by them that a saturated layer is formed at the surface of the solid. The velocity of the change is then simply the velocity with which solute molecules diffuse out into the liquid. Bruner and St. Tolloczko* substantiated this conclusion by examining the rate of dissolution of a variety of compounds in water. The velocity was found by them to be directly proportional to the area (A) of the surface:

$$\frac{dx}{dt} = kA(a_s - x). \qquad (12)$$

Since unimolecularity is obeyed during the complete process, it appears that the effective area remains constant, although the actual surface of the solid becomes eroded.

A general theory of the kinetics of heterogeneous reactions was developed by Nernst† upon analogy with the effects observed during dissolution.

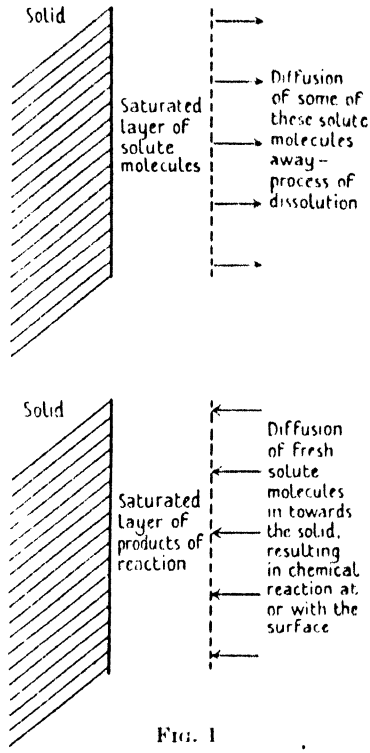


FIG. 1

The principal postulate is that chemical reaction proper takes place very rapidly at the surface, the liquid in the immediate neighbourhood thus becoming soon choked with the products of reaction, and hindering further chemical change. Fresh molecules of solute can, however, diffuse slowly through this saturated layer, with a velocity which is small compared with that of the chemical change, and diminishes as the concentration of dissolved substance falls off. The theory therefore predicts that such reactions must

* *Ibid.*, **35**, 283, (1900). † *Ibid.*, **47**, 52, (1904).

be unimolecular, with a velocity which is equal to the velocity of diffusion. Nernst's views have been variously received by different investigators. Brunner* and others have enthusiastically adopted it as the correct and final answer to the phenomena of all chemical reactions occurring between solids and dilute solutions. Wildermann† is inclined to discredit the theory altogether, pointing out, quite rightly, that the unimolecular behaviour can be explained in other ways. Experiments carried out during later years, a review of which is given by Centnerszwer,‡ show that some reactions can readily be understood upon the Nernst theory, whereas others seem to contradict it. The crux of the matter depends on how much truth there is in the assumption that the actual chemical reaction (or the actual process of dissolution of a solid in a liquid) takes place rapidly compared with the process of diffusion.

Instances are known where the agreement with theory is complete, and the assumption in these cases seems to be amply justified. It will be shown later that the postulate does not accord with the facts in other cases: the actual chemical change at the interface may completely determine the velocity of reaction, the question of diffusion not entering into the problem at all.

The theory of Nernst may be described in the following words. Consider a solution of volume V litres, containing c gram molecules of solute per litre. Between the solution and a solid of area A sq. cm., there is a layer of thickness δ, formed by the accumulation of reaction products during initial stages. In the subsequent stages, fresh molecules of solute can only reach the solid by diffusion through this layer. The

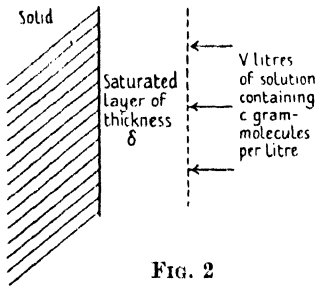


FIG. 2

* *Z. physikal. Chem.*, **47**, 56, (1904). † *Ibid.*, **66**, 445, (1909).
‡ *Ibid.*, **A**, **141**, 297, (1929).

number of gram molecules reaching the solid in time dt seconds is ds. This transfer reduces the concentration of the solute by an amount ds in V litres, i.e. the fall in concentration in this time is ds/V. Now by Fick's law

$$\frac{ds}{dt} = DA\frac{dc}{dz}, \tag{13}$$

where dc/dz is the concentration gradient. Hence

$$\frac{dc}{dt} = \frac{1}{V}\frac{ds}{dt} = \frac{DA}{V}\frac{dc}{dz}. \tag{14}$$

The concentration gradient at any instant being c/δ, we have

$$\frac{dc}{dt} = \frac{DA}{V\delta}c \tag{15}$$

and

$$k_{\text{uni}} = \frac{dc}{dt}\frac{1}{c} = \frac{DA}{V\delta}. \tag{16}$$

It should be noticed that k is independent of the concentration of the solute, V being the total volume of the solution and not the volume containing 1 gram molecule of solute. We will return to a fuller discussion of this equation later. For the present, it need be pointed out that the velocity corresponding to an area of 1 sq. cm. and a total volume of 1 litre is given as

$$\delta = \frac{D}{k}, \tag{17}$$

an equation which has been used by Brunner to calculate the thickness of the saturated layer. For a number of reactions in water at 20°, δ is about 3×10^{-3} cm. The magnitude of δ, of course, is no proof that the theory is correct, but the fact that k is of the same order of magnitude for a number of different solutes is what is to be expected if diffusion governs the processes. This is the really significant result. The absolute value of δ may well be regarded as improbable, since it represents a layer which is about 50,000 molecules thick.

A further important test of Nernst's theory is afforded by

the influence of temperature upon the velocity of heterogeneous reactions. Provided the thickness of the interfacial layer is independent of temperature, dk/dT should equal dD/dT, and the observed critical increment should thus have a value of 4,600 calories at 25° C. Many heterogeneous reactions do in fact have about this value for E, but it is quite possible, of course, for reactions to possess a real energy of activation of this value. Homogeneous reactions in solution are known with zero critical increment (p. 207). The argument is therefore not unambiguously in favour of the diffusion theory even when the temperature coefficient is of this amount. A third characteristic of reactions with rates governed by the diffusion process is that k varies with the rate at which the solution is stirred. The constant s in the equation: rate of reaction = constant × (rate of stirring)^s has been given values of 1 (Wildermann), $\frac{2}{3}$ (Brunner), and $\frac{4}{5}$ (von Name).

Nernst's theory is open to criticism which cannot be given before dealing first with its application in various directions.

The Reactions between Metals and Iodine Dissolved in Aqueous Potassium Iodide.

The velocity of the reaction between metals and iodine has been studied by von Name and his collaborators.* The significant results are that numerous metals, such as mercury, cadmium, zinc, copper, and silver react at approximately the same velocity at the same temperature. The velocity increases with a rise in temperature to the same extent as the diffusion coefficient. Furthermore, bromine attacks the metals more rapidly than iodine. All these facts are adequately explained in terms of Nernst's diffusion theory, and there is no doubt that the interpretation is correct. We must, however, examine some of the results more closely.

* von Name and Edgar, *J. Amer. Chem. Soc.*, **38**, 253, (1916); von Name and Bosworth, *Am. J. Sci.*, **32**, 207, (1911); von Name and Hill, *ibid.*, **36**, 543, (1913).

Von Name's* data on the rate of reaction between cadmium and iodine are very complete. A disk of cadmium of diameter 3·83 cm. (area therefore equals 23·0 sq. cm.) was rotated 200 times per minute in a solution containing 0·5 gram molecules of potassium iodide per litre, 0·01 of sulphuric acid, and 0·02 of iodine. The halogen was therefore present almost entirely in the form of the tri-iodide ion I_3^-. The reaction was found to be unimolecular; the value being that given by the equation

$$k = \frac{2{\cdot}303}{t_2 - t_1} v \log_{10} \frac{[I_2]_1}{[I_2]_2}. \qquad (18)$$

t is the time in minutes, and v the volume of the solution in c.c. Von Name's values are:

$t°$ C.	0	15	25	35	45	55	65
k	3·72	5·87	7·62	9·55	11·81	14·26	16·93.

The critical increment (4,040 calories) thus compares very favourably with the heat of diffusion (equation (8)), which, although not quite constant, has an average value of 4,240 calories over this range.

It is when we come to consider the absolute value of the velocity of reaction that the first departure from an otherwise complete agreement with theory becomes noticeable. At 15° C., we may take the diffusion coefficient to be approximately 5×10^{-6} cm.^{2} per second. The velocity constant given by von Name must be divided by $(60 \times 1{,}000 \times 23)$ in order to reduce the time to seconds, the volume to litres, and the area of the surface to 1 sq. cm. $k_{15°}$ then becomes $4{\cdot}25 \times 10^{-6}$. By equation (17) the thickness δ of the saturated layer would appear to be about 1 cm., which of course is absurd. A saturated layer of a few molecules seems in all respects to be the true interface. Let us therefore assume δ to be of the order of magnitude of 10^{-7}. The observed velocity of reaction is consequently lower by this factor than what would be anticipated on the basis of Nernst's theory.

* *Am. J. Sci.*, **43**, 453, (1917).

In other words, only about one in ten millions of the ions I_3^- which diffuse on to the metallic surface succeeds in detaching an atom of the metal. Why this should be is not clear, although many explanations suggest themselves. The whole picture remains intact, however, since the number of ions which do react is still proportional to the number that reach the surface. Quantitative agreement between calculated and observed rates implies, not only that the reaction at the surface is rapid, but also that every molecule which reaches the surface reacts.

If, in the reactions studied by Brunner, the efficiency of collisions is less than one, the saturated layers will have a true thickness which is smaller than the published values in proportion to the inefficiency.

The Reaction Between Metals and Dilute Aqueous Acids.

The factors governing the rate of evolution of hydrogen from metals in acid solution have received much attention, partly on account of the importance attaching to the allied phenomena of metallic corrosion and passivity. A wide diversity of results has been discovered. It may be said that the general reproducibility of data obtained within recent years is singularly good. The velocity of reaction most frequently is unimolecular with respect to the acid, although changes of higher order have been reported. Many metals and some alloys are attacked by acids at approximately the same rate, indicating, along with other results, the predominance of the part played by diffusion.

A polished disk of metal, partially covered by a mixture of wax and rubber, is rotated in the solution of acid. The course of the reaction may be determined by weighing the disk at various intervals, or, as is more frequently done, by measuring the volume of hydrogen evolved. The velocity of the reaction between zinc and hydrochloric acid has been investigated using both methods. Some of the results are compared in Table I.

Table 1

The Rate of Reaction between Zinc and Hydrochloric Acid referred to 1 *sq. cm. of Metal Surface*

Reference	Temperature ° C.	Initial concentration of HCl (gram mol./litre)	Observed no. of H_3O^+ disappearing per second	Calculated no. of H_3O^+ striking unit area per second	Ratio
(1)	23	0·175	$3{\cdot}10 \times 10^{17}$	$1{\cdot}52 \times 10^{23}$	$4{\cdot}9 \times 10^{5}$
(2)	16	0·5	$1{\cdot}36 \times 10^{18}$	$4{\cdot}20 \times 10^{24}$	$3{\cdot}2 \times 10^{6}$
(3)	25	0·5	$1{\cdot}08 \times 10^{18}$	$4{\cdot}36 \times 10^{24}$	$4{\cdot}0 \times 10^{6}$

(1) King and Braverman, *J. Amer. Chem. Soc.*, **54**, 1744, (1932).
(2) Fischer, *Z. Elektrochem.*, **35**, 502, (1929).
(3) Centnerszwer, *Z. physikal. Chem.*, **A, 141**, 297, (1929).

The figures in the fourth column have been computed from the number of c.c. of hydrogen evolved per minute: those in column 5 have been obtained from the expression $n_s\sqrt{(RT/2\pi M)}$, where n_s is the number of hydrogen ions per c.c. of solution (equation (9), Chap. I). As in the reaction between metals and iodine, only a very small fraction of those ions which reach the surface result in chemical change. In the present example, two hydrogen ions must become engaged before one atom of zinc is dissolved, which suggests that the low efficiency of the reaction may be attributed to the smaller probability of what is in effect a ternary collision. This explanation, however, is improbable, for the same tardiness is revealed in the process of dissolution of a salt in water. The origin of the delay at the surface seems to be due to the necessity of activation of the solid molecules. In the most favourable case, the minimum value of the energy of activation would be equal to the heat of fusion of the solid plus the heat of solvation. When E is large, the reaction at the surface will be slow, and possibly much slower than diffusion, which does not therefore enter into the scheme. In the instance under examination, however, the actual chemical change at the surface, although relatively slow, is still much faster than the rate of diffusion. Hence nothing is known of the true energy of activation. King and

Braverman* have shown this reaction to be free from kinetic salt effects and due entirely to hydrogen ions.† From their values of k_{25}/k_{15} (= 1·285), and k_{35}/k_{25} (= 1·260), we have an apparent energy of activation of 4,230 calories, in close agreement with the heat of diffusion, which is 4,600 calories in this temperature range. Further proof that the measurable velocity is influenced by diffusion is afforded by the effect of stirring and of the addition of substances which alter the viscosity.

Table 2

Time (minutes)	$\frac{\Delta v}{\Delta t}$ (c.c. of H_2 per minute)	$k = \frac{\Delta v}{\Delta t} \cdot \frac{1}{[HCl]}$	
10	1·249	—	
20	1·169	—	
30	1·426	—	
40	1·600	—	
50	1·796	—	
60	1·805	4·28	
70	1·777	4·33	
80	1·777	4·42	
90	1·651	4·42	
100	1·553	4·41	4·36
110	1·483	4·40	
120	1·408	4·38	
130	1·333	4·36	
140	1·235	4·33	
150	1·216	4·32	

The alloying of zinc with small amounts of silver, lead, arsenic, and other metals diminishes the velocity of reaction to a slight extent.‡ The results of a typical run are given in Table 2, which is due to Centnerszwer§ and refers to an alloy of 0·4 per cent. of silver in zinc, dissolving in 200 c.c. of 0·5N hydrochloric acid at 25° C. As is frequently found, the rate of reaction increases during the initial stages before the unimolecular condition is established. Calculations

* *Loc. cit.*

† The proportionality between velocity of dissolution and concentration of acid is disputed by Guertler and Blumenthal (*Z. physikal. Chem.*, **A, 152,** 197, (1931)), who emphasize the role played by the overvoltage of hydrogen.

‡ Fischer, *loc. cit.* § *Loc. cit.*

directed at evaluating the thickness of the Noyes-Whitney layer on the assumption that the early period in the reaction corresponds with the time taken to form the layer show the assumption to be false. It is much more probable that the reaction under ideal circumstances is actually unimolecular throughout its course, but in such cases as these the law is partially obscured by the incomplete removal of those factors which when present in a more acute form give rise to entire passivity. Further discussion of this interesting phenomenon would be out of place here, but it is worth while noticing that the effect is definitely connected with the surface of the metal only, and that the potential difference set up between the metal and the solution of its ions may be the sole cause. The rate of dissolution of metals in acids is modified by the application of an external electromotive force, the magnitude of the modification being proportional to the applied E.M.F.*

Centnerszwer† claims that the reactions between cadmium and hydrochloric acid and between tin and hydrochloric acid are of the fourth order with respect to the acid, but the evidence adduced is not convincing. The absolute rate is slower by a factor of about 10^3 than the rate with zinc and other metals, and is definitely a function of [HCl] raised to a power greater than unity. The other fact which is definitely established is that the temperature coefficient of the solution of tin in hydrochloric acid is much greater than that of diffusion. Centnerszwer's results give a value of $E = 7{,}210$ calories, from which it is found that the ratio of the number of activating collisions to the number of molecules reacting is about 10^5.

Experiments which have been carried out on the dissolution of metals‡ and of amalgams§ in non-aqueous solutions of acids are few in number. They clearly indicate a marked solvent effect.

* Thiel and Eckell, *Z. physikal. Chem.*, **132**, 78, (1928).

† *Ibid.*, **A, 141**, 297, (1929).

‡ Zecchini, *Gazz. chim. ital.*, **27**, 466, (1897).

§ Brönsted and Kane, *J. Amer. Chem. Soc.*, **53**, 3624, (1931).

The Reaction between Solid Calcium Carbonate and Dilute Hydrochloric Acid.

When a crystal of marble dissolves in hydrochloric acid, the rate of evolution of carbon dioxide is found to be proportional to the area of the surface of the solid and to the concentration of the acid. Equimolecular solutions of strong acids have all the same effect.

$$\frac{d[CO_2]}{dt} = kA[HCl]. \qquad (19)$$

Spring* worked with parallelepipeds of Carrara marble, waxed all over but for one facet, which was exposed to a 5 per cent. solution of hydrochloric acid. The facet measured 19 mm. by 16 mm. and at 35° C. gave off carbon dioxide at the rate of 25 c.c. in 54 seconds. This is equal to $1{\cdot}11\times10^{19}$ molecules per second. From the temperature coefficient of this rate, it is found that $E_{15-35^\circ} = 6{,}300$ calories and $E_{35-55^\circ} = 6{,}400$ calories. Over a temperature range of 40°, therefore, there is a constant critical increment of about 6,350 calories, which is definitely greater than the slightly variable heat of diffusion. It is therefore worth while making the supposition that the velocity of the actual chemical change is the important factor in the case, and calculating the rate of disappearance of hydrogen ions by means of the equation

$$-\frac{dn_s}{dt} = An_s\sqrt{\left(\frac{RT}{2\pi M_s}\right)}e^{-E/RT}. \qquad (20)$$

A is the area of the solid (here equal to 3·04 sq. cm.), and $n_s\sqrt{\frac{RT}{2\pi M}}$ is the number of hydrogen ions which strike unit surface per second (here equal to $1{\cdot}22\times10^{25}$). If the chemical change consists of the removal of carbonate ions from the crystal

$$CO_3^{--} + H_3O^+ \rightarrow HCO_3^- + H_2O,$$

the subsequent decomposition of the soluble bicarbonate

* *Z. physikal. Chem.*, **1**, 209, (1887).

may be assumed rapid, so that one molecule of carbon dioxide is produced for each hydrogen ion which disappears as a result of collision with the surface. The result of these calculations is that about one ion out of every 93 which strike the surface with energy greater than E results in chemical change. This factor is quite a reasonable one. The important conclusion is that the necessity of postulating the existence of an interfacial layer is superfluous. Diffusion does not determine the velocity of reaction in this case. Brunner,* whose absolute rates are about 4 times as great as those of Spring—possibly due to the stirring†—favours the diffusion view, although his study of the temperature effect is hardly extensive enough to warrant the conclusion.

Since the predominance of the diffusion effect may in general be expected when the energy of activation of the reaction taking place at the surface is small, we must look for examples of heterogeneous reactions with a large critical increment. Several of these have been investigated but with the solid present in the dispersed rather than the massive form.

The Decomposition of Sodium Hypochlorite in Aqueous Solution, Catalysed by Cobalt Peroxide.

Reference has already been made (p. 49) to the very slow decomposition of aqueous solutions of sodium hypochlorite, and to the marked catalytic effect of nickel peroxide. Howell‡ has studied the velocity of decomposition of sodium hypochlorite ($2\,ClO^- \rightarrow 2\,Cl^- + O_2$) under the influence of cobalt peroxide.

A suspension of CoO_2 containing 0·033 gram molecule per litre was found to be quite stable, and to give reproducible

* *Ibid.*, **47**, 56, (1904).

† It is open to question whether it is strictly logical to apply to reactions carried out with violent stirring the value of the diffusion coefficient which has been determined in quiet solutions. The diffusion of a solid in a stirred liquid is discussed by Schumann, *Physical Rev.*, **37**, 1508, (1931).

‡ *Proc. Roy. Soc.*, **A, 104**, 134, (1923).

results when the rate of stirring was not less than 1,600 revolutions per minute. When the concentration of catalyst is low, the decomposition is unimolecular with respect to hypochlorite, the value of the unimolecular constant being directly proportional to the concentration of catalyst over a sixfold range in $[CoO_2]$. At 40° C., 1 c.c. of the catalyst preparation added to 60 c.c. of hypochlorite solution gives $k_{\text{unl}} = 3{\cdot}51 \times 10^{-3}$ (minutes^{-1}: $\ln_e$). Howell measured the velocity of reaction at temperatures of 25, 30, 35, 40, 45, and 50° C., and found the Arrhenius critical increment to be 16,574 calories.

The molecular statistics of this reaction may now be discussed, provided the size of the catalyst particles can be estimated. From the stability of the preparation, it may safely be inferred that the diameters are less than 10^{-6} cm., for particles of this size coagulate rapidly. Ascribing a value of 5×10^{-7} cm. to the diameter of the cobalt peroxide suspensoid, and assuming it to have unit density, it follows that under the experimental conditions (1 c.c. of 0·033 molar preparation added to 60 c.c. of hypochlorite solution) 1 c.c. of the reaction mixture contains $7{\cdot}52 \times 10^{14}$ units of catalyst The observed unimolecular constant is $5{\cdot}85 \times 10^{-5}$ seconds^{-1}. The unimolecular constant which would be observed when the concentration of catalyst is 1 particle per c.c. is thus $7{\cdot}78 \times 10^{-20}$ seconds^{-1}.

Let us now calculate the velocity upon the assumption that each ion ClO^- which strikes the catalyst with energy greater than 16,574 calories/gram molecule brings about the formation of one molecule of oxygen. The number of molecules striking unit area per second is $n_s \sqrt{\frac{RT}{2\pi M_s}}$, where n_s is the number of hypochlorite ions per c.c. and M_s is the ionic weight. The number which strikes a sphere of area $\pi\sigma^2$ is $n_s\sigma^2 \sqrt{\frac{\pi RT}{2M_s}}$. Taking σ to be 5×10^{-7} cm., and $T = 313°$, this becomes $7{\cdot}05 \times 10^{-9} n_s$. The fraction of this number with

the requisite energy is $e^{-16,574/RT} = 2{\cdot}46\times10^{-12}$; the number of activating collisions upon one particle per second is $1{\cdot}73\times10^{-20}\times n_s$. Hence

$$\frac{dn_s}{dt} = 1{\cdot}73\times10^{-20}\, n_s$$

or

$$k = 1{\cdot}73\times10^{-20},$$

which is in excellent agreement with the observed velocity constant. The closeness of the agreement, however, is not important and may well be accidental. The result nevertheless is conclusive enough in demonstrating that the order of magnitude of the reaction velocity is governed by the rapidity of the chemical change, and not by the diffusion process.

The general form of the equation which is applicable to similar cases is

$$\frac{dn_s}{dt} = \sigma_c^2 n_s n_c \sqrt{\left(\frac{\pi RT}{2M_c}\right)} e^{-E/RT}, \qquad (21)$$

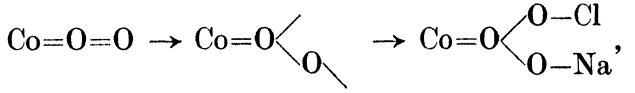
where n_s and n_c are the numbers of substrate and catalyst units present per c.c., and σ_c is the diameter of the catalyst. It will be noticed that the collision term in this equation is the same as that derived for gaseous molecules,

$$\sigma_{1,2}^2 n_1 n_2 \sqrt{\left\{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}},$$

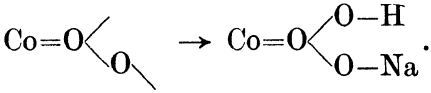
under such extreme conditions as will allow us to ignore $1/M_2$ as negligibly small, and to take the sum of the molecular radii as equal to the radius of the larger molecule.

Howell found that the addition of sodium chloride accelerated the reaction, the velocity constant being linearly related to the amount of added salt, thus affording an interesting example of the linear salt effect in heterogeneous catalysis. The catalyst suffers no injury when the usual poisons—potassium cyanide, mercuric chloride, arsenious oxide, and hydrogen sulphide—are added. Alkalis, however, retard the reaction markedly, possibly, as Howell

suggests, due to selective adsorption. In the absence of alkali, the following mechanism is suggested:



which in its presence is hindered by the preferential adsorption of the hydroxyl ion:



The explanation is consistent with the fact that hydrogen peroxide is much more labile in alkaline than in acid solution.

Chirnoaga's repetition of this work* gives results which agree in the main with those of Howell, although E is found to be somewhat less (15,840). With nickel peroxide as catalyst E becomes 16,580 calories, but the reaction is no longer unimolecular, the rate being given approximately as $dc/dt = kc^{0.47}$. The difference is rather surprising in view of the similarity in the two catalysts and in the apparent heats of activation.

The Freundlich adsorption isotherm has been found to represent the equilibrium between adsorbed molecules and those in solution in the reaction between formaldehyde and alkalis at the surface of copper oxide,† in the decomposition of formic acid solutions at the surface of rhodium‡ and of sodium hypophosphite at the surface of palladium.§

Other examples of heterogeneous reactions, the rates of which are not governed by diffusion, are the oxidation of hydrocarbons by potassium permanganate,‖ the hydrolysis of emulsions of esters in water,** and the dissolution of arsenious oxide.††

* *Trans. Chem. Soc.*, 1693, (1925).
† Birstein and Lobanov, *Z. anorg. Chem.*, **195**, 173, (1931).
‡ Blackadder, *Z. physikal. Chem.*, **81**, 385, (1912).
§ Sieverts and Peters, *ibid.*, **91**, 199, (1916).
‖ Meyer and Saam, *Berichte*, **30**, 1935, (1897).
** Goldschmidt, *Z. physikal. Chem.*, **31**, 235, (1899).
†† Drucker, *ibid.*, **36**, 693, (1901).

The Kinetics of Dissolution.

The theory of Noyes and Whitney, as we have seen, offers an explanation of the kinetics of dissolution of solids in terms of the diffusion of solute molecules away from an interfacial layer of a saturated solution which is found in the early stages of the process. There are two important facts, however, which need to be pointed out in any general consideration of the kinetics of dissolution.

In the first place, a unimolecular velocity is to be expected for the process in any case, whether a saturated layer is held to the surface or not. Adopting Langmuir's phraseology* we have

$$\text{rate of evaporation of solid molecules} = k_1 A$$

$$\text{rate of condensation of solute molecules} = k_2 A n.$$

A is the area of the surface, and n is the number of dissolved molecules in 1 c.c. of the solution.

$$\text{rate of dissolution} = \frac{dn}{dt} = k_1 A - k_2 A n. \qquad (22)$$

When the whole solution is saturated, statistical equilibrium is maintained between the number of molecules leaving the solid surface and the number deposited upon it; $dn/dt = 0$, and

$$k_1 = k_2 n_s,$$

where n_s is the number of molecules present per c.c. of saturated solution. While the solution is still unsaturated,

$$\frac{dn}{dt} = k_2 A(n_s - n)$$

or

$$k_2 = \frac{1}{tA} \ln \frac{n_s}{n_s - n}, \qquad (23)$$

which is the equation of Bruner and St. Tolloczko (equation 12).

Secondly, the Noyes-Whitney hypothesis assumes the actual process of dissolution to be rapid compared with the

* *J. Amer. Chem. Soc.*, **38**, 2221, (1916).

rate at which the dissolved molecules move off. This has not yet been proved, and there are facts which cast doubt upon its validity. The most thorough examination of the influence of temperature upon the rate of dissolution of benzoic acid in water has been made by Wildermann* from whose results at intervals from 0 to 60° C. it is found that E is 5,630 calories. Solubility measurements taken over the same range† show the heat of solution to be 5,970 calories. It is therefore quite likely that the true velocity of dissolution is governed largely by the rate at which molecules of solid in the surface layer acquire sufficient energy to become dislodged, and the problem thus becomes similar in some respects to the velocity of dissociation of salt hydrates, the molecular statistics of which have been discussed by Topley.‡

Discussion of the Nernst Theory.

The chief objection to the theory of Nernst, which claims to be applicable only when the true chemical change is rapid, is the high values which result for the thickness of the saturated layer. Films of 10^{-3} cm. are not likely to be stable, and moreover, the time which would be taken to form a layer of this thickness is often a major portion of the time of reaction when the products are fairly soluble. As we have seen, one of the reasons for the high values is that the calculations imply that all the molecules which reach the surface react. Another reason may be due to the limited applicability of the equation (16): $\delta = \frac{AD}{Vk}$, which has not really been tested adequately. If δ has a fixed value, this equation implies that the unimolecular constant diminishes indefinitely as the total volume of the solution is increased. The constancy of Vk has hitherto been demonstrated only within fairly narrow experimental conditions. It would be

* *Z. physikal. Chem.*, **66**, 445, (1909).

† Bourgoin, *Ann. Chim. Phys.*, **15**, 171, (1878).

‡ *Proc. Roy. Soc.*, **A, 136**, 413, (1932).

instructive to learn whether a limiting value of k is definitely reached long before the solution has the infinite volume which according to this equation it should have. In all probability the value of δ thus obtained would be less than the high values usually found, and would be more consistent with the modern views of an adsorbed layer.

Reaction Velocity at a Liquid-Liquid Interface.

The following characteristics are to be sought in selecting a reaction suitable for investigation:* (1) the two solvents must be immiscible and non-emulsifiable; (2) each reactant must be soluble in one phase and insoluble in the other; (3) the products of reaction must be soluble in at least one of the solvents; (4) there must be no hydrogen ions present, or other ions which have a disturbing effect upon surface conditions. There is also, of course, the desirability that the change shall proceed with measurable velocity at temperatures below the boiling-point of either solvent. From a number of reactions which is thus very restricted, Bell chose to study the oxidation of benzoyl-*o*-toluidine into benzoylanthranilic acid (in benzene solution) by potassium permanganate (in aqueous solution). The reaction was found to be unimolecular with respect to the permanganate, the initial velocity increasing with increase in concentration of the organic reactant up to a point (5·6 grams per litre) beyond which further addition of benzoyl-*o*-toluidine caused no change in the rate. The results are interpreted on the assumption that the velocity depends upon the number of permanganate ions which strike a layer of benzoyl-*o*-toluidine molecules adsorbed at the interface. The rate of stirring has little effect upon the reaction velocity, but the influence of temperature is great, hence the rate is not determined by diffusion. Bell calculated a value of 9,500 calories for the critical increment from the ratio of the number of fruitful collisions to the number of total collisions.

* Bell, *J. Physical Chem.*, **32**, 882, (1928).

The observed value was 43,700 calories, but upon this figure no great reliance was placed. Kassel and Schaffer* repeated the experiments, with results which are mainly confirmatory, except that the observed critical increment has a value of 11,500 calories at about 20° C., increasing gradually to 16,200 calories at about 40° C., and thus demonstrating the reaction to be composite. There can be no doubt that these low values of E are the more accurate ones. The investigation of other reactions at liquid-liquid interfaces would yield valuable information concerning matters which are at present but dimly understood.

The Decomposition of Hydrogen Peroxide.

Pure liquid hydrogen peroxide and aqueous solutions decompose with a slow but measurable velocity under ordinary conditions. A wide variety of substances catalyse the reaction to varying extents. The influence of the halogen acids upon the rate has been fully discussed in Chapter VII. Berzelius saw in the similarity of the catalytic action of platinum and organic 'ferments' a possible way of studying the nature of enzyme action, which was subsequently adopted by Bredig and his collaborators. It will be shown presently that, as far as this reaction goes, enzymes and colloidal metals are not only qualitatively similar, but actually bring about the destruction of the same number of hydrogen peroxide molecules under comparable conditions. The experimental matter may be dealt with under the following divisions: the decomposition (*a*) in the absence of catalysts, (*b*) under the influence of colloidal platinum, (*c*) under the influence of liver catalase and plant catalase, (*d*) under the influence of massive platinized platinum. The reaction is invariably unimolecular with respect to hydrogen peroxide.

(*a*) *Decomposition in the Absence of Catalyst.* The decomposition of aqueous solutions in glass vessels is partly heterogeneous, and is affected by the surface of the vessel

* *J. Amer. Chem. Soc.*, **41**, 965, (1929).

and by dust particles suspended in the solution.* In quartz vessels, the change is apparently homogeneous.† The velocity is also very susceptible to traces of hydroxyl ion, which is sometimes present as an impurity in the form of ferric hydroxide.‡ Using great precautions to purify the peroxide and to ensure a reproducible surface, fairly constant velocities of decomposition have been found by Williams§ and by Pana,‖ some of whose results are given in Table 3. Approximately 1-molar solutions were employed, so that the unimolecular velocity coefficient in waxed vessels at 25° C. takes on the value of $3{\cdot}45 \times 10^{-9}$ seconds^{-1}.

Table 3

Surface of vessel	Initial rate of decomposition at 40° C. (grams of H_2O_2 per c.c. per minute $\times 10^7$)	E Calories per gram molecule
Silica	3·50	16,800
Glass	1·05	17,000
Paraffin wax	0·30	18,000

(*b*) *Decomposition Catalysed by Colloidal Platinum.* Highly reproducible results were obtained by Bredig and von Berneck** in their important researches on the catalytic influence of stable platinum sol. One gram atom of the metal dissolved in many millions of litres of solution has a pronounced catalytic effect, which is not, however, directly proportional to the quantity of catalyst present, but varies in a manner consistent with the adsorption conditions of a Freundlich isotherm. Velocity measurements taken at temperatures of 25, 45, 65, and 85° C. give an Arrhenius A of 5,899, whence the critical increment is 11,700 calories. This has been corrected for the spontaneous (uncatalysed)

* F. O. Rice, *J. Amer. Chem. Soc.*, **48**, 2099, (1926); *J. Physical Chem.*, **31**, 1507, (1927).

† Robertson, *J. Amer. Chem. Soc.*, **53**, 382, (1931).

‡ Clayton, *Trans. Faraday Soc.*, **11**, 164, (1915).

§ *Ibid.*, **24**, 245, (1928). ‖ *Ibid.*, **24**, 486, (1928).

** *Z. physikal. Chem.*, **31**, 258, (1899).

decomposition of the peroxide, but not for the coagulation of the sol, which may introduce a considerable error.* At 25° C., with 1/38,000 gram atom of platinum per litre, and a concentration of 1/50 gram molecule of hydrogen peroxide per litre, the unimolecular constant is $6{\cdot}10\times10^{-3}$ (minutes^{-1}, $\log_{10}$) or $2{\cdot}34\times10^{-4}$ (seconds^{-1}, $\ln_e$).

In order to compare this figure with the theoretical value, it is first necessary to know the number of colloid particles present. Their average diameter is known to be about $8{\cdot}8\times10^{-6}$ cm.† Let us assume that each atom of platinum in the colloid is associated with three molecules of water, the density of the particles being about 10 grams/c.c. On this basis, the number of colloid particles in each c.c. is $1{\cdot}84\times10^{9}$. The number of molecules of hydrogen peroxide destroyed per c.c. per second is

$$(1/50)\times(1/1000)\times6{\cdot}06\times10^{23}\times2{\cdot}34\times10^{-4}=2{\cdot}83\times10^{15}.$$

One colloid particle therefore brings about the decomposition of $1{\cdot}54\times10^{6}$ molecules of hydrogen peroxide per second. The number of H_2O_2 molecules colliding per second against a sphere of diameter σ is $Z=\sigma^2 n_s\sqrt{(\pi RT/2M)}$.

$$\sigma=8{\cdot}8\times10^{-6},\qquad n_s=1{\cdot}21\times10^{19},\qquad M=34.$$

Hence $$Z=3{\cdot}17\times10^{13}.$$

The fraction of this number with energy equal to 11,700 calories is $e^{-E/RT}=2{\cdot}46\times10^{-9}$. The number of activating collisions per second per colloid particle is thus $7{\cdot}78\times10^{4}$. Rather than conclude, as would probably be legitimate in the absence of adsorption, that each activating collision causes the destruction of 20 molecules of hydrogen peroxide—thus indicating a chain reaction—it must simply be concluded that the theory of collisional activation leads to a value of the velocity which lies as close to the experimental one as the nature of the assumptions will allow.

* Cf. P. J. R. Butler, *Trans. Faraday Soc.*, **34**, 656, (1930), upon the influence of temperature on the rate of coagulation of gold hydrosol.

† Lewis, *A System of Physical Chemistry*, vol. i, p. 333, (1923).

(*c*) *Decomposition Catalysed by Catalase.* The results of Willstätter and Pollinger,* of Zeile and Hellström,† and of Williams,‡ upon the enzymic decomposition of hydrogen peroxide have been analysed and interpreted by Haldane.§ Zeile and Hellström have shown that horse-liver catalase is an iron-porphorin compound with a spectrum resembling that of alkaline haematin, and that the quantity of iron present can be estimated photometrically by converting the enzyme into pyridine-haemochromogen. Haldane makes the assumption that a molecule of catalase contains one atom of iron, and on this basis shows that at 0° C. and at the optimum *p*H (6·6) one molecule of catalyst destroys $5{\cdot}42\times10^4$ substrate molecules per second. Plant catalase is slightly more active. A comparison of this figure with the one calculated above shows that inorganic catalysts and enzymes behave very similarly. The following figures refer to a solution which is 1/100-molar with respect to hydrogen peroxide at 0° C.:

One platinum colloid destroys $1{\cdot}26\times10^5$ molecules of hydrogen peroxide per second.

One unit of liver catalase destroys $0{\cdot}54\times10^5$ molecules of hydrogen peroxide per second.

One unit of plant catalase destroys $1{\cdot}7\times10^5$ molecules of hydrogen peroxide per second.

If the enzyme molecules contain, like haemoglobin, four atoms of iron per molecule, the reactivity is commensurably greater, but of the same order of magnitude.

A careful examination of these figures shows the agreement to be largely accidental. When hydrogen peroxide is decomposed by colloidal platinum, it appears from the foregoing calculations that every molecule of the peroxide which strikes the colloid with an energy equal to 11,700 calories

* *Annalen*, **430**, 290, (1923).
† *Z. physiol. Chem.*, **192**, 171, (1930).
‡ *J. General Physiol.*, **11**, 209, (1928).
§ *Proc. Roy. Soc.*, **B**, **108**, 559, (1931).

is decomposed. The chemical efficiency of the activating colloid-substrate encounter is not less than unity, and all parts of the colloid surface seem to be equally effective catalytically. Now the energy of activation for the decomposition by liver catalase is about 5,500 calories (Williams), so that we should expect one molecule of catalase to be more efficient than a platinum sol unit by the factor $e^{\Delta E/RT}$, where $\Delta E = 11{,}700 - 5{,}500$. The value of the exponential is $9{\cdot}6 \times 10^4$. By an independent line of argument, without reference to colloidal platinum, Haldane has estimated the efficiency factor to be about $6{\cdot}6 \times 10^4$. Apparently, therefore, only one out of about 90,000 molecules of hydrogen peroxide which strike the catalase molecule with sufficient violence is decomposed. In the case of the hydrolysis of sucrose by saccharase the factor is about 7,000.* After allowing for the possible error in E, which may be considerable even at the optimum pH, there remains justifiable evidence for concluding that enzymes are in fact less efficient than inorganic catalysts. The principal reason is that only a small fraction of the enzyme surface is catalytically active. This constitutes a major distinction between enzymes and inorganic catalysts.

(*d*) *Decomposition Catalysed by Massive Platinized Platinum.* In most respects this reaction is typical of the changes the rates of which are governed by the process of diffusion,† as we should expect, since the chemical change occurring at the surface must be extremely rapid if massive platinum is catalytically comparable with the colloidal metal. The catalyst is poisoned by hydrocyanic acid, mercuric chloride, and iodine. Chloroform and alcohols are without effect, while formic acid, hydrazine, and dilute nitric acid have a promoting action, and have been termed catalytic tonics. The poisoning, or negative catalytic, effect is best understood in terms of selective adsorption. Promoter action may well

* Moelwyn-Hughes, *Ergebnisse der Enzymforschung*, **2**, 1, (1933).

† Bredig and Teletow, *Z. Elektrochem.*, **12**, 582, (1906).

be independent of the surface of the platinum, and due to separate catalysis in the homogeneous phase. The injury by the poisons is not permanent, and the health of the catalyst can readily be restored.

Enzyme Reactions.

Until some of the mysteries which still enshroud simple chemical changes have been cleared up, it is obviously unprofitable to deal at any great length with the application of chemical dynamics to the enormously complicated problem of enzyme reactions. The subject has recently been reviewed* on the supposition that the collision theory, even if proved to be ultimately inapplicable, can be regarded at least provisionally as a useful guide.

A fundamental difficulty is that of discovering the precise significance of the observed critical increment. When ethyl butyrate is hydrolysed by pancreatic lipase—a reaction which is probably typical of the enzymic hydrolysis of fats—the closeness of E to the heat of diffusion† shows the reaction to be definitely heterogeneous, with a velocity governed solely by the diffusion. On the other hand, E for the hydrolysis of sucrose by saccharase is not only greater than the heat of diffusion, but is apparently independent of temperature, provided attention is confined to the region of optimum pH.‡ Moreover, the system is probably homogeneous.§ Most enzyme reactions occupy positions between these least and most favourable examples, E being neither equal to the heat of diffusion nor independent of temperature. The suggestion that the fairly persistent fall in the critical increment with a rise in temperature could be attributed to the operation of a large number of internal

* Moelwyn-Hughes, *loc. cit.*

† Kastle and Loevenhart, *J. Amer. Chem. Soc.*, **24**, 491, (1900).

‡ Nelson and Bloomfield, *ibid.*, **46**, 1025, (1924).

§ Michaelis, *Biochem. Z.*, **115**, 269, (1921); solutions of albumin (Sørensen) and of pepsin are also considered to be homogeneous (Northrop, *Ergebnisse der Enzymforschung*, **1**, 322, (1932)).

degrees of freedom,* though leading to reasonable values for the velocity of reaction,† is inconsistent with the general theory of catalysis, and must now be discredited.

Although the kinetics of most enzyme reactions must for the present be studied individually, there are two simple equations which have an extensive applicability.

The first of these‡ affords another illustration of the usefulness of the intermediate-complex theory. The equation is derived in the following manner, by postulating the instantaneous velocity (v) of reaction to be proportional to the concentration of a complex formed by the union of enzyme and substrate:

Enzyme	Substrate	Complex
$(e-p)$	s	p

$$K = \frac{(e-p)s}{p} \qquad v = kp = \frac{kes}{K+s}. \tag{24}$$

When K is either very large or very small, the relation reduces to $v = (k/K)es$ and $v = ke$ respectively. The bimolecular condition ($v \propto es$) more often prevails, i.e. K is small; hence the union between enzyme and substrate, although intimate, is a loose one. An equation of the same form results even when the rates of the reactions comprising the equilibrium are commensurate with the velocity of decomposition of the complex.§

The second equation, known as Schütz's law,‖ refers to systems wherein the proportion of substrate to enzyme is high. It expresses the results found for the velocities of fermentation and hydrolysis of sugars,** but has chiefly been used in connexion with the tryptic and peptic digestion of proteins.†† Schütz's law connects the time (t) with quantity

* Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 81, (1929).
† Haldane, *Proc. Roy. Soc.*, **B, 108**, 559, (1931).
‡ Michaelis and Menten, *Biochem. Z.*, **49**, 333, (1913).
§ Briggs and Haldane, *Biochem. J.*, **69**, 443, (1926).
‖ Schütz, *Z. physiol. Chem.*, **30**, 1, (1900).
** Armstrong, *Proc. Roy. Soc.*, **B, 73**, 507, (1904).
†† Northrop, *J. General Physiol.*, **6**, 723, (1923–4).

(x) of substrate hydrolysed, in the following manner:

$$k_s = \frac{x}{\sqrt{(et)}}, \tag{25}$$

which implies that the velocity (v) is inversely proportional to the concentration of the products.* By assuming that reactants and resultants are both highly adsorbable, but the latter more so than the former, the equation can be deduced theoretically on the basis of Langmuir's theory, regarding enzymes as colloids on the surface of which reaction takes place.† The true energy of activation is equal to twice the critical increment calculated from the Schütz constant (k_s), plus the heat of formation of the enzyme-products complex.‡

It has been suggested that oxidative processes catalysed by enzymes proceed by way of a chain mechanism.§ The hypothesis is of singular interest in view of the large number of enzyme reactions which obey Schütz's law. The theoretical explanation is then to be found in the special case of negative catalysis, when the products of reaction are the inhibitors (i.e. $C = x$ in equation (32), p. 265).

Enzymes are differentiated from inorganic catalysts by their specificity and instability. Although stable in the crystalline state, in aqueous solution they undergo spontaneous transformation which modifies or completely destroys their catalytic properties. The change is known as inactivation, and frequently complicates the mechanism of the reactions which they catalyse.

The Inactivation of Enzymes.

As might be expected, enzymes become inactivated unimolecularly. Superficially at least, the process does not seem

* Differentiating with respect to t, we have $\frac{dx}{dt} = \frac{k_s^2 e}{2x}$. Schütz's law can therefore not hold for the initial stages of reaction.

† Langmuir, *J. Amer. Chem. Soc.*, **38**, 2221, (1916).

‡ Moelwyn-Hughes, Pace, and Lewis, *J. General Physiol.*, **13**, 323, (1930).

§ Willstätter and Haber, *Berichte*, **64**, 2844, (1931).

to differ markedly from other reactions of the first order. With enzymes carefully purified by adsorption methods, the inordinately large and variable critical increments previously found with impure preparations are not obtained, but reasonable values of E are recorded,* which are sensibly independent of the pH, within certain limits, and of the presence of large amounts of glycerol. The lability of the enzymes is characterized by the large values of the term S of the Arrhenius equation. The velocity of inactivation is catalysed by hydroxyl ions and hydrogen ions, the catalytic coefficients being in the order $k_{OH} > k_H > k_{H_2O}$, as for simpler processes.

The calculation of theoretical velocities of inactivation necessitates, of course, a knowledge of the energy of activation, which may be very different from the observed critical increment if the reaction is heterogeneous. It is therefore unfortunate that the temperature coefficient of k has not been examined over a wide range. Assuming the observed E to refer to a simple unimolecular reaction governed by collisions between enzyme and water molecules, the rates can be accounted for by supposing that from 9 to 15 internal degrees of freedom are involved. The values of F are interesting in spite of their uncertainty. The elimination of carboxylpolypeptidase from trypsin-kinase ($F = 12$) yields proteinase, for which $F = 9$; the decrease corresponds to the paralysing of at least one active centre on the parent enzyme.

The frequency of collisions (*ca.* 10^{14}) between enzyme and water molecules given by equation VIII (p. 28) agrees with that found by combining equation V with the correction for the persistence of velocity, which in these examples is naturally very large (*ca.* 10^3).

In some respects, the inactivation of enzymes resembles

* 45,900 calories for pancreatic lipase (McGillivray, *Biochem. J.*, **24**, 891, (1930)); 40,800 calories for trypsin (Pace, *ibid.*, **24**, 606, (1930)); 38,000 calories for pancreatic proteinase (Pace, *ibid.*, **25**, 1485, (1931)).

the denaturation of proteins,* which probably corresponds with a conversion from the molecular to the unaggregated, micellar state.† The distension of the enzyme, consequent upon the entrance of water molecules, would be sufficient to destroy that delicately balanced orientation of surface groups upon which catalytic activity depends. Pace independently concludes that the core of the enzyme is affected. The kinetics of inactivation, if this hypothesis should prove to be correct, must then be very much more complicated than the straightforward experimental results imply.

A Comparison of the Sucrose-Saccharase Reaction with Simple Bimolecular Reactions.

The chemical change now to be considered is that catalysed by an enzyme under conditions such that the inactivation may be neglected. A favourable case to examine is the enzymic inversion of sucrose, for which the efficiency of activating collisions has been shown to be one in about 7,000. The familiar calculations upon which this figure is based involve certain assumptions which may rightly be challenged. It is therefore desirable to learn how this reaction, judged solely upon experimental facts, compares with simple bimolecular processes. During the initial stages, the reaction is definitely unimolecular with respect to the sugar, k_{uni} being directly proportional to the amount of enzyme employed. The value of the constant at 37° C. and *p*H 4·5 is $2{\cdot}1\times10^{-4}$ seconds^{-1},‡ when the solution contains 0·06 gram of crude saccharase per 100 c.c. By a method which is fully described elsewhere,§ it can be shown that this represents a concentration of pure saccharase not exceeding 5×10^{-9} gram molecule per litre. The bimolecular constant is thus at least $4{\cdot}2\times10^{+4}$ litres/gram molecule-

* P. S. Lewis, *Biochem. J.*, **20**, 965, (1926).

† Loughlin and Lewis, *ibid.*, **26**, 476, (1932).

‡ Nelson and Born, *J. Amer. Chem. Soc.*, **36**, 393, (1914); Nelson and Vosgurgh, *ibid.*, **39**, 790, (1917).

§ *Ergebnisse der Enzymforschung*, **2**, 1, (1933).

second. In Table 3 this value is compared with the velocities of simple bimolecular reactions in solution and in the gaseous phase. Column 3 gives the fraction of the total

Table 3

Reaction	E (calories per gram mol.)	$k_{37°C}$ (litres per gram mol.-second)	$e^{-E/RT}$	$\left(\frac{k}{e^{-E/RT}}\right)$
Inversion of sucrose by saccharase in aqueous solution	8,700	$4{\cdot}2\times10^{+4}$	$7{\cdot}0\times10^{-7}$	$0{\cdot}6\times10^{11}$
Combination of sodium ethoxide with ethyl iodide in ethyl-alcoholic solution	20,650	$3{\cdot}5\times10^{-4}$	$2{\cdot}3\times10^{-15}$	$1{\cdot}5\times10^{11}$
Decomposition of hydrogen iodide in the gaseous phase	44,450	$4{\cdot}2\times10^{-21}$	$3{\cdot}5\times10^{-32}$	$1{\cdot}2\times10^{11}$

number of molecules with a critical energy of E in two square terms. The enzyme reaction is seen to fall in line with the others. Its great speed is due primarily to the relatively large proportion (approximately one in a million) of the molecules which are in the active state at any instant. The parallelism between the figures in columns 3 and 4 is explicable in terms of the general theory of activation, of which the collision theory is one variant. The approximate constancy of the quantities in the last column becomes intelligible in the light of the collision theory. The figures for the two simple reactions lie close together merely because the collision frequency in the two systems is nearly the same. The much greater collision frequency predicted by theory for the enzyme reaction is almost exactly counterbalanced by the inefficiency of activating collisions. It is well to recall that the results given in this table are based entirely upon experimental facts; although best understood in terms of the collision hypothesis, they possess an intrinsic value, independent of any theory.

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