

420. *The Rate of Reactions in Solution.*

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SEVERAL attempts have recently been made to explain the rate of reactions in solution by a collision mechanism. The explanations generally adopted (Christiansen, *Z. physikal. Chem.*, 1924, **113**, 35; Jowett, *Phil. Mag.*, 1929, **8**, 1059. For a review, with full references, see Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, 1933) fall into two groups: (a) for bimolecular reactions, the collision frequency is taken to be the same as in the gaseous phase at the same concentration, and (b) for collisions between solute and solvent, which determine in some cases the rate of unimolecular reactions, the collision frequency is given by ${}_1Z_s = 3\pi\eta\sigma/2m_1$, where η is the viscosity of the medium, σ the diameter and m_1 the mass of a solute molecule. An alternative formula is given by ${}_1Z_s = 8RT(M_1 + M_s)/3\pi DM_1M_s$, where M_1 and M_s are the molecular weights of solute and solvent respectively, and D is the diffusion coefficient of the solute. The two formulæ are seen to be roughly equivalent when D is replaced by its value $RT/3\pi\eta N\sigma$ given by Einstein.

The explanations (a) and (b) are open to the objection that insufficient attention has been paid to the molecular theory of liquids. Explanation (a) is a broad generalisation which requires detailed investigation. Even if it gives a numerical result which is approxi-

mately correct, the formula probably does not represent the true behaviour of collisions in solution where the mean free path is less than the diameter (see, *e.g.*, Harper, *Proc. Camb. Phil. Soc.*, 1932, 28, 223). Moreover, explanations (a) and (b) seem dissociated from one another. It is difficult also to believe that the viscosity enters explicitly into the theory, since the viscosity of a liquid is a measure of the resistance offered to changing the chaotic motion of the molecules into an ordered one (Scatchard, *J. Amer. Chem. Soc.*, 1923, 45, 1580) and it is doubtful whether such a conception can be applied to the chaotic motion itself. In other words, it would seem incorrect to apply the diffusion theory of colloidal particles, in so far as it embodies Stokes's law, to molecular diffusion; the modifications of the law proposed by Cunningham, Lenard, Millikan, and Epstein (Epstein, *Physical Rev.*, 1924, 23, 710) suffer from the same objection.

An exact formulation of the dynamical theory of the liquid state is so difficult that some degree of approximation is necessary. It is possible, however, as an alternative, to avoid the introduction of viscosity by the following approximate argument, which, in effect, considers a liquid to possess a quasi-solid structure; Bernal and Fowler's work on the structure of water (*J. Chem. Physics*, 1933, 1, 515) shows that this view can give good results. In this paper, because of special complications, ionic reactions will not be considered in detail.

Free Space, Oscillation Frequency, and Collision Frequency in Liquids.—As a rough model of the liquid it may be assumed that the molecules are spherical and close-packed. Each molecule, for the closest packing, is surrounded by twelve others, and the motion of the molecule within this enclosure resembles a vibration of high frequency and continually changing axis; hence, around each molecule may be drawn a sphere representing the confines of this oscillatory motion. The effect of temperature will be to increase the amplitude, and conversely the latter may be inferred by extrapolating the virtual radius of the molecule, calculated from the density, to the absolute zero. Fortunately, the virtual radius usually varies linearly with the temperature, and a wide extrapolation is possible. The results obtained by this method will probably be of the right order.

In addition to this oscillatory motion, a small fraction of the molecules will be undergoing self-diffusion. As will be seen later, the energy required for a molecule to break through the surrounding envelope is such that less than 1% of the molecules will be undergoing a net displacement relative to the molecules immediately surrounding them, and for the calculation of the collision frequency in a pure liquid this fraction may be neglected.

Let a be the mean double amplitude of the oscillation of a molecule, v^2 the mean square velocity, and τ the mean half-period of the oscillation. Then

$$mv^2 = 3RT/N \text{ and } \tau = a/v = a(mN/3RT)^{\frac{1}{2}} \quad (1)$$

For hexagonal close-packing, r , the virtual radius of a molecule, is equal to $(\frac{2}{3} \times 0.74M/N\pi\rho)^{\frac{1}{2}}$, where N is the Avogadro number, and M and ρ are the molecular weight and density of the liquid. If r varies with temperature according to $r = r_0(1 + bT)$, then $a_T = 2(r - r_0)$. This makes a proportional to the temperature, and therefore to the kinetic energy, giving $ac = \frac{1}{2}mv^2$, where c is a constant. This may be used as a basis for a more refined calculation, in which the last relation is applied to individual molecules. The number of molecules per c.c. with kinetic energy between E and $E + dE$ per g.-mol. is $dn = nE^{-\frac{3}{2}}e^{-E/RT} \cdot dE / (\pi RT)^{\frac{3}{2}}$, where n is the total number of molecules per c.c. These dn molecules will have periods between τ' and $\tau' + d\tau'$, where $\tau' = a'/v' = \frac{1}{2}mv'/c = (Em/2N)^{\frac{1}{2}}/c$. Hence τ , the true mean half-period, is equal to

$$\int_0^{\infty} \left(\frac{Em}{2N}\right)^{\frac{1}{2}} \cdot \frac{1}{c} \cdot \frac{E^{-\frac{3}{2}}}{(\pi RT)^{\frac{3}{2}}} \cdot e^{-E/RT} \cdot dE = \left(\frac{mRT}{2\pi N}\right)^{\frac{1}{2}} \cdot \frac{1}{c} = \frac{a}{v} \cdot \left(\frac{2}{3\pi}\right)^{\frac{1}{2}} \quad (2)$$

which will be used instead of the approximate equation $\tau = a/v$.

The number of collisions per second which each molecule makes with the surrounding molecules is therefore $(v/a)(3\pi/2)^{\frac{1}{2}}$, and

$$\text{total no. of collisions/c.c./sec.} = (\frac{1}{2}vn/a)(3\pi/2)^{\frac{1}{2}} \quad (3)$$

(since in summing over one c.c. each molecule is counted twice).

The above calculation gives results which are in accordance with our conception of internal pressure. The external pressure, p , of a liquid may be written in the form $p = \text{kinetic pressure} + \text{cohesive pressure}$ [*e.g.*, in Beattie and Bridgman's equation (*J. Amer. Chem. Soc.*, 1927, **49**, 1665) the last term is A^1/V^2]. Since the vapour pressure of a liquid is usually small at room temperature, the two terms will be almost equal. The kinetic pressure must therefore, like the cohesive pressure, be large (of the order of 1000 atmospheres) (Hildebrand, "Solubility," Chap. ix, Chemical Catalog Co., 1924).

The internal kinetic pressure may be calculated roughly as follows. Imagine a molecule enclosed in a cubical box of edge about 5 Å.U. This will simulate the conditions in a liquid. At each impact with the wall of the box the change of momentum is $2mv$, and the change per second is $\frac{2}{3}mv(v/2a)$. With $a = 0.5$ Å.U., this gives a pressure of about 2000 atm., which is of the correct order.

The Rate of Reactions in the Liquid Phase and the Rate of Unimolecular Reactions in Solution.—Formula (3) may be applied at once to the case of reaction in the liquid phase. Each molecule will contribute two squared terms to the collision energy available for activation, kinetic and oscillation potential energy, if as a first approximation it is assumed that the potential energy is a quadratic in the displacement co-ordinates. This introduction of squared terms differs essentially from Moelwyn-Hughes's treatment, in that it is the same for all reactions and does not include internal degrees of freedom. The latter may be operative in some cases, but their allocation is so uncertain that it is thought better to consider only the simple case of collision between oscillators.

On the assumption that all collisions in which the energy exceeds the critical increment E are effective for reaction, the velocity constant is given by

$$k = \frac{v}{a} \left(\frac{3\pi}{2} \right)^{\frac{1}{2}} \cdot \frac{E}{RT} \cdot e^{-E/RT} \dots \dots \dots (4)$$

Since $d \log_e k/d(1/T) = -E/R + 3T/2$ (a is proportional to T , and v to $T^{\frac{1}{2}}$) the true value of E is obtained by adding $\frac{3}{2}RT$ to the value derived from the slope of the approximate straight line given by plotting $\log_e k$ against $1/T$; this is denoted by E_1 .

An example is provided by the conversion of *d*-pinene into dipentene. The following table shows good agreement between r , obs., the virtual radius, calculated from the density and r , calc., derived from the linear relation $r = 3.239 + 1.18 \times 10^{-3}T$:

T , absolute	273°	290.9°	332.4°	352.6°
r , obs., Å.U.	3.561	3.583	3.632	3.657
r , calc., Å.U.	3.561	3.582	3.631	3.655

(The data for the density were those given by Beilstein for *l*-pinene, since more values were available for this than for *d*-pinene.)

At $T = 457.5^\circ \text{K.}$, $r = 3.779$ Å.U. E_1 for the liquid was not measured, but for the gas it was 43,710 and for petroleum solution 41,210 cal./g.-mol. The true value will probably not be far from the latter, which gives a collision frequency z^* of 1.4×10^{14} per sec. (obs. 5.52×10^{14} ; Smith, *J. Amer. Chem. Soc.*, 1927, **49**, 43; Conant and Carlson, *ibid.*, 1929, **51**, 3464).

In the case of unimolecular reactions the assumption that collisions between solute and solvent molecules with energy greater than E are effective for reaction gives a velocity constant

$$k = \frac{v}{a} \left(\frac{3\pi}{2} \right)^{\frac{1}{2}} \frac{E}{RT} e^{-E/RT} \dots \dots \dots (5)$$

The factor $\frac{1}{2}$ is not included. As an example the reaction $\text{CCl}_3 \cdot \text{CO}_2\text{H} \longrightarrow \text{CHCl}_3 + \text{CO}_2$ in aniline solution will be considered. For trichloroacetic acid, $r = 2.755 + 0.9575 \times 10^{-3}T$, and for aniline, $r = 2.790 + 0.8 \times 10^{-3}T$ (both ± 0.001) at 60° ; for 25° , the values for r are respectively 3.040 and 2.988 (density data from Beilstein). If it is assumed that the shell of aniline molecules is sufficiently rigid to limit the vibrations of a trichloroacetic acid molecule (the two values of r at 25° are very nearly the same, and the change in a for the

* That is, z in the equation $k = ze^{-E/RT}$.

acid from the value in the pure liquid is very small) a for the acid may be calculated to be 0.466 Å.U. The value of E_1 is 28,350 cal./g.-mol.; hence E at 25° is about 29,230 cal./g.-mol., which gives $k = 1.5 \times 10^{-7}$ sec.⁻¹ (obs., 6.7×10^{-7} sec.⁻¹; Goldschmidt and Bräuer, *Ber.*, 1906, **39**, 109).

The decomposition of diethylmalonic acid in water affords another example: $\text{CEt}_2(\text{CO}_2\text{H})_2 \longrightarrow \text{CHEt}_2\cdot\text{CO}_2\text{H} + \text{CO}_2$; r may be calculated from Beilstein's density value for the isomeric ethyl malonate—the error in a is probably not serious—giving $r = 3.204 + 1.133 \times 10^{-3}T$, *i.e.*, at 60°, $r = 3.581$. Since r for water is about half this, it is clear that the normal cluster of four water molecules (Bernal and Fowler, *loc. cit.*) cannot accommodate an acid molecule inside; hence a will be taken to be the same as for the acid at the same temperature; E_1 is 33,430 cal./g.-mol. This gives $k = 0.71 \times 10^{-8}$ sec.⁻¹ at 60° (obs., 2.0×10^{-8} sec.⁻¹; Moelwyn-Hughes, *op. cit.*, p. 164).

For most of the substances data are lacking for the temperature variation of the density. The calculation may, however, be reversed, and values of a calculated from the observed values of k . The applicability of the method is demonstrated by the agreement to within a factor of 5 of reasonable values of a in many cases (Table I). This method has the advantage that the assumed linear variation of a with T enters only by increasing E by $\frac{1}{2}RT$. Even if a is assumed to be a constant, practically the same agreement of calculated values of a with reasonable results is obtained.

TABLE I.

(Cf. Moelwyn-Hughes, *op. cit.*, p. 164.)

Decomposing substance.	Solvent.	E_1 (cals. per g.-mol.).	k (obs.) (sec. ⁻¹).	a (Å.U.).
Camphorcarboxylic acid	PhCOMe	28,960	1.59×10^{-6}	2.37
.....	H ₂ O	29,640	3.31×10^{-7}	4.14
2 : 4 : 6-Trinitrobenzoic acid.....	H ₂ O	29,970	3.33×10^{-6}	0.18
.....	PhNO ₂	34,990	4.07×10^{-9}	0.11
Triethylsulphonium bromide	AcOH	31,060	8.51×10^{-7}	0.20
Acetonedicarboxylic acid	H ₂ O	23,320	5.48×10^{-2}	0.34
Benzenediazonium chloride	H ₂ O	23,360	3.43×10^{-3}	5.11
<i>o</i> -Toluenediazonium chloride	H ₂ O	23,440	8.97×10^{-3}	1.73
"	H ₂ O	22,800	8.89×10^{-3}	4.58
Mesoxalic acid	H ₂ O	33,700	1.82×10^{-8}	0.24

In some cases the errors are larger; *e.g.*, for the decomposition of 2 : 4 : 6-trinitrobenzoic acid in toluene, $a = 42$ Å.U. (contrast Table I). However, for every 1000 cal. error in E_1 , a will be in error by a factor of about 6.5 at 60°. The above theory, moreover, is not intended to be a comprehensive one, but rather a method of approach to the problem—essentially different from that adopted by Moelwyn-Hughes—which may need elaboration in special cases; *e.g.*, deactivating collisions with the solvent and the effect of internal degrees of freedom have not been considered. In contrast to the method adopted by Moelwyn-Hughes, the collision frequency z is independent of the viscosity, and $\log z$ varies only slightly with the temperature (Moelwyn-Hughes, *op. cit.*, p. 159, gives the formula $k = 3\pi\eta\sigma e^{-E/RT}/2m$ and allows for the variation of η with temperature). On the above view (equation 5) the solvent molecules immediately in contact with a solute molecule supply the energy required for activation, and diffusion through the solvent need not be considered; it will be shown below that only a small fraction of the solute molecules are undergoing diffusion. On the other hand, diffusion is the controlling factor in bimolecular reactions in solution and will be considered below as a natural extension of the conception of vibration frequency and solvent envelope.

Diffusion in Solution.—Whereas the viscous resistance offered to a solute molecule is difficult to formulate in terms of viscosity, the diffusion coefficient is a readily intelligible concept. On the above theory, diffusion will occur when a solute molecule has sufficient energy, E_2 , to break through the envelope of solvent molecules surrounding it. Thus diffusion relative to the surrounding molecules will proceed by a series of jumps, each equal to d , from one energy trough to another. Consider a tube one sq. cm. in cross section

containing the solution (Fig. 1; not drawn to scale), and suppose that diffusion occurs from right to left. Select two planes, 1 and 2, a distance d apart, and let the concentrations of the solution at 1 and 2 be c_1 and c_2 respectively. If we divide the solute molecules at plane 1 into six groups, three pairs at right angles, the number of solute molecules leaving plane 1 from right to left in time τ , the oscillation frequency of the solute, is $\frac{1}{6}dc_1e^{-E_2/RT}$, since the number of solute molecules at plane 1 may be taken as dc_1 ; the dotted lines, a distance d apart, define the limits of the solute molecules relegated to plane 1. The allocation of the molecules into six groups is, of course, an approximation, which will, however, only slightly affect the order of the result. Similarly the number of molecules leaving plane 2 from left to right in time is $\frac{1}{6}dc_2e^{-E_2/RT}$. Diffusion at right angles to the axis of the tube does not influence c . Diffusion of the type considered still continues in the absence of a concentration gradient across the tube, but of course there is no net flow. The net flow along the tube is therefore $d(c_1 - c_2)e^{-E_2/RT}/6\tau$ per sec. per sq. cm. = $D(c_1 - c_2)/d$, where D is the diffusion coefficient. Hence

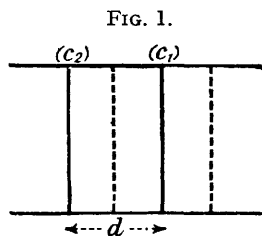


FIG. 1.

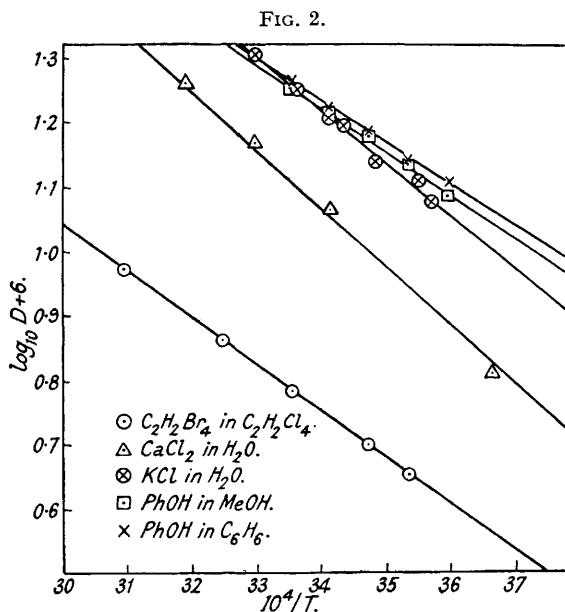
FIG. 1. A diagram of a tube with two vertical planes, 1 and 2, separated by a distance d . Plane 1 is on the left and plane 2 is on the right. The concentration of the solution at plane 1 is c_1 and at plane 2 is c_2 . Dotted lines are drawn at a distance d from each plane, defining the limits of solute molecules relegated to plane 1. The diagram illustrates the diffusion process and the allocation of molecules into six groups.

FIG. 2. A graph showing the logarithm of the diffusion coefficient, $\log_{10} D + 6$, plotted against $10^4/T$. The y-axis ranges from 0.6 to 1.3, and the x-axis ranges from 30 to 37. Five data series are shown, each represented by a different symbol and a straight line with a negative slope. The symbols used are circles, triangles, squares, and crosses.

$$D = \frac{d^2}{6\tau} \cdot e^{-E_2/RT} = \frac{d^2v(3\pi)^{\frac{1}{2}}}{6a\left(\frac{2}{2}\right)^{\frac{1}{2}}} e^{-E_2/RT} \quad \dots \quad (6)$$

The factor E_2/RT is not introduced as in equation (4) since the calculation considers the fraction of solute molecules of sufficient energy to pass through the barrier. A molecule cannot be activated by collision with the barrier for the process of diffusion through it, for the receipt of energy from the barrier would occasion reflexion, although such energy would be available for unimolecular decomposition. In contrast to the deduction of D by use of Stokes's law, formula (6) does not involve the viscosity explicitly.

Although diffusion in solution is not usually supposed to vary exponentially with temperature, since D is usually written in the form $RT/3\pi\eta N\sigma$, and the temperature variation of D/T is usually attributed to η (Williams and Cady, *Chem. Reviews*, 1934, 14, 171), the results support equation (6). A similar law is found for such a "physical" process as the diffusion of the inert gases through solids. On plotting $\log D$ against $1/T$, a straight line is obtained in many cases (Fig. 2). The data are taken from the International Critical Tables except those for phenol in methyl alcohol (Thovert, *Ann. Physique*, 1914, 2, 369). The true value of E_2 is $E_3 + \frac{1}{2}RT$, where E_3 is taken from the slope of the graph. Strictly, $\log D - \frac{1}{2} \log T$ should be plotted against $1/T$; however, this scarcely affects the final result. The variation of d with temperature is negligible. Results are summarised in Table II; D is given by $D = D_0 e^{-E_2/RT} / T^{\frac{1}{2}}$, and L is the latent heat per g.-mol. of the solvent. L is seen to be roughly twice E_2 ; D_0 (obs.) in Table II refers to values of D_0 calculated from this formula, by using the values of E_2 determined from Fig. 2. Values of D_0 may be calculated as before from the values of a as determined from the temperature dependence of the density (Beilstein), and are given under D_0 , calc., in Table II. This gives the following values of r :





d has been taken to be equal to the sum of the virtual radii of solute and solvent.

TABLE II

Solute.	Solvent.	E_3 (cals. per g.-mol.).	$100D_0$, obs.	$100D_0$, calc.	L , cals.
PhOH	MeOH	3,151	6.44	9.5	8,410
PhOH	C_6H_6	3,078	9.44	10.4	7,360
<i>s.</i> - $\text{C}_2\text{H}_2\text{Br}_4$	<i>s.</i> - $\text{C}_2\text{H}_2\text{Cl}_4$	3,365	5.16	10.6	7,350
CaCl_2	H_2O	4,410	62.8	—	9,710
KCl	H_2O	3,960	2.51	—	9,710

Values of D_0 for the ionised molecules have not been calculated owing to complications (see below). In view of the nature of the assumptions, the agreement in the other cases is good. The selection of a in the case of solutions is somewhat arbitrary: when the solute and solvent have nearly the same virtual radius, it is assumed that the envelope of solvent molecules determines the amplitude of vibration of the solute molecules. When r for the solute is much greater than for the solvent, a is taken to be the same for the solute at the same temperature, *i.e.*, the solute molecule accommodates solvent molecules around it. In any case, the order of the result will not be affected, and the above calculation for D may be applied with confidence to the calculation of the rate of bimolecular reactions in solution. It is noteworthy that, owing to the exponential term, only a small fraction of the solute molecules are undergoing diffusion (about 0.5%).

The Rate of Bimolecular Reactions in Solution.—In fairly dilute solution any molecule of solute will be surrounded by solvent molecules almost entirely, and solute will diffuse up to this envelope.

Let n_1 and n_2 be the number of reactants per c.c., and D_1 and D_2 their diffusion coefficients. Smoluchowski (*Z. physikal. Chem.*, 1918, **92**, 129) showed that the number of molecules of species 2, diffusing in time Δt up to a distance d of a molecule of class 1 (d is measured from centre to centre) is

$$4\pi d(D_1 + D_2)n_2\Delta t + 8\pi^{\frac{1}{2}}D^{\frac{1}{2}}d^2n_2(\Delta t)^{\frac{3}{2}} \quad \dots \quad (7)$$

(but Harper, *Trans. Faraday Soc.*, 1934, **30**, 636, considers this is erroneous by a factor of 4). If $\Delta t \gg d^2/D$, the last term is negligible. The chance that any particular molecule of species 2 will collide with the molecule 1 after diffusing up to the distance d from it is 1/12 on the basis of hexagonal close-packing and equal radii for all species of molecule. It is assumed that at the position of instantaneous rest of each vibration molecule 1 makes a collision. Hence the number of collisions of molecules of species 2 with 1 in time Δt is

$$\frac{1}{2} \times 4\pi d(D_1 + D_2)n_1n_2/12 \quad \dots \quad (8)$$

where the factor $\frac{1}{2}$ allows for counting each molecule twice.

If the rate is expressed in the form $dn/dt = kn_1n_2/1000N$, then

$$k = \frac{\pi}{6}(D_1 + D_2) \frac{Nd}{1000} \cdot \frac{E}{RT} \cdot e^{-(E+E_2)/RT} \quad \dots \quad (9)$$

where E and E_2 are the activation energies for reaction and diffusion; E_2 is actually the sum of the diffusion activation energies of the two solutes. As before, E_3 , calculated from the slope of $\log k$ plotted against $1/T$, is equal to $E + E_2 - \frac{3}{2}RT$, so if the velocity constant is expressed in the form $k = ze^{-E_3/RT}$, where z is taken to be independent of T ,

$$z = \frac{\pi}{36} \left(\frac{d_1^2v_1}{a_1} + \frac{d_2^2v_2}{a_2} \right) \cdot \left(\frac{3\pi}{2} \right)^{\frac{1}{2}} \cdot \frac{Nd}{1000} \cdot \frac{E}{RT} \cdot e^{-3/2} \quad \dots \quad (10)$$

and T may be taken as 298. Also E may be taken as about 3000 cal., for a variation in 1000 cal. affects z only to the extent of about 5%. Further, $d_1 = r_1 + r_s$, $d_2 = r_2 + r_s$, and $d = r_1 + r_2$, where r_1 , r_2 , and r_s are the virtual radii of solutes 1 and 2 and of the solvent.

A result similar to equation (8) was obtained by Ölander (*Z. physikal. Chem.*, 1929, *A*, **144**, 118), who gave for the collision frequency per sec. per c.c. the formula $z = n_1 n_2 \frac{\pi k'T}{6\eta} \cdot \frac{(r_1 + r_2)^2}{r_1 r_2}$, where k' is the gas constant. On eliminating η by means of the equations $D_1 = k'T/6\pi\eta r_1$, $D_2 = k'T/6\pi\eta r_2$ (which is the basis on which Ölander's result was obtained), we find $z = \pi^2(D_1 + D_2)(r_1 + r_2)$, which differs from (8) only in a numerical factor.*

The above calculation will not apply as it stands to small ions such as multivalent cations, to which a sphere of polar solvent molecules, *e.g.*, water, will be attached with a much firmer binding than that already considered. This envelope of solvent molecules directly in contact with the ion may accompany it as it diffuses through the solvent, an outer and more weakly oriented envelope of solvent molecules being built up and again dispersing. The energy required for the ion to break through the inner envelope will be greater than for a neutral molecule, and the range of the motion of the ion will be more restricted ($1/\tau$ greater than for a neutral molecule). For larger ions (anions) solvation need not be considered, and the charge will affect only the value of E_2 . The influence of the ionic atmosphere need not be considered, since the displacements of the ion are very small and infrequent (in contrast to the conditions obtaining when a potential difference is applied), and after each jump from one position of mean equilibrium to another the ion may have to wait some time before again escaping from its envelope. Consequently considerations of relaxation time (Onsager, *Trans. Faraday Soc.*, 1927, **23**, 341) do not affect the form of the diffusion equation. Since density data are lacking for the cases in question, a will be calculated from the observed value of z by means of equation (10). For simplicity, it will be assumed that $d_1 = d_2 = d = 5 \text{ \AA.U.}$, and $a_1 = a_2 = a$. Suitable examples of bimolecular reactions between un-ionised molecules are rare. The reaction $\text{Et}_2\text{S} + \text{EtBr} \rightarrow \text{Et}_3\text{SBr}$ has been studied in benzyl alcohol (Moelwyn-Hughes, *op. cit.*, p. 79): $E_3 = 24,470$ and $z = 0.31 \times 10^{11}$; this gives $a = 12.1 \text{ \AA.U.}$

TABLE III.

Reaction.	Solvent.	$z \times 10^{-11}$.	E_3 (cals. per g.-mol.).	a (calc.), \AA.U.
$\text{MeONa} + 1 : 2 : 4\text{-C}_6\text{H}_3(\text{NO}_2)_2\text{Cl}$	MeOH	1.91	17,450	2.3
$\text{EtONa} + \text{ " " " "}$	EtOH	1.80	16,760	1.6
$\text{EtONa} + \text{MeI}$	"	2.42	19,490	1.4
$\text{EtONa} + \text{EtI}$	"	1.49	20,650	2.5
$\text{EtONa} + \text{C}_6\text{H}_5\text{-CH}_2\text{I}$	"	0.15	19,900	22.8
$\text{PhONa} + \text{PrI}$	"	3.53	22,450	0.9
$\text{PhONa} + \text{Pr}^\beta\text{I}$	"	1.74	22,100	2.4
$\text{PhONa} + \text{C}_6\text{H}_{11}\text{I}$	"	2.78	22,430	1.0
$\text{C}_6\text{H}_5\text{-CH}_2\text{-ONa} + \text{BuI}$	"	2.92	21,560	1.0
$\text{C}_6\text{H}_5\text{-CH}_2\text{-ONa} + \text{iso-BuI}$	"	2.45	21,350	1.1
$\text{C}_6\text{H}_5\text{-CH}_2\text{-ONa} + \text{C}_{16}\text{H}_{33}\text{I}$	"	1.26	21,090	1.9
$\text{o-C}_6\text{H}_4\text{Me-ONa} + \text{MeI}$	"	1.30	21,180	2.2
<i>m-</i> " "	"	2.27	19,490	1.1
<i>p-</i> " "	"	8.49	20,900	0.3
$\beta\text{-C}_{10}\text{H}_7\text{ONa} + \text{EtI}$	MeOH	0.10	21,010	25.1
$\text{CH}_3\text{-[CH}_2\text{]}_3\text{-Cl} + \text{I}'$	COMe ₂	2.24	23,500	1.5
$\text{C}_6\text{H}_5\text{-CO-[CH}_2\text{]}_2\text{-Cl} + \text{I}'$	"	10.5	22,160	0.3
$\text{C}_6\text{H}_5\text{Br}_2 + \text{I}'$	MeOH	1.07	25,100	2.8
$\text{CH}_2(\text{OH})\text{-CH}_2\text{Cl} + \text{OH}'$	H ₂ O	25.5	19,870	0.2
$\text{C}_2\text{H}_5\text{Br} + \text{OH}'$	EtOH	4.30	21,400	1.4

Most of the other examples appear to be reactions involving the formation of quaternary ammonium salts. It is well known that these are "abnormal," in the sense that the rates cannot be interpreted on a simple kinetic hypothesis, since in the gaseous phase, where the collision mechanism is well established, abnormally slow rates are obtained for the formation of tetraethylammonium iodide (*idem, ibid.*, p. 109). It is necessary, therefore, to turn to ionic reactions for examples, and no serious difficulty is introduced if one of the reactants

* Moelwyn-Hughes (*op. cit.*, p. 119) states that Ölander's result is dimensionally incorrect; but since $n_1 = L^{-3}$, $n_2 = L^{-3}$, $\eta = ML^{-1}t^{-1}$, $k'T = ML^2t^{-2}$, z has the dimensions $t^{-1}L^{-3}$, *i.e.*, number per c.c. per sec., which is correct.

is an un-ionised molecule, and the ions considered are not strongly solvated. This is due to the fact that no corrections are necessary for an uneven distribution of molecules of solute 2 around a molecule of solute 1. The same result follows from Brönsted's theory, according to which the velocity of the reaction $A + B \longrightarrow C + D$ via a complex is given by $v = k_0 c_A c_B \cdot f_A f_B / f_C$, where the f 's are activity coefficients, *i.e.*, $v = k_0 c_A c_B e^{2\alpha z_A z_B \mu^{\frac{1}{2}}}$ (*idem, ibid.*, p. 197), where z_A and z_B are the charges on A and B, μ is the ionic strength, and α is a constant for the solvent in question. On putting $z_A = 0$, the result follows. This does not mean, of course, that the rate will be the same whether one reactant is ionised or not, owing to the influence of E .

Examples of the reaction between an ion and an un-ionised molecule are given in Table III, and values of a are calculated as before. In many cases agreement with a reasonable value of a is obtained. The reactions $\text{RONa} + \text{R}'\text{X} \longrightarrow \text{ROR}' + \text{NaX}$ are probably mainly ionic. Acree (*Amer. Chem. J.*, 1912, **48**, 352) gives for $\text{PhONa} + \text{MeI}$ the value $k_{\text{ionic}}/k_{\text{molecular}} = 5.95$ at 25° . The values of the degree of ionisation, however, are of doubtful significance, for interionic attraction was not allowed for. In general, the agreement with a reasonable value of a is of the same order as the agreement of z , as calculated by Moelwyn-Hughes, with z observed. Thus the above theory offers an alternative picture for reaction mechanism in solution in simple cases.

SUMMARY.

The rate of reaction in solution is calculated by a method which takes into account the molecular structure of liquids and avoids the introduction of viscosity.

The rate of a unimolecular reaction in which activating collisions are supplied by the solvent is $\frac{v}{a} \left(\frac{3\pi}{2}\right)^{\frac{1}{2}} \cdot \frac{E}{RT} \cdot e^{-E/RT}$, where v^2 is the mean square velocity of a solute molecule, a the amplitude of vibration, and E the energy of activation. Agreement is found in many cases.

It is shown that diffusion in solution can be interpreted in a similar way, and agreement is found between observed and calculated diffusion coefficients. The latter are given by $\frac{d_2 v}{6a} \left(\frac{3\pi}{2}\right)^{\frac{1}{2}} e^{-E_2/RT}$, where d is the distance a solute molecule moves from one position of mean equilibrium to another, and E_2 is the activation energy for diffusion.

The rate of a bimolecular reaction is deduced to be

$$\frac{\pi}{36} \left(\frac{d_1^2 v_1}{a_1} + \frac{d_2^2 v_2}{a_2} \right) \left(\frac{3\pi}{2} \right)^{\frac{1}{2}} \frac{Nd}{1000 RT} e^{-(E+E_2)/RT}$$

where $d_1 = r_1 + r_s$, $d_2 = r_2 + r_s$, $d = r_1 + r_2$, and r_1 , r_2 , r_s are the virtual radii of the reactant and of the solvent molecules, N is Avogadro's number, E_2 the sum of the diffusion activation energies of the two solutes, and E the activation energy for reaction. Agreement is found for many examples of reactions between a large ion and an un-ionised molecule.

The general theory of ionic reactions is not considered.

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