

13. *The Kinetics of Reactions involving Collisions
between Solute and Solvent Molecules.*

By E. A. MOELWYN-HUGHES.

THE collision theory of chemical reaction rate, to which the explanation of experimental results for gaseous reactions is to be credited (Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," 2nd edtn., Oxford, 1929), shows every promise of being able to account also for the rates of reactions in solution (Moelwyn-

Hughes, *Chem. Reviews*, 1932, in the press). When considering, for example, a reaction between two solutes, the bimolecular velocity coefficient can be evaluated by assuming that chemical change takes place whenever two of the reacting molecules collide with the necessary increment of energy. The dissolved molecules are regarded as moving with the same average velocity as neutral gaseous molecules at the same temperature, so the collision rate is the same for a dilute solution as for the gas. Now it is well known that when the concentration, or partial pressure, of one molecular species is much greater than that of the other, the reaction will appear to be unimolecular. It may therefore be argued that several reactions which have been measured only in solution and which appear to be unimolecular are in fact bimolecular. In the simplest possible case we would expect such reactions to have rates dependent on the number of collisions between solute and solvent molecules.

Jowett (*Phil. Mag.*, 1929, 8, 1059) calculates the number of collisions between dissolved molecules and solvent molecules in the following manner. Two independent methods have shown that the coefficient of diffusion for a dilute solution is the same as that of self-diffusion in gases. After introduction of a correction necessitated by a tendency of the velocity to persist after collision (Jeans, "The Dynamical Theory of Gases," 4th edtn., Cambridge, 1925), the coefficient of diffusion is given by the relation

$$D = 1.051\lambda u/3(1 - \theta) \dots \dots \dots (1)$$

in which λ is the mean free path of the dissolved molecule, and u is its root-mean-square velocity; θ , the average persistence of velocity, is approximately equal to $M_1/(M_1 + M_s)$, where M_1 is the mass of the solute molecule and M_s that of the solvent molecule. The number of solvent molecules encountered per second by each solute molecule is

$$Z = u/\lambda \dots \dots \dots (2)$$

Thus $Z = 0.892RT(M_1 + M_s)/M_1M_sD$.

This is the form in which the equation has been used by Jowett to calculate the collision rates for numerous solutes in water at 18°. If we now combine this with the Sutherland-Einstein equation (the validity of which can be assumed for the moment), in which η is the viscosity of the solvent and r the radius of the solute molecule, viz.,

$$D = RT/6\pi\eta rN \dots \dots \dots (3)$$

we have

$$Z = 0.892(M_1 + M_s) \times 6\pi N\eta r/M_1M_s.$$

Replacing N by 6.06×10^{23} , we then have

$$Z = 5.1 \times 10^{24}(M_1 + M_s)\sigma\eta/M_1M_s \dots \dots (4)$$

This equation enables us to calculate the collision rate for a dilute solution from a knowledge of the diameter (σ) of the solute molecule and the viscosity of the solvent.

The most interesting consequence of this equation is, as Jowett points out, that the collision frequency should be directly proportional to the viscosity and should possess the same (negative) temperature coefficient. This result is rather an unexpected one, but the same conclusion is attained by an alternative though perhaps less rigorous treatment.

Einstein (*Z. Elektrochem.*, 1908, **14**, 235) has shown that the mean displacement $\overline{\Delta x}$, measured along one axis, of a dissolved molecule in time t seconds due to solvent bombardment is

$$\overline{\Delta x}^2 = 2RTt/CN \quad . \quad . \quad . \quad . \quad (5)$$

where C , the resistance factor, is equal to $6\pi\eta r$ in the case of a molecule which is spherical and large in comparison with a solvent molecule. Hence $\overline{\Delta x}^2 = 2RTt/6\pi N\eta r$. For the actual displacement $\overline{\Delta s}$ in three dimensions, we have as an average value

$$\overline{\Delta s}^2 = 3\overline{\Delta x}^2 = RTt/\pi N\eta r \quad . \quad . \quad . \quad . \quad (6)$$

The displacements measured by Perrin during his investigation 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/u . Substituting these values in equation (6), we have

$$\lambda = RT/\pi N\eta r u \quad . \quad . \quad . \quad . \quad (7)$$

Combination with equation (2) gives $Z = \pi N\eta r u^2/RT = 3\pi N\eta\sigma/2M_1$ or

$$Z = 2.9 \times 10^{24}\sigma\eta/M_1 \quad . \quad . \quad . \quad . \quad (8)$$

The similarity to equation (4) will be at once apparent. The absolute values of the collision frequencies given by the two equations differ by a factor of $0.57(1 - \theta)$, the magnitude of which depends on the relative masses of solute and solvent molecules, and will not generally be large. The conclusion that collision rate for dilute solutions is proportional to the viscosity of the solvent is one which cannot be avoided: unlike the corresponding quantity for gaseous systems, the collision frequency in solution 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, the conclusion reached means that the effect of temperature on the free space is the important factor. Considering the viscosity of pure liquids, it is not certain whether the increased separation of the molecules is sufficient to account entirely for its negative temperature coefficient. But while the matter is still undecided from the theoretical standpoint, there is much evidence for believing 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.

It now remains to show how this result bears on the problem of calculating the rates of reactions in dilute solutions.

The total number of collisions per c.c. per sec. between solute and solvent molecules is Zn , where n is the number of solute molecules present in 1 c.c. of solution. If every such collision, with the appropriate energy conditions, leads to reaction, we have for the instantaneous rate of disappearance of reactant molecules

$$-dn/dt = Zn \cdot e^{-E'/RT} \dots \dots \dots (9)$$

The term E' differs from the Arrhenius value for the energy of activation, as will be shown presently. The unimolecular velocity coefficient for the reaction is

$$k = -1/n \cdot dn/dt = Z \cdot e^{-E'/RT} \dots \dots \dots (10)$$

The terms constituting Z are all independent of temperature, except the viscosity. We have, thus, by either equation (4) or equation (8),

$$k = \text{constant} \times \eta \cdot e^{-E'/RT} \dots \dots \dots (11)$$

The importance of this equation lies in the fact that, in order to determine the true energy of activation for this type of reaction, we must take into account the temperature coefficient of the viscosity of the medium. The simplest analytical method of doing this is to plot $\ln(k_{\text{obs.}}/\eta)$ against the reciprocal of the absolute temperature ($1/T$). The slope of the curve will be $-E'/R$, and, if theory and observation are in harmony, the value of $(k_{\text{obs.}}/\eta)$ corresponding to $T = \infty$ should be comparable with the term $5.1 \times 10^{24}(M_1 + M_s)\sigma/M_1M_s$ or $2.9 \times 10^{24}\sigma/M_1$. The effect of this alteration in the usual procedure for dealing with experimental velocity coefficients is, as Jowett foresaw, to lead to a critical increment value which is greater than the Arrhenius term E .

We shall now proceed to apply equation (10) to certain experimental data, employing the values of Z given by equations (4) and (8). In the absence of a more precise method, we shall estimate the diameter of the solute molecule, which is assumed to be unhydrated, from a knowledge of the molecular volume V_m of the solute in the pure liquid or solid state :

$$\sigma = 1.36 \times 10^{-8} V_m^{1/3} \quad . \quad . \quad . \quad (12)$$

This equation is known to give values which are certainly of the correct order of magnitude, and are probably exact to within about 30%.

It will be recalled that the deductions of both the collision formulæ given above imply the validity of the Sutherland-Einstein expression. Now, although this records in a satisfactory manner the variation with temperature of the diffusion coefficient, yet it is strictly applicable only to dilute solutions in which the motion of the dissolved molecule obeys Stokes's law. We shall therefore expect the agreement between observed and calculated values of the velocity coefficients to be closer when the solute molecule is large compared with the solvent molecule.

The Decomposition of Ozone in Carbon Tetrachloride Solution.—The decomposition of ozone in the gaseous state is predominantly a bimolecular reaction, the energy of activation having been given as 27,800 cal. (Belton, Griffith, and McKeown, *J.*, 1926, 3153) and 29,600 cal. (Wulf and Tolman, *J. Amer. Chem. Soc.*, 1927, **49**, 1650). It has recently been shown that the reaction in carbon tetrachloride solution is unimolecular, the value of E being now 26,160 cal. (Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc.*, 1931, *A*, **134**, 211). The apparent change in order could, according to the investigators, be explained if collisions between ozone molecules and solvent molecules lead to reaction. The interpretation of this suggestion in a quantitative manner entails, in the first place, a correction in the observed critical increment value for the change with temperature of the viscosity of the solvent. Applying this in the manner described, E becomes 28,750 cal. for the reaction in solution; this is in rather striking agreement with the values for the gaseous reaction, being, in fact, equal to the average of the two figures quoted above. Inserting this value for E in equation (11), and employing the collision rates given by equations (4) and (8), we obtain the calculated values given below.

Temp.	$\eta \times 10^3$.	Unimolecular velocity constant (secs. ⁻¹).		
		Obs.	Calc. by eqn. (4).	Calc. by eqn. (8).
54.7°	6.33	1.82×10^{-5}	1.77×10^{-6}	8.45×10^{-7}
71.0	5.24	1.24×10^{-4}	1.34×10^{-5}	5.82×10^{-6}

It will be seen that the theoretical velocity coefficients are lower than the observed values by factors of 10 and 22 respectively. Equation (4) is thus seen to be, in this instance, in somewhat better agreement with experiment than equation (8). Greater harmony cannot be expected when it is remembered that the ozone molecule is small ($\sigma = 3.5 \times 10^{-8}$ cm.) compared with the solvent molecule ($\sigma = 6.1 \times 10^{-8}$ cm.), and that the reaction in solution—like the gas reaction—is not entirely free from minor complications.

Bowen, Moelwyn-Hughes, and Hinshelwood (*loc. cit.*) found that ozone reacts to some extent with the carbon tetrachloride, and concluded that this was "either a relatively unimportant side-reaction . . . or . . . the first stage of a chain reaction in which about seventeen molecules of ozone are decomposed for each initial act." The latter suggestion is of interest in view of the factors 10 and 22 just found.

The Decomposition of Dibromosuccinic Acid in Aqueous Solution.—The rate at which dibromosuccinic acid decomposes into bromomaleic and hydrobromic acids in water, $\text{CO}_2\text{H}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H} \rightarrow \text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CO}_2\text{H} + \text{HBr}$, was found by van 't Hoff ("Studies in Chemical Dynamics," London, 1896) to be unimolecular with respect to the dibromosuccinic acid. His velocity-constant data, converted into natural logarithms and reciprocal seconds, are given in the third column of Table I, along with the rates calculated on the assumption that every collision between a dibromosuccinic acid molecule ($\sigma = 7 \times 10^{-8}$ cm.) and a water molecule leads to reaction when the kinetic energy exceeds 24,830 cal. per g.-mol. The

TABLE I.
Unimolecular velocity constant (secs.⁻¹).

Temp.	$\eta \times 10^3$.	Obs.	Calc. by eqn. (4).	Calc. by eqn. (8).
15°	11.4	1.61×10^{-7}	2.91×10^{-5}	7.75×10^{-7}
40	6.57	1.41×10^{-6}	5.31×10^{-4}	1.41×10^{-5}
50	5.50	4.15×10^{-6}	1.54×10^{-3}	4.09×10^{-5}
60.2	4.64	1.09×10^{-5}	4.31×10^{-3}	1.15×10^{-4}
70.1	4.05	2.82×10^{-5}	1.11×10^{-2}	2.95×10^{-4}
80	3.56	7.67×10^{-5}	2.74×10^{-2}	7.30×10^{-4}
89.4	3.19	1.74×10^{-4}	6.18×10^{-2}	1.64×10^{-3}
101	2.81	5.30×10^{-4}	1.61×10^{-1}	4.28×10^{-3}

experimental results are in greater harmony with an equation of the form $k = \text{constant} \times \eta \cdot e^{-E/RT}$ than with the Arrhenius equation, which gives a critical increment of 22,840 cal. Equation (8) is in better agreement with experiment than equation (4), and gives values for theoretical rates which are about 10 times as great as the experimental values. The important point is that the reaction proceeds at a rate which does not exceed that given by

postulating a very simple collision mechanism of activation. The reaction is slightly complicated at high temperatures by a tendency in the organic acids to eliminate carbon dioxide.

The Conversion of Chloropurpleochromichloride into Roseochromichloride $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ (Freundlich and Pape, *Z. physikal. Chem.*, 1914, **86**, 458).—The two reactions which have been already studied involved collisions between two molecular species with the chemical transformation of only one, *i.e.*, the solute. For reactions of the type studied here, and for hydrolytic reactions generally, the two colliding types of molecules disappear, and allowance should strictly be made for the diminution in the concentration of the solvent. For dilute solutions, however, only about 1 mol. of solvent in several hundreds is used up, so that the correction can be ignored. The critical increment for this reaction is 21,570 cal. by the Arrhenius equation, and 25,580 cal. by the viscosity equation (11). Putting $M_1 = 224$ and $\sigma = 7 \times 10^{-8}$ cm., we obtain the calculated constants given below. It will

Temp.	$\eta \times 10^3$.	Unimolecular velocity constant $\times 10^6$ (secs. ⁻¹).		
		Obs.	Calc. by eqn. (4).	Calc. by eqn. (8).
25.0°	8.94	9.7	29	1.1
30.3	7.95	18	55	2.1
35.0	7.24	33	95	3.7

be seen that both equations lead to values of the velocity coefficient which are of the right order of magnitude, the factor $k_{\text{calc.}}/k_{\text{obs.}}$ being 3 and 1/9 respectively. The data for two other reactions of the same type (Freundlich and Bartels, *ibid.*, 1922, **101**, 177) are in equally good agreement with theory.

The Hydrolysis of Monochloroacetic Acid.—The Arrhenius critical increment (26,310 cal.) for this reaction, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} \longrightarrow \text{CH}_2(\text{OH})\cdot\text{CO}_2\text{H} + \text{HCl}$, is lower by 3,370 cal. 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 monochloroacetic acid molecule being taken as 5.4×10^{-8} cm. [equation (12)], equations (4) and (8) give calculated rates which are greater by factors of 16 and 2.5 (see Table II)

TABLE II.

Temp.	$\eta \times 10^3$.	Unimolecular velocity constants (secs. ⁻¹).		
		Obs.	Calc. by eqn. (4).	Calc. by eqn. (8).
80°	3.56	8.52×10^{-7}	1.36×10^{-5}	2.13×10^{-6}
90	3.16	2.31×10^{-6}	3.81×10^{-5}	6.00×10^{-6}
100	2.84	6.64×10^{-6}	1.03×10^{-4}	1.63×10^{-5}
110	2.56	1.67×10^{-5}	2.69×10^{-4}	4.23×10^{-5}
120	2.32	4.03×10^{-5}	6.56×10^{-4}	1.03×10^{-4}
130	2.14	9.10×10^{-5}	1.59×10^{-3}	2.50×10^{-4}

than those determined experimentally by Buchanan (*Ber.*, 1871, 4, 340; see van 't Hoff, *op. cit.*, p. 130). The reaction appears to be free from complications.

The Hydrolysis of Carbonyl Sulphide, $\text{COS} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2\text{S}$.—Buchböck's velocity-constant data (*Z. physikal. Chem.*, 1897, 23, 123) at seven temperatures are faithfully represented by the equation

$$k_{\text{obs.}} = 2.37 \times 10^{17} \cdot \eta \cdot e^{-27,190/RT}.$$

The collision frequencies by equations (4) and (8) are $1.59 \times 10^{16}\eta$ and $2.08 \times 10^{15}\eta$ respectively, and are thus considerably lower than the experimental value. The reaction may proceed in consecutive stages, as Buchböck himself suggested. This is the first instance encountered of a simple reaction which goes at a rate much faster than the collision theory will allow, but it should be remembered that the solute molecule ($\sigma = 3.41 \times 10^{-8}$ cm.) is of about the same size as the solvent molecule, so that it is not legitimate to use the Stokes expression for the resistance of the solvent to the motion of the dissolved molecules. Furthermore, it has not been possible to correct the observed constants for the part played by the hydroxyl ion, which is known to catalyse the reaction to some extent.

The Hydrolysis of Substituted Benzyl Chlorides.—Olivier (*Rec. trav. chim.*, 1922, 41, 301, 646; 1923, 42, 516, 775) has measured the rate of hydrolysis of a large number of compounds of this class in 50% aqueous alcoholic mixtures at 30° and 83°. Within this range, the temperature coefficients of the viscosity of ethyl alcohol

TABLE III.

Reactant.	E (Arrhenius).	$k_{30} \times 10^7$ (secs. ⁻¹).			$\frac{k_{\text{calc.}}(8)}{k_{\text{obs.}}}$.	$\sigma \times 10^8$.
		Obs.	Calc. by eqn. (4).	Calc. by eqn. (8).		
$\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{Cl}$	19,900	18.5	4770	125	6.8	5.3
$o\text{-CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$	19,790	91.7	2180	140	1.5	5.5
<i>m</i> - ,,	20,190	24.0	1140	73.6	3.1	5.5
<i>p</i> - ,,	20,390	173	807	52.0	0.4	5.5
$o\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$	22,250	0.867	40.5	2.18	2.5	6.3
<i>m</i> - ,,	21,780	1.05	86.7	4.76	4.5	6.3
<i>p</i> - ,,	21,990	0.818	62.8	3.37	4.1	6.3
$m\text{-CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$	21,350	3.15	164	8.89	2.8	5.7
<i>p</i> - ,,	21,560	2.02	116	6.29	3.1	5.7
$o\text{-Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$	21,110	3.93	351	12.7	3.2	6.5
<i>m</i> - ,,	21,870	2.45	98.9	3.58	1.5	6.5
<i>p</i> - ,,	21,550	7.62	168	6.08	0.8	6.5
2 : 6- $\text{Br}_2\text{C}_6\text{H}_3 \cdot \text{CH}_2\text{Cl}$	22,460	1.19	30.7	1.04	0.9	7.0
2 : 4- ,,	22,490	1.82	29.3	0.99	0.6	7.0
3 : 5- ,,	22,450	0.53	30.7	1.04	1.8	7.0

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 cal. Table III indicates that equation (8) predicts rates which are always within a small factor of the observed values, the absolute rates varying about 300-fold. 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 (12) 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 reactions which have been discussed proceed at rates which can be accounted for in a satisfactory manner on a very simple collision mechanism. The greatest disparity is found in the case of the hydrolysis of carbonyl sulphide, the molecular diameter of which is so small compared with that of the solvent molecule that neither collision formula is strictly applicable. There is little to choose between equations (4) and (8) as far as harmony with the experiment goes, although the scanty evidence available shows that the latter equation—that based on Einstein's treatment of the Brownian movement—agrees somewhat better with the facts.

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.

All 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 energised 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. This idea—introduced into chemical dynamics by Polanyi (*Z. Physik*, 1920, **1**, 337), who calculated that seven such degrees of freedom are required to account for the rate of dissociation of bromine molecules—has been independently developed and presented in the form of a generalised theory by Hinshelwood (*Proc. Roy. Soc.*, 1926, **113**, 230) and by Fowler and Rideal (*ibid.*, p. 570). On this hypothesis, which has received ample confirmation from experiments with gaseous reactions, the rate at which activated molecules are produced by collisions is

$$\frac{dn}{dt} = Zn \cdot e^{-E/RT} \cdot \left(\frac{E}{RT}\right)^F \cdot \frac{1}{F} \cdot \dots \quad (13)$$

For the kind of reaction with which we are concerned, Zn is the total number of collisions between solute and solvent molecules per second, and $E = E' + F \cdot RT$, where F is one less than the number of degrees of freedom involved. If this be equated to the observed rate of chemical change

$$dn/dt = kn \dots \dots \dots (14)$$

it becomes possible to evaluate the minimum number of degrees of freedom which must be concerned in the activation process:

$$k = Z \cdot e^{-E/RT} \cdot \left(\frac{E}{RT}\right)^F \cdot \frac{1}{F} \dots \dots \dots (15)$$

The values of F thus found for a number of unimolecular reactions in solution are given in Table IV. The collision rate used has been that given by equation (8).

The observed critical increment (E , Arrhenius) 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 cals. The viscosity data have been taken from the "International Critical Tables," Vol. 7, 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 ($E' - E$) varies from 880 cals. for chloroform at 40 — 70° to 5,680 cals. for acetophenone at 70 — 140° . The numbers in the last column of Table IV are the nearest integers which will satisfy equation (15) when the observed velocity coefficients are substituted for k ; $k_{\text{calc.}}$ is the value assumed by k when this value of F is used in the same equation.

TABLE IV.

Reactant.	Solvent.	E (Arrhenius).	E' .	$\eta_{80} \times 10^3$.	k_{80}^* .		F .
					Obs.	Calc.	
Triethylsulphonium bromide ¹	PhNO ₂	28,290	31,340	10.94	2.11×10^{-4}	2.96×10^{-4}	4
	C ₂ H ₅ Cl ₄	30,350	33,180	9.90	2.19×10^{-4}	1.66×10^{-4}	6
	CHCl ₃	33,010	33,890	4.50	2.07×10^{-4}	9.84×10^{-5}	7*
	Pr-OH	33,120	37,600	9.16	1.53×10^{-4}	2.14×10^{-5}	7
	CH ₃ -CO ₂ H	31,060	33,820	7.16	8.51×10^{-7}	5.43×10^{-7}	3
2 : 4 : 6-Trinitrobenzolic acid ²	H ₂ O	29,970	33,080	4.69	3.33×10^{-6}	3.91×10^{-6}	4
	Ph-COMe	25,450	31,130	10.80	5.79×10^{-7}	4.39×10^{-7}	2
	PhNO ₂	34,990	37,120	10.94	4.07×10^{-9}	8.61×10^{-9}	3
	Ph-CH ₃	31,600	33,620	3.80	1.62×10^{-9}	4.20×10^{-9}	1
	Ph-COMe	28,960	32,620	10.80	1.59×10^{-6}	2.39×10^{-6}	3
Camphorcarboxylic acid ³	H ₂ O	29,640	32,690	4.69	3.31×10^{-7}	2.18×10^{-7}	2
	PhNH ₂	28,350	32,950	15.40	1.05×10^{-4}	9.44×10^{-5}	5
Trichloroacetic acid ⁴	H ₂ O	23,320	27,240	4.69	5.48×10^{-3}	2.05×10^{-3}	4
Acetonedicarboxylic acid ⁵	"	28,820	31,620	4.69	1.41×10^{-7}	2.11×10^{-7}	1
Malonic acid ^{6, 7}	"	27,970	30,820	4.69	2.46×10^{-7}	5.03×10^{-7}	1
Allylmalonic acid ⁷	"	33,430	36,250	4.69	2.00×10^{-8}	4.34×10^{-6}	4
Diethylmalonic acid ⁷	"	33,700	36,330	4.69	1.82×10^{-8}	1.33×10^{-6}	3
Mesoxalic acid ⁷	"	23,360	27,110	4.69	3.43×10^{-3}	6.70×10^{-3}	3
Benzenediazonium chloride ⁸	"	23,440	27,310	4.69	8.97×10^{-3}	5.00×10^{-3}	3
<i>o</i> -Toluenediazonium chloride ⁸	"	22,800	26,670	4.69	8.89×10^{-3}	1.22×10^{-3}	3
<i>m</i> -Toluenediazonium chloride ⁸	"	27,680	31,150	4.69	5.20×10^{-4}	5.51×10^{-4}	5
<i>p</i> -Toluenediazonium chloride ⁸	"	29,960	31,620	4.50	1.04×10^{-3}	1.38×10^{-3}	7
Phenylbenzylmethylallyl-ammonium bromide ⁹	CHCl ₃						

¹ von Halban, *Z. physikal. Chem.*, 1909, **67**, 129.² Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, 1931, **131**, A, 186.³ Fajans, *Z. physikal. Chem.*, 1910, **73**, 25; also private communication from Professor Freudenberg.⁴ Goldschmidt and Bräuer, *Ber.*, 1906, **39**, 109.⁵ Wiig, *J. Physical Chem.*, 1930, **34**, 596; 1928, **32**, 961.⁶ Bernouilli and Wege, *Helv. Chim. Acta*, 1919, **2**, 511.⁷ Knaus, *Thesis*, Bale, 1923; vide *Tables Annuelles*, 1928.⁸ Cain and Nicoll, *J.*, 1902, **81**, 1412.⁹ von Halban, *Ber.*, 1908, **41**, 2417.

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 emphasised 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, $k_{\text{calc.}}$ 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 (Hinshelwood, *loc. cit.*; Ramsperger and Leermakers, *J. Amer. Chem. Soc.*, 1931, **53**, 2061).

For reactions of the true unimolecular type, the rate of decomposition is entirely independent of the collision frequency, since it is clearly impossible in dealing with solutions to attain that low total pressure of the system at which both quantities become comparable. The decomposition of nitrogen pentoxide would appear at first sight to be an example of this kind of behaviour, the velocity coefficient and the heat of activation of the gaseous reaction being not very different from the corresponding quantities for the reaction in carbon tetrachloride solution (Daniels and Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53; Lueck, *ibid.*, 1922, **44**, 757; White and Tolman, *ibid.*, 1925, **47**, 1240). If this is the true mechanism, it becomes unnecessary to correct the critical increment for the change in viscosity of the solvent, but the collision formulæ can still be applied to calculate the total number of encounters between nitrogen pentoxide and carbon tetrachloride molecules, and the minimum value of F can be determined as before. The observed rate of reaction at 60° in this solvent is 3.80×10^{-3} sec.⁻¹, and E is 25,500 cal. The collision frequency, by equation (8), is 9.56×10^{12} , if the diameter of the solute molecule be taken as 6×10^{-8} cm. If we now ascribe values of 2 and 3 to F , the calculated rate of reaction becomes, by equation (15), 1.73×10^{-3} and 9.14×10^{-3} respectively. There is some doubt as to the correct value of F for the gaseous reaction; even by ascribing large values to the molecular diameter, F becomes about 14; it would therefore appear that the reaction in solution is somewhat simpler than that in the gas. A careful examination of the experimental data for this reaction in the gas phase and in solution indicates that they bear sufficient precision to allow of these two conclusions: (1) The reaction in solution is faster than the gaseous reaction by a factor of 1.3; (2) the critical increment for the reaction in solution is 800 cal. greater than E for the gaseous reaction. These results, coupled with the fact that E for the same reaction in certain other solvents is some 4,000 cal. greater than the value for the gaseous reaction, may be taken as evidence that the type of collision in the two systems is, as we have assumed above, different.

Reverting to the values of F given in Table IV, 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 rôle 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 can therefore be 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. This view is not inconsistent with the fact that enzymic reactions—in which complex formation is fairly well established—apparently involve a large number of degrees of freedom (Moelwyn-Hughes, *Trans. Faraday Soc.*, 1929, **25**, 503; Haldane, *Proc. Roy. Soc.*, 1931, *B*, **108**, 559).

The most interesting feature of the figures given in Table IV, however, is that they emphasise an analogy between reactions in solution and those in the gaseous phase. Experimental evidence for such a parallelism has long been extant in the case of unimolecular reactions, and has been extended recently to cover instances of a bimolecular reaction and a more complicated one.

Summary.

An extension of Einstein's relation for the motion of a particle in the Brownian movement leads to an equation giving the rate of collision between solute and solvent molecules. The equation is similar to one deduced by Jowett from a treatment of diffusion, with a correction for the persistence of velocity.

The rates of numerous unimolecular reactions in solution in various solvents can be accounted for in a satisfactory manner by assuming that every collision between a solute and solvent molecule which obeys the necessary energy conditions leads to reaction.

When the reaction is of an elementary character, the critical increment is regarded as the lowest value of the total kinetic energy in a successful collision. For more complicated reactions, the minimal number of internal degrees of freedom required to account for a sufficiently rapid rate of activation is evaluated by means of the Hinshelwood-Fowler-Rideal equation. These numbers, which vary from solvent to solvent, range from 2 to 8, and suggest an analogy with gaseous reactions.

The critical increment used in these calculations is greater than the Arrhenius value by a quantity dependent on the temperature coefficient of the viscosity of the solvent.

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