

23. Some Kinetic Consequences of Complex Formation in Solution.

By E. A. MOELWYN-HUGHES and ALBERT SHERMAN.

EXPERIMENT shows that the influence of a solvent on the mechanism of a chemical change proceeding in its presence is specific, having a magnitude dependent on the properties of the solute and solvent molecules. It is the object of this paper to classify the various types of solvent action, for which purpose we require a knowledge of the different kinds of intermolecular forces which are hypothetically possible. The solvent effect can be formulated quantitatively in certain simple cases.

Where the topics of discussion coincide, our conclusions are in harmony with those of Nathan and Watson (J., 1933, 890, 1248) and of Waters (*ibid.*, p. 1551).

Classification of Chemical Bonds.—The occurrence of a chemical reaction always entails the making or breaking of a bond, and very often two such changes take place simultaneously. A classification of chemical reactions should thus constitute a logical corollary to any scheme of bond classification. We outline below the accepted scheme of bond classification, admitting (Lennard-Jones and Sherman, Reports of the London Physical Society, 1935) that it is too idealistic, because, in practice, no bond is entirely of one type.

A. *Homopolar bonds.* That the homopolar or covalent bond (*e.g.*, H–H, C–H) is due to a pair of electrons, was suggested empirically by Lewis in 1915. The nature of the interaction has been understood only with the recent advent of quantum mechanics. It is noteworthy that almost all the quantum-mechanical treatments of valency have been confined to the homopolar bond (for review, see van Vleck and Sherman, *Rev. Mod. Physics*, 1935, 7, 167).

B. *Electrostatic attractions.* The three sources of electrostatic attractions are ions, permanent dipoles, and induced dipoles. Electrostatic attractions arise from all possible interactions in pairs.

1. Ion-ion bond (*e.g.*, Na⁺Cl⁻ in the sodium chloride crystal; for summary, see J. Sherman, *Chem. Reviews*, 1933, 11, 93). The energy of this bond is due to the Coulomb attraction between two ions of opposite charge.

2. Dipole-dipole bond (*e.g.*, intermolecular compounds, such as are formed between ether and chloroform ($\text{C}_2\text{H}_5\overset{\rightarrow}{\text{O}}$, HCCl_3). The Coulomb attraction between two molecules, each of which has a permanent dipole, is responsible for this bond. The most familiar example is afforded by the association of alcohols, but numerous instances of the behaviour described parenthetically above are also known. It will be shown that they are of importance in the study of the kinetics of reactions in solution.

3. Induced dipole-induced dipole bond. The forces operating here are Coulomb forces between dipoles induced in neutral atoms or molecules. They are relatively small in magnitude, and give rise to bonds so weak that the compounds are largely dissociated except at low temperatures. These so-called van der Waals forces account for the liquefaction of the rare gases and for the existence of the molecules Hg₂ and O₄.

4. Ion-dipole bond. The Coulomb attraction between an ion (*e.g.*, Cu⁺⁺) and a molecule possessing a permanent dipole (*e.g.*, NH₃) results in the formation of compounds such as the tetramminocupric ion, Cu(NH₃)₄⁺⁺. The relation between the bond so formed and the co-ordinate link will be discussed later.

5. Ion-induced dipole bond. The presence of an ion may induce a dipole in a molecule which is otherwise non-polar; and the interaction between the ion and the induced dipole gives rise to an attractive force which makes compound formation possible. For purposes of discussion, we may consider the stability of the tri-iodide ion (I₃⁻) as due, in part, to the attraction between the iodide ion and the dipole which it induces in the iodine molecule. The example is not a clear-cut one, because there is some doubt as to whether the iodine molecule in water is really non-polar. The ion-induced dipole bond is weaker than, and is always superimposed upon, the ion-dipole bond.

6. Dipole-induced dipole bond. This case differs from the preceding one only in that the dipole is induced by a permanent dipole rather than by an ion. The formation of the

hydrates of the rare gases and of the halogens affords evidence for the existence of this type of bond.

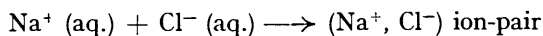
The six types of electrostatic attraction discussed here are effective at relatively great separations; when the ions, dipoles, or induced dipoles are brought close together, strong repulsive forces come into effect. The interplay between attractive and repulsive forces thus gives rise to six types of bond. The magnitudes of the attractive forces are inversely proportional to the dielectric constant of the medium; hence we expect all the six bonds to be weaker in solution than in the gas phase. Nevertheless, atoms, molecules, or ions which are held together by quite small forces may form complexes which are of great importance in determining the course of chemical change.

Chemical Reactions involving the Rupture or Formation of Homopolar Bonds in Un-ionised Molecules.—The main contribution to the energy of the homopolar bond arises from a non-classical resonance, and is usually of such magnitude that we can anticipate the bond to be largely uninfluenced by a solvent environment. The potential energy of a diatomic molecule is known to be represented by an equation of the Morse type, *viz.*,

$$V(r) = D'\{e^{-2a(r - r_0)} - 2e^{-a(r - r_0)}\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D' is the strength of the bond (including zero-point energy), a is a constant, and r_0 is the equilibrium separation of the nuclei. The velocity of chemical change, in general, depends on the attainment of a certain minimum potential energy, characteristic of the reacting system, and on the probability of transformation of the critical configuration, towards the formation of which the energy has been expended. Our knowledge of such probabilities is meagre, and the phrase at present is little more than a confession of ignorance. But the critical energy can often be computed in a satisfactory manner; its magnitude is dependent on the magnitude of the various D' terms involved in the reaction. Eyring and Polanyi's method of calculating the energy of activation shows that, provided an ionic mechanism does not intervene, the influence of the solvent upon the energy of activation is not very great. This conclusion harmonises with the somewhat scant experimental information (cf. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, 1933). As far as it is possible to generalise, it may be said that reactions which do not involve an ion on either side of the chemical expression are less sensitive to solvent influences than those in which ions are produced or consumed. For instance, nitrogen pentoxide, chlorine monoxide, and pinene decompose at the same rate in the gas phase as in certain solvents (*op. cit.*, p. 51); the Beckmann transformation (Chapman, J., 1934, 1550) and certain catalysed mutarotations (*op. cit.*, p. 229) proceed in solution by the same mechanism as would be predicted for their behaviour in gases; the elimination of nitrogen from diazonium halides is largely insensitive to a change in the solvent medium (*op. cit.*, p. 157); and the decomposition of nitrous acid is unaffected by drastic changes in the ionic environment (*op. cit.*, p. 201). All these changes can be formulated as occurring by the breaking and making of essentially homopolar bonds, in the absence of ionic intervention. Conversely, the decomposition of triazole compounds (*op. cit.*, p. 133) and of carboxylic acids (*op. cit.*, p. 166) is influenced by a change in the solvent medium, and it may be concluded that electrostatic influences due to the solvent atmosphere have been superimposed on the chemical reaction proper.

Reactions between Two Ions in Solution.—It has been pointed out (*op. cit.*, p. 172) that there exists a fundamental distinction between true ionic reactions and reactions occurring between charged particles. Failure to recognise the distinction has led to some confusion. True ionic reactions have been defined as those wherein the attractive forces are solely the Coulomb influence between the ions, *e.g.*, the formation of the sodium chloride ion-pair in water



With such reactions alone is it logical to introduce the Debye-Hückel expression for the activity into the general equation for the velocity of a bimolecular reaction proceeding by way of an intermediate complex. No data are available on this type of reaction. The formation of ion-pairs is known to proceed rapidly, but not necessarily instantaneously,

because, if the sum of the ionic solvation energies exceeds the crystal energy, the reactions will be endothermic, and may involve considerable activation. The physical reason for the necessity of activation is that the formation of an ion-pair requires the partial removal of the solvation shells. With an activation energy of the order of magnitude of the equipartition value, it would be necessary to work with concentrations of the order of magnitude of 10^{-14} g.-mol./l. in order to follow the course of reaction by ordinary methods. The method of Hartridge and Roughton, however, may prove to be helpful in the study of true ionic reactions, since a half-life of 10^{-8} sec. can be measured by its aid, and correspondingly higher concentrations of reactants could be employed. von Halban and Eisner (*Helv. Chim. Acta*, 1935, **18**, 724) have recently applied this technique to the study of fast reactions, both inorganic and organic. Their estimated values of the activation energy agree with the conclusions of this paragraph.

The simplest ionic reactions which have hitherto been examined are shown below. They refer to aqueous solutions (for more detailed information, see "The Kinetics of Reactions in Solution," pp. 37, 218, and 220). All three reactions take place between ions which have charges of the same sign, so a portion of the activation energy must be expended in overcoming the Coulomb repulsion between the ions. The energy required

Ionic Reactions.

Reaction.	Observed energy of activation (cals./g.-mol.)
(1) $\text{ClO}' + \text{ClO}' \longrightarrow \text{Cl}' + \text{ClO}_2'$	22,500
(2) $\text{AsO}_3''' + \text{TeO}_4''' \longrightarrow \text{AsO}_4''' + \text{TeO}_3''$	14,400
(3) $\text{Sn}'' + 2\text{Fe}'' \longrightarrow \text{Sn}'' + 2\text{Fe}''$	29,200

to bring an ion of charge $z_A e$ up to a distance r_0 from a second ion of charge $z_B e$, in a medium of dielectric constant D , is

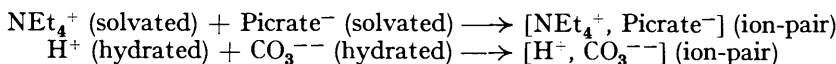
$$\epsilon = z_A z_B e^2 / D r_0 \quad \dots \quad (2)$$

With r_0 in Å.,

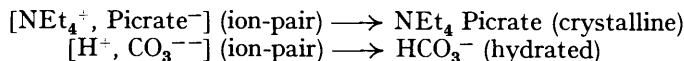
$$\epsilon = 329 \cdot 7 z_A z_B / D r_0 \text{ kg.-cals./mol.}$$

If, e.g., $z_A = z_B = 2$, $r_0 = 2$ Å., and $D = 80$, ϵ becomes 8,260 cals.; hence, the interionic repulsion accounts for a considerable fraction of the activation energy. However, none of these reactions can be regarded as a true ionic reaction. Examples 1 and 2 obviously involve the breaking of covalency bonds. Example 3 is *prima facie* the most appropriate case to examine, because it involves a change in electrovalency without a change in covalency. Recent work, however, has shown that the reaction is kinetically complicated (Robinson and Law, *Trans. Faraday Soc.*, 1935, **31**, 899). The velocity constants given by experiment refer, not to the step written in the above table, but to some intermediate stage in the total reaction, which bears many of the distinguishing features of a chain reaction, though it has not yet been viewed in this light.

Such data as are available, from *E.M.F.* and conductivity measurements, suggest that the formation of ion-pairs, although a rapid process, may be the rate-determining step in several chemical processes. For example, the processes subsequent to the following reactions



which are crystallisation and the formation of a covalent link respectively,



may well proceed rapidly in comparison with the first stage, since the subsequent stage depends only on the transference of an electron, whereas the primary stage, as stated above, involves partial desolvation.

Reactions between Two Dipoles in Solution.—Molecular complexes, long known to chemists, have recently gained new prominence because the magnitude of the dielectric constant of dilute solutions cannot be interpreted without postulating their existence.

We are here concerned with the relation between the energy of formation of such complexes and the velocity of the relevant reactions.

The potential energy of two molecules held together in a head-on position by the mutual interaction of two dipoles (μ_A and μ_B) in a medium of unvarying dielectric capacity D is

$$\epsilon = \frac{2\mu_A\mu_B}{Dr_0^3} \dots \dots \dots (3)$$

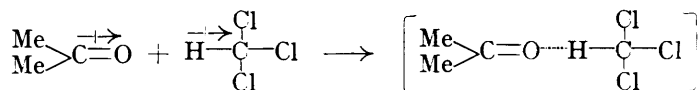
With r_0 in Å., and μ in Debye units, $\epsilon = 28.9 \frac{\mu_A\mu_B}{Dr_0^3}$ kg.-cals./mol.

We are usually concerned with permanent moments ranging in magnitude from about 0.2 to about 3 (Debye units), and with equilibrium separations (r_0) of 1–4 Å. in media where D may have any value from 2 to 80. Hence ϵ lies within the approximate limits of 200 and 15,000 cal./g.-mol.

Complexes formed with the evolution of only 200 cal. can obviously not be regarded as stable at ordinary temperatures, although they may be kinetically influential. The next most stable type of complex corresponds to that postulated by Debye, where the approach is not head-on, but broad-side on, thus $\uparrow\downarrow$. Sakurada (*Z. physikal. Chem.*, 1935, B, 28, 104) found the exothermic heat of formation of double molecules of phenyl halides in carbon tetrachloride solution to vary from 1,078 to 1,714 cal.; and, although there is some force in the criticism of Heitet and Dumont (*ibid.*, 29, 15), Sakurada's values are certainly correct as regards order of magnitude. These associated compounds are fairly stable at room temperatures, but their exothermicity is scarcely large enough to constitute an important factor in determining the reactivity of the phenyl halides, where fairly large energies of activation are usually found (cf. the discussion above on the influence of solvent atmosphere on the strength of the covalent bond).

The heats of formation of complexes formed between trinitrobenzene and dibenzyl, tolan, and stilbene, vary from 600 to 3,170 cal. (Briegleb and Kambeitz, *ibid.*, 1934, 27, 161). The energy of association of a series of seven alcohols ranges from 5,000 to 5,900 cal. in hexane solution, and from 3,400 to 4,000 cal. in benzene solution (Wolf, Pohlke, and Wehago, *ibid.*, 1935, 28, 1). The magnitude of these energy terms, and the fact that they are independent of the nature of the alcohol, are consistent with the idea that the complexes are formed by the mutual action of two solute dipoles.

The vapour pressure, viscosity, and mutual solubility of acetone–chloroform mixtures are anomalous, in the sense that they bear no apparent relation to the composition of the mixture and to the individual properties of its components. The mixed solvent has also an anomalous effect on the velocity of reactions which proceed in it. Assuming the vapour pressure of each species to be proportional to the molar fraction in the condensed phase, Schulze (*ibid.*, 1919, 93, 370) determined the equilibrium constant $K = n_1n_2/n_{1,2}$ at various temperatures. Applying the van't Hoff relation, we find that the postulated complex is formed exothermically, with $Q = 4,070$ cal. Let us assume that the complex is formed by the head-on union of the two dipoles ($\mu_{\text{COMe}_2} = 2.75$; $\mu_{\text{CHCl}_3} = 1.05$), that the moments



remain unchanged, and that the heat of formation may be identified with the mutual electrostatic potential energy of the system. Equating Q to $2\mu_A\mu_B/Dr_0^3$, we find $r_0 = 1.0$ Å., which is in good agreement with the accepted separation of the hydrogen and the oxygen nucleus in most compounds.

The formation of a similar complex between ethyl ether and chloroform has been postulated by McLeod and Wilson (*Trans. Faraday Soc.*, 1935, 31, 596), who determined the heat of reaction calorimetrically. The exothermicity is 6,070 cal./g.-mol. The dielectric constant of a mixture of 50% ether + 50% chloroform is 5.58 (Philip, *Z. physikal. Chem.*, 1897, 24, 18). With $\mu_{\text{Et}_2\text{O}} = 1.32$ and $\mu_{\text{CHCl}_3} = 1.05$, we find $r_0 = 1.05$ Å., which again is a reasonable value.

More extensive, if less accurate, information is available relating to complexes formed between nitro-compounds and hydrocarbons, and between nitrogen bases and alkyl and

aryl halides. We confine attention to the latter class, and quote but two illustrative examples from the abundant data given by Bramley (J., 1916, **109**, 11, 434). The heat of reaction, calculated from the equation $d \log_e K/dT = Q/RT^2$, using the experimental values of the equilibrium constant K , are shown in Table I. The fall in Q may be due to error in experiment or in the computation of K . It may equally well be genuine, indicating the omission of relevant factors, such as the temperature variation of the viscosity. The freezing-point curves of these mixtures show compound formation at equimolecular proportions. A 1 : 1 compound also separates in the case of *o*-chlorophenol with aniline and

TABLE I.

Heats of Formation of Intermolecular Complexes.

Quinoline and <i>o</i> -chlorophenol.			Pyridine and <i>o</i> -chlorophenol.		
Temp.	K .	Q .	Temp.	K .	Q .
60°	0.014	13,300	40°	0.0236	9,400
80	0.043	13,300	60	0.0670	8,100
110	0.189	10,800	80	0.134	7,600
150	0.712		110	0.313	

with dimethylaniline. Similarly, *o*-cresol and pyridine give only a 1 : 1 eutectic, but phenol and pyridine give a complex $C_5H_5N, 2C_6H_5 \cdot OH$. The behaviour is fairly general, and there is no reason to dispute that its origin is to be traced to the dipole-dipole attraction under discussion.

In considering the effect of molecular compounds upon the velocity of bimolecular reactions in liquid systems, we may first re-examine the results of Lowry and Traill (*Proc. Roy. Soc.*, 1931, *A*, **132**, 398) upon the mutarotation of beryllium benzoylcamphor under the influence of catalysts in various solvents. In carbon tetrachloride solution, the reaction is kinetically very simple: with catalysts such as cresol, pyridine, and alcohol, catalytic coefficients are found which agree with those calculated by making the usual assumptions about collision frequencies. The α - and the β -form of the reactant have equal stability in carbon tetrachloride and in hexane, but in chloroform solution the symmetrical equilibrium is displaced, indicating, as the authors point out, that the solvent now combines with both forms, but preferentially. The lessened catalytic activity of pyridine in chloroform, as compared with carbon tetrachloride, has been quantitatively ascribed to the presence of a complex, which, moreover, has been isolated in the form of a crystalline solvate with two molecules of chloroform.

We next consider the reactions between nitrogen bases and alkyl or aryl halides in various solvents. Their velocities are usually lower than those calculated by means of the equation

$$k = \sigma_{1,2}^2 \{8\pi kT(1/m_1 + 1/m_2)\}^{1/2} \cdot e^{-E/RT} \dots \dots \dots (4)$$

and many attempts have been made to account for this apparent slowness. These have all been based on the assumption that the critical increment (E_A) as given by the Arrhenius equation is a true measure of the activation energy. In a general review of bimolecular reactions in solution (Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 260) it was pointed out that these "observed critical increments are false, in the sense that, by some unknown mechanism, they have been depressed from their normal values." The interaction of the dipole of either reactant with the solvent seems to supply the missing mechanism. The reaction scheme can be formulated in the familiar way by assuming that the net change $A + B \longrightarrow AB$ proceeds *via* the reversible formation of a complex of either A or B with the solvent, S, say,



whence it follows that

$$k_{obs.}[A][B] = \text{rate} = k_2 [AS][B] = k_2 K[S][A][B]$$

Hence

$$k_{obs.} = k_2 K[S]$$

and

$$E_A = E_2 - Q \dots \dots \dots (5)$$

Taking the true value of the activation energy E_2 as that given by equation (4), we have thus a means of calculating Q from kinetic measurements. Hundreds of examples have been investigated, and it is a simple matter to calculate Q in each case. Unfortunately, however, the corresponding values of Q determined independently from non-kinetic data do not appear to exist in any single instance, so we can only illustrate our ideas in a general way. Combining equations (3) and (5), we have

$$E_2 - E_A = 2\mu_A\mu_B/Dr_0^3 \dots \dots \dots (6)$$

Substituting into equation (4), we have

$$k = \sigma_{1,2} \{8\pi kT(1/m_1 + 1/m_2)\}^{1/2} \cdot e^{-(E_A + 2N_0(\mu_A\mu_B/Dr_0^3))/RT} \dots \dots (7)$$

where N_0 is the Avogadro constant. We have ignored the fact that both the collision frequency and the dielectric constant vary with the temperature; since D varies exponentially with T (Lowry and Jessop, J., 1930, 782; Åkerlöf, *J. Amer. Chem. Soc.*, 1932, 54, 4125), the correction can be conveniently included. It has been omitted, partly because it is relatively small, but chiefly so as not to cloud the issue. After making as impartial a survey of the data as is possible, we conclude that, in a general way, equation (7) summarises satisfactorily the salient points revealed by the slow reactions of the Menschutkin type; *e.g.*, it explains the comparative rapidity of these reactions in solvents of high dielectric capacity, where $2\mu_A\mu_B/Dr_0^3$ is small, and the velocity approaches what has been termed the normal value, *i.e.*, that given by equation (4). It also explains the observation (Grimm, Ruf, and Wolf, *Z. physikal. Chem.*, 1931, B, 13, 301) that, in solvents of similar dielectric constant (*e.g.*, the phenyl halides), the velocity increases with a decrease in the dipole moment of the solvent molecules.

The application of equation (7) to Cox's data (J., 1921, 119, 142) on the aniline-bromoacetophenone reaction is illustrated in Table II. It will be observed, first, that the magnitude

TABLE II.

The Reaction between Aniline and Bromoacetophenone in Various Solvents.

Solvent.	E_2 .	E_A .	$(E_2 - E_A)$.	D .	$\mu_s \times 10^{18}$.
C_6H_6	24,590	8,090	16,500	2.28	0.2 (C-H)
$CHCl_3$	23,970	10,760	13,210	5.05	0.95
$COMe_2$	22,210	11,080	11,130	<i>ca.</i> 20	2.75
$CH_3 \cdot OH$	21,420	12,440	8,980	33.7	1.60
$C_2H_5 \cdot OH$	21,440	13,910	7,530	26.8	1.60
$C_6H_5 \cdot CH_2 \cdot OH$	21,810	14,290	7,520	15.9	—
$C_6H_5 \cdot NO_2$	22,500	13,470	9,030	36.1	1.9 (?)

of $(E_2 - E_A)$ lies near that of the non-kinetic quantity Q , of Table I. A more significant observation is that the expected parallelism between $(E_2 - E_A)$ and $2\mu_A\mu_B/Dr_0^3$ is maintained in solvents of low dielectric capacity (those placed above the line) and breaks down for the hydroxylic solvents and nitrobenzene. The explanation we offer is that the dipole-dipole interaction between reactant and solvent is now so great as to cause actual ionisation, *e.g.*, $C_6H_5 \cdot NH_2 + CH_3 \cdot OH \rightleftharpoons C_6H_5 \cdot NH_3^+ + OH^-$ (cf. $NH_3 + HOH \rightleftharpoons NH_4^+ + OH^-$). In fact, the velocity of reaction in alcoholic solution approaches the value to be anticipated if one of the reactants were completely ionised, and is consistent with the idea of partial, or incipient, ionisation as described here. If the present explanation is correct, the reactions between halides and nitrogen bases are intermediate in character between reactions which are wholly non-polar and those where one of the participants is unambiguously ionic. Accepting Cox's data, and applying the admittedly approximate method of calculation described here, we obtain the following values for the critical separation of the dipoles in the intermediate complex: 0.73 Å. in benzene, 2.26 Å. in chloroform, and 3.33 Å. in nitrobenzene. The agreement is sufficiently close to enable us to conclude that these reactions, which have been usually referred to as "slow," have normal velocities, provided the correct energy of activation is used in the calculation.

New and more accurate experimental material for testing equation (7) has been provided

by Winkler and Hinshelwood (J., 1935, 1147) on the union of amines and halides in benzene solution. Of the numerous predictions of the theory, three examples of which are illustrated in Table III, only two are not in agreement with experiment. Change of the iodine atom

TABLE III.

Reaction.	E_A .	$(E_2 - E_A)$.	$\mu \times 10^{18}$.	Reaction.	E_A .	$(E_2 - E_A)$.	$\mu \times 10^{18}$.
NMe ₃ + MeI	8,790	11,490	1.6 (MeI)	NMe ₃ + MeI	8,790	11,490	0.82 (NMe ₃)
NMe ₃ + EtI	11,400	11,520	1.7 (EtI)	NEt ₃ + MeI	9,300	12,700	0.90 (NEt ₃)
NMe ₃ + Pr ⁿ I	11,200	13,140	1.85 (Pr ⁿ I)	C ₅ H ₅ N + Pr ⁿ Br	15,900	12,150	1.97 (Pr ⁿ Br)
				C ₅ H ₅ N + Pr ⁿ I	16,100	10,770	1.85 (Pr ⁿ I)

from the α - to the β -position should cause $(E_2 - E_A)$ to increase about 7%, whereas experiment shows it to decrease by this amount. Secondly, our elementary calculations have not succeeded in explaining the difference observed on passing from an aliphatic amine to an aromatic one. The intermolecular complex in the latter case possibly requires some other geometric arrangement, or a simple 1 : 1 complex is not formed.

Similar considerations apply to the apparently unimolecular decomposition of carboxylic acids in various solvents. The difference between the critical increment for the decarboxylation of camphorcarboxylic acid in water and in aniline is 8,700 cal. (*op. cit.*, p. 156). Accepting the value in water as the standard value, because it is nearly equal to that in the fused state, we may ascribe the catalytic effect of aniline to the exothermic formation of a molecular complex, prior to decomposition. Taking $\mu_1 = 1.5$, $\mu_2 = 2.5$, and $D_{N-H,Ph} = 7.25$, we find, from $\Delta E = 2\mu_1\mu_2/Dr_0^3$, that $r_0 = 1.20 \text{ \AA}$.

It is to be noted that the occurrence, rather than the velocity, of dipole-dipole interaction is the significant fact in the study of the kinetics of the formation of quaternary ammonium salts.

Reactions involving the Interaction of a Dipole and an Induced Dipole.—The term non-polar solvent is apt to be misleading, because the very existence of the liquid state implies a certain polarity; *e.g.*, carbon tetrachloride is only effectively non-polar, owing to the fact that its four live dipoles are equal and symmetrically oriented. In the presence of foreign molecules, the symmetry may be disturbed and the molecule as a whole become slightly polar. The effect is due to the superposition on the permanent dipole of an additional dipole induced by the presence of neighbouring molecules or ions. The polar inducibility of bonds in compounds which are normally non-polar is a subject of some importance in general chemistry. We propose to gather here some of the unco-ordinated facts.

The dipole moment of certain substances is greater in non-polar solvents such as heptane than in the vapour phase, indicating an influence due to the alleged non-polar solvent (Jenkins, *Trans. Faraday Soc.*, 1934, **30**, 739; Smythe and McAlpine, *J. Chem. Physics*, 1935, **3**, 320). The polarisability of bonds such as C-Cl in carbon tetrachloride and of C-H in hydrocarbons probably accounts for the fact that the union of amines and halides in these solvents is quite different from what it is in the "vapour" phase. One of the reactants has clearly induced a dipole in the solvent molecules. In their behaviour towards reactions of the Menshutkin type, solvents such as carbon tetrachloride, hexane and benzene are certainly not inert. On the other hand, solutes such as chlorine monoxide in carbon tetrachloride exhibit no such effect, and the velocity and mechanism of decomposition in the gas phase and in solution are the same.

The following interesting facts have been pointed out by Sidgwick ("The Covalent Link in Chemistry," Cornell University Press, 1933, p. 135) :

Iodine in hexane is non-polar; in benzene, $\mu = 1$.

Aluminium bromide in hexane is non-polar; in benzene, $\mu = 4.89$.

The first observation can be correlated with the solubility of iodine in various solvents: in carbon tetrachloride, it is sparingly soluble; in chloroform at room temperature it is about twice as soluble (Briner, *Z. physikal. Chem.*, 1898, **26**, 147); in methylene iodide it is very soluble, and in methane abundantly soluble. The solubility of iodine is thus

closely linked with the presence of the C-H bond in the solvent molecule and with the high polarisability of the iodine molecule. The conclusion is of interest in connection with Hinshelwood's suggestion that the catalytic action of iodine molecules in the gaseous decomposition of ethers and aldehydes (which, of course, contain C-H bonds) may be connected with the high polarisability of the catalyst. The other halogens have not such a marked catalytic effect.

The variability of the dipole of aluminium bromide is suggestive in view of the fact that this compound typifies the most effective catalyst for reactions of the Friedel-Crafts category, *e.g.*, $R \cdot COCl + C_6H_6 \longrightarrow R \cdot CO \cdot C_6H_5 + HCl$. Reactions of this type are also catalysed, in order of diminishing efficacy, by aluminium, antimonous, and arsenious chlorides. The compounds $C_6H_6 \cdot 2SbCl_3$ and $C_6H_6 \cdot 2SbBr_3$ have been isolated, and their existence is in all probability due to the interaction between the permanent dipole of the inorganic molecule and the dipole which it induces in the organic molecule. In the case of aluminium bromide in benzene solution (above), the magnitude of the dipole is so great that if it were, so to speak, concentrated in one bond, it would render ionisation in benzene solution fairly facile. In solution in nitrobenzene, which possesses greater dielectric capacity, we are therefore entitled to expect substances like aluminium bromide to exist largely in the ionic form. The absolute velocity of the reaction $Cl_2 + C_6H_5 \cdot NO_2 \longrightarrow HCl + m\text{-}C_6H_4Cl \cdot NO_2$ (Goldschmidt and Larson, *Z. physikal. Chem.*, 1904, **48**, 424) catalysed by ferric, stannic, or aluminium chloride in nitrobenzene solution can be shown to be, in fact, consistent with values calculated on the basis of a termolecular mechanism involving an ion.

In a table containing much data, Hildebrand ("Solubility," Chemical Catalog Company, New York, 1924, p. 63) shows that the greatest deviation from Raoult's law occurs in the case of the mutual solubility of stannic chloride and benzene. Neither of these substances shows a resultant dipole moment alone, but in the presence of one another mutually induced dipoles determine the property to a large extent.

The existence of crystalline hydrates of methane and of the rare gases argon, krypton, and xenon (Sidgwick, "The Electronic Theory of Valency," Oxford, 1927) must be attributed to the interaction of the dipole of the water molecule and the dipole which it induces in the normally non-polar molecule or atom. The magnitude of the induced dipole depends on the polarisability of the atom in question; hence it is easy to understand why hydrates of helium and neon (which have low polarisabilities) are not known.

Reactions between an Ion and a Dipole.—The energy of attraction between an ion of charge ze and a permanent dipole μ situated at a distance r from it is

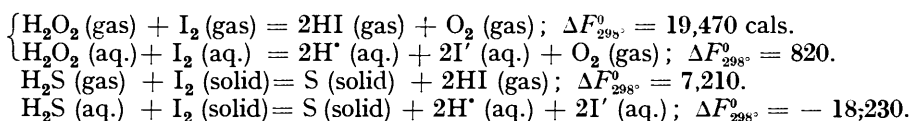
$$\epsilon = ze\mu / Dr^2 \quad \dots \dots \dots (8)$$

With r in Å., and μ in Debye units, $\epsilon = 70 \cdot 3ze\mu / Dr^2$ kg.-cals./mol.

when the ion lies on the projected axis of the dipole. The most important class of compounds which owe their existence to such interactions are solvated ions.

All ions in aqueous solution exist in the hydrated form (ion, nH_2O). The electrostatic attraction is due to the ionic charge and to the permanent dipole of the water molecules, and, as will be shown, is usually fairly large. The phenomenon of solvation is not, of course, confined to water, but is a general property of all solvents the molecules of which possess permanent dipoles (non-polar solvent molecules are discussed below). The hydration of ions in solution has been investigated by a variety of methods, depending on the determination of properties such as the density, viscosity, freezing point, electrical conductivity, electrical transport, and the influence of neutral salts on solubility. In no case, however, can one decide quantitatively about the number of water molecules which are combined with a particular ion. The term n is, in fact, a statistical number. Furthermore, as equation (8) implies, each ion is attracted by all the solvent molecules in the system, to an extent depending on the separation. Some quantitative idea of the magnitude of the energy of hydration may be obtained by ascribing the electrostatic effect solely to those solvent molecules which are adjacent to the ion, and gauging their number from our knowledge of crystal structure; *e.g.*, the lattice energy of the sodium bromide crystal is 170,000 cal./

g.-mol. (J. Sherman, *loc. cit.*). The heat of dissolution of this salt at infinite dilution is practically zero, the exact value being 100 cal. (Fajans and Schwartz, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 717), hence the sum of the heats of hydration of the bromide and sodium ions must be about 170,000 cal. If we assume that this quantity is equally shared between the two ions, and further, that a shell consists of six water molecules, we have a value of about 14,000 cal. for the energy of interaction of the ion and a single dipole. In many cases, the process of dissolution is exothermic (*e.g.*, 11,700 cal. for lithium bromide and 14,800 cal. for lithium iodide in water), but it is always small compared with the lattice energy. From a consideration of similar magnitudes, Guggenheim ("Chemistry at the Centenary Meeting of the British Association," 1931, p. 58) has concluded that all monatomic ions in water are thoroughly hydrated. Because of these large heats of hydration, many reactions are rendered possible in solution, which could not occur in the gas phase. The importance of this conclusion has been demonstrated by Ogg and Polanyi (*Trans. Faraday Soc.*, 1935, **31**, 511). The profound change in the equilibrium position of certain reactions, due to the presence of a solvent, is further illustrated by the following examples :



Ions are hydrated, not only in solution, but in crystal hydrates such as $\text{BaCl}_2 \cdot \text{H}_2\text{O}$; $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$, etc. In these cases, also, it is reasonable to ascribe the dominant rôle to the interaction between ions and dipoles. Table IV gives the magnitudes of the heats of hydration (cal./g.-mol.) of a few ionic crystals. Analogous compounds are $\text{AgCl} \cdot 3\text{NH}_3$; $\text{CaCl}_2 \cdot 6\text{NH}_3$, etc.; and instances of compounds containing chloroform of solvation have already been cited.

TABLE IV.

Hydrate	KF, 2H ₂ O	NaBr, 2H ₂ O	NaI, 2H ₂ O	LiBr, 2H ₂ O	BaCl ₂ · 2H ₂ O
Heat of hydration	4,600	4,520	5,230	10,050	7,000
Hydrate	BaCl ₂ · H ₂ O	SrCl ₂ · 2H ₂ O	SrCl ₂ · H ₂ O	MgSO ₄ · H ₂ O	
Heat of hydration	3,170	9,060	5,260	6,980	

Reactions between an Ion and an Induced Dipole.—The moments of dipoles induced by ions are usually less than those of the permanent dipoles. Where a permanent dipole exists in the absence of an ion, the two interactions are superimposable, but an ion-induced dipole interaction may exist without a permanent dipole being present. In order to induce a moment μ , an energy $\mu^2/2\alpha$ must be expended, where α is the polarisability. The energy of combination of an ion of charge e and a dipole μ is given (see above) by $\epsilon = e\mu/r^2$. Hence the total energy gained by the process of polarisation and attraction of the ion and the induced dipole (in a vacuum) is

$$\frac{e\mu}{r^2} - \frac{\mu^2}{2\alpha} = \frac{\alpha e^2}{r^4} - \frac{\alpha^2 e^2}{2\alpha r^4} = \frac{\alpha e^2}{2r^4} = 164.9/r^4 \text{ kg.-cals./mol.} \quad (9)$$

for $\alpha = 1$ (r in Å.).

The Relation between the Electrostatic Attraction of Ion and Dipole and the Attraction designated as a Co-ordinate Link.—It is the object of this section to show that there is no incompatibility between the ideas of an ion-dipole bond and of the co-ordinate linkage. Let us consider the formation of the ammonium ion from a proton and a molecule of ammonia, $\text{H}^+ + \text{NH}_3 \longrightarrow [\text{NH}_4]^+$. According to the principle outlined here, the newly-formed bond exists in virtue of the compensating effect of a repulsive force (which is dominant at small separations) and an electrostatic attractive force (dominant at great separations). The ammonium ion, however, is symmetrical; all the bonds in it are equal, and they must be covalent bonds, hence the ion-dipole bond must be a precursor of a covalent bond when the latter is formed in the presence of an ion. According to the conventional theory of valency, the formation of the ammonium ion is due to the sharing of the two lone

electrons in the ammonia molecule between this molecule and the proton. Sidgwick, to whom the term co-ordination is due, has been careful to apply it to the process of formation and has, rightly, not insisted that the bond, once formed, is in any way different from a covalent bond formed when two atoms unite. The terms "electron donation" and "ion-dipole attraction" are thus not mutually exclusive, but are alternative attempts to describe the same phenomenon. The present approach is more helpful in some respects. For example, it enables us to understand why the complex $[\text{Cu}(\text{NH}_3)_4]^{++}$ exists, and why there is no such complex as $[\text{Cu}(\text{He})_4]^{++}$. On the other hand, the present view would never have led us to Sidgwick's covalency rule.

From the quantum-mechanical aspect, the state of system $[\text{Cu}(\text{NH}_3)_4]^{++}$ can be represented by a wave function ψ . Supposing that it is possible for the system to exist in two states which have very nearly the same energies, the wave function of the system may be expressed approximately as a linear combination of the functions ψ_a and ψ_b , thus $\psi = a\psi_a + b\psi_b$. If ψ_a denotes the ion-dipole state, and ψ_b the co-ordinate state, the two states can clearly co-exist, or the system may be entirely of one kind (*e.g.*, $a = 1$, $b = 0$) or the other ($a = 0$, $b = 1$).

Conclusion.—It has been our object to emphasise the importance of considering the variety of electrostatic attractions in dealing with systems in the condensed phase. The scheme of classification of chemical equilibria which such considerations make possible includes the difficult problems of solubility, solvation and the kinetics of reactions in solution. Each of these will ultimately require careful quantitative treatment, and we have therefore here confined ourselves to a purely descriptive outline of the principles involved. At least one of the numerous problems raised here has already been the subject of quantitative examination, *viz.*, the kinetics of ion-dipole reactions, investigated by Ogg and Polanyi (*loc. cit.*). The success which has attended their work is encouraging, and indicates the necessity of similar treatments for the numerous problems which, according to the present scheme, are outstanding. One or two of these we hope to deal with in a forthcoming publication.

Scant attention has here been paid to reactions involving only the making or breaking of covalent bonds (in the absence of ions) because, as previously stated, we believe them to reveal no features peculiar to solutions.

SUMMARY.

If the kinetics of reaction are different in the gas phase and in solution, the solvent is responsible for the disturbance, which, in general, is electrostatic in nature.

Electrostatic attractions are of six kinds, depending on the interactions of ions, permanent dipoles, and induced dipoles, taken in pairs. The balancing of these six attractive forces by the repulsive force which characterises all interatomic systems at low separations gives rise to six types of bond, which are, however, not strictly different, though it is convenient to regard them as such. The various types of bond are severally discussed in relation to the influence of complexes on the kinetics of reactions in solution. In dealing with ionic reactions, it is pointed out that the Debye-Hückel expression refers to purely interionic attractions, whereas the so-called ionic reactions, in the kinetic study of which the expression has been so extensively applied, usually involves the interaction between an ion and a dipole as well. The interaction between two molecules, both of which possess permanent dipoles, is held responsible for the formation of several intermolecular complexes, and for the apparently slow velocity of certain bimolecular reactions in solution. The catalytic effect of substances such as aluminium chloride towards the Friedel-Crafts reaction, the existence of hydrates of methane and the rare gases, and certain solubility effects can be traced to the interaction of a permanent dipole with an induced dipole. The solvation of ions and the formation of crystalline hydrates imply an ion-permanent dipole interaction, the relation of which to the co-ordinate link is discussed.