STATISTICAL MECHANICS AND REACTION RATES IN LIQUID SOLUTIONS[1]

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A discussion of the relation of statistical mechanics to the problems of the kinetics of reactions in liquid solutions seems very timely. By bringing together what has been accomplished and by showing as clearly as possible which conclusions come from the theory and which from extraneous assumptions, the author hopes to smooth somewhat the way for further advances. In his opinion the three great advances in the theory of reaction rates in liquid solutions have been the classical law of mass action, the theory of the temperature coefficients of reaction rates, and the theory of Brönsted (1). The first two are discussed in every textbook of physical chemistry and are so familiar that no references need be given. For theoretical purposes the first may be considered as a special case of the third, and the second should be considered as a problem in gaseous reactions. So we shall be concerned largely with the relation of statistical mechanics to Brönsted's theory.

Before applying statistical mechanics we must picture the conditions necessary for a chemical reaction. We may say that molecules react if they approach within a certain distance, with a certain relative orientation, and with a certain amount of energy distributed in a certain way (or with a definite deformation of the molecules). Each of these conditions should be considered as extending over a small range of the corresponding coördinates. It is possible that the molecules must remain in this state during

a very short but finite time necessary for reaction. There is also a possibility that there are two or more states, quite different in some respects, which lead to the same reaction. These conditions seem general enough to cover all cases. If the approach of the molecules follows the reception of energy and the deformation and orientation, there is a "reaction on collision"; if the approach precedes any of the other steps, there is a "preliminary complex formation." Much has been written (2, 3) on the question whether this reacting state or complex is to be regarded as a "physical constellation" or as a "chemical compound." The distinction seems to the author to be quite unimportant and dependent entirely upon the language with which we define a chemical compound. It seems equally unimportant whether the rate be calculated from the concentration of reacting complexes (2) or from the number of collisions with the necessary orientation and energy multiplied by a factor for the duration of a collision (4).

We know that for reactions slow enough to give measurable rates the reacting state is a very improbable one. We must assume that it differs only slightly from other states whose total probability is very much greater than that of the reacting complex and which are in statistical equilibrium. We may then treat the reacting complex as though it also were in equilibrium. This is the one general assumption which might be questioned.

THE THEORY OF BRÖNSTED

The above picture of a reacting complex seems to the author identical with the "critical complex" of Brönsted (1), and we may derive his theory directly from this picture and the postulate that statistical equilibrium and thermodynamic equilibrium are the same. The theory states that the rate of reaction at constant temperature is proportional to the product of the activities of the reactants divided by the activity coefficient of the critical complex. We will take as example the simple reaction

$$A + B \rightarrow (X) \rightarrow D + E$$
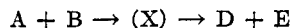
$$-\frac{dC_A}{dt} = K'C_X = KC_A C_B \frac{f_A f_B}{f_X} \tag{1}$$

where C means concentration, f activity coefficient, and the subscripts refer to the substances in the reaction above. If there be more than one reacting complex which leads to the same reaction, they may all be grouped as a single critical complex. This might complicate the calculation of f_X, but it should give no other difficulty.

Brönsted (1b) further concludes that the constant K may be divided into two factors, thus,

$$K = K_r K_m$$

the first of which depends only on the reaction and the second only on the medium. It seems to the author impossible that there should be any constant which is the same for all reactions which is not also the same for all media. As illustration let us consider a catalyzed reaction. It is only a matter of convenience, although one of enormous convenience, that we consider the catalyst as one of the reactants. Equation 1 must be equally true if the catalyst is not included, provided that the activity coefficient f_X is properly expressed. One might, of course, prefer to express the catalytic effect in K_m. However, we know that catalytic effects, although the same for a reversible reaction in both directions, are not the same for all reactions. Therefore, it seems much more logical to consider K a function only of the reaction and the temperature, and to ascribe all changes with changing medium to f_X. This is always possible if X is sufficiently specified. From the fact that our definition of activity coefficient demands a different standard state for each temperature, the greatest part of the temperature variation must be ascribed to K. This is an advantage and, for theoretical discussions, the standard state should be chosen as that of an infinitely dilute gas. Thus we may consider temperature coefficients as outside the scope of the theory of liquid solutions.

APPLICATION OF STATISTICAL MECHANICS

We have seen that Brönsted's theory follows from our assumptions without any use of statistical mechanics other than the general postulate that statistical equilibrium implies thermody-

namic equilibrium. A derivation of Brönsted's equation from statistical mechanics, such as that of Bjerrum (2), seems quite unnecessary. There is, however, a great opportunity for the application of statistical mechanics to our problem. Thermodynamics tells us nothing of the value of f_X; the activity coefficient of a complex that disappears immediately it is formed can certainly never be measured. There remain as methods of determining it only empirical generalization and statistical mechanics. So far the application has been limited to those cases in which the ratio of the number of critical complexes to the total number of complexes with the same distance of approach may be regarded as independent of the medium, that is, where the orientation, the quantity of energy, and the distribution of it within the complex are independent of the medium. The application has been further limited to those cases in which the concentration of complexes with a given distance of approach may be calculated from the theories of Debye.

Reactions between ions

Brönsted himself computed the effect of dilute electrolytes on a large number of reactions with the assumption, first reached by empirical generalization and then from the Debye-Hückel theory (5), that the activity coefficient in dilute electrolyte solutions depends only on the valence type. The theoretical expression for very dilute solutions is

$$\ln \frac{f_A f_B}{f_X} = \frac{-\epsilon^2}{2 DkT} [z_A^2 + z_B^2 - (z_A + z_B)^2] \kappa = \frac{\epsilon^2 z_A z_B}{DkT} \kappa \qquad (2)$$

where z is the valence, ϵ the protonic charge, D the dielectric constant, k Boltzmann's constant, T the absolute temperature, and κ has its usual significance in the Debye theories. We see immediately that the addition of an electrolyte increases the rate of reaction if the reactants have valences of the same sign, decreases the rate if they have opposite signs, and has no effect proportional to the square root of the concentration if either reactant has the valence zero. It may be noted that Brönsted's conclusion that the activity coefficient of the critical complex depends only

on its valence in very dilute solutions is at variance with the conclusion of Bjerrum (2, 6) that the activity coefficient of a "Zwitterion" or of a polyvalent ion approaches the product of the activity coefficients of the ions of which it is composed as the distance of separation increases. Detailed calculations by Kirkwood and Scatchard (7), however, agree with Brönsted that the term proportional to the square root of the concentration depends only on the valence, provided that the distance of separation is finite and the same as in the standard state.

For our present purposes we may follow the much simpler procedure of Christiansen (4) and calculate the concentration of the complex directly from equations given by Debye and Hückel (5). This concentration is proportional to the bulk concentration of A molecules multiplied by the average concentration of B molecules at a distance r from an A molecule, where r is the distance of approach characteristic of the complex. According to Debye and Hückel this is

$$C_X = K'' C_A C_B \, e^{-\frac{\psi_r \, \epsilon \, z_B}{kT}} = K'' C_A C_B \, e^{-\frac{\epsilon^2 z_A z_B}{DkT} \frac{e^{-\kappa r}}{r} \frac{e^{\kappa a}}{1 + \kappa a}} \tag{3}$$

where ψ_r is the mean electrostatic potential at the distance r from an A ion, and a is the closest distance of approach of the other ions to an A ion. When $\kappa = 0$, equation 3 reduces to

$$C_X^0 = K'' C_A^0 C_B^0 \, e^{-\frac{\epsilon^2 z_A z_B}{DkTr}} \tag{4}$$

From this it follows that

$$\ln \frac{f_A f_B}{f_X} = \ln \frac{C_X}{C_A C_B} - \ln \frac{C_X^0}{C_A^0 C_B^0} = \frac{\epsilon^2 z_A z_B}{DkTr} \left[1 - \frac{e^{-\kappa r} e^{\kappa a}}{1 + \kappa a} \right] \tag{5}$$

To compare with Brönsted's result we expand in series

$$\ln \frac{f_A f_B}{f_X} = \frac{\epsilon^2 z_A z_B}{DkT} \left[\frac{\kappa - \frac{\kappa^2}{2!} \frac{(r-a)^2}{r} + \frac{\kappa^3}{3!} \frac{(r-a)^3}{r} - \cdots}{1 + \kappa a} \right] \tag{6}$$

$$\cong \frac{\epsilon^2 z_A z_B}{DkT} \kappa \tag{7}$$

Christiansen, who also obtains equation 7 as the limiting law, omits the factor $\dfrac{e^{\kappa a}}{1 + \kappa a}$ from equation 3. It is hard to justify the neglect of κa when κr is considered, for the distance to which two ions must approach in order to react must be of the same order of magnitude as, and is probably not many per cent different from, the closest distance of approach of the ions. We should consider here the criticism of Gross (8), namely, that this method must be wrong in principle because if the sizes of the two ions are not the same the answer for more concentrated solutions depends upon which ion is chosen as the central one. This would be obvious from equations 5 or 6 if a were different for the two ions. However, when *all* the ions in the solution do not have the same size there is, strictly speaking, no a for any ion (9), and the proper value must be in doubt by at least the difference between these two answers. Gross also criticizes this whole method of approach for a reaction between two ions, and claims that the averaging for the calculation of reaction rates must be different from that for activity coefficients. His criticism of the application of the Debye-Hückel theory to reaction rates may well be compared to Fowler's (10) criticism of its application to activity coefficients with which Gross appears to disagree absolutely. Considering concentrations rather than potentials, it seems obvious that the rate of reaction depends upon the same average concentration of B ions around an A ion as does the activity coefficient. How accurately this average is given by the Debye-Hückel theory is a question into which we need not enter here.

It is very probable that the forces of repulsion vary so rapidly with the distance that the ions may be regarded as perfectly rigid spheres which must touch in order to react, so that r may be taken equal to a. In this case equation 5 reduces to

$$\ln \frac{f_A f_B}{f_X} = \frac{\epsilon^2 z_A z_B}{DkT} \frac{\kappa}{1 + \kappa a} \tag{8}$$

which is the form that the author (11) used for less dilute solutions, deriving it through the assumption that the complex might also

be regarded as a spherical ion with the characteristic distance a. The assumption used in the present method is much more probable. It must be understood, of course, that the applicability of the equations is limited to solutions so dilute that other deviations from the laws of ideal solutions may be neglected, including in these other deviations the Gronwall-LaMer correction for small size or large charge (12).

We may consider the theory well established in so far as it concerns the term that is proportional to the square root of the concentration and that depends on no properties of the ions other than their valences. It is probable that any variation of the ratio of the number of critical complexes to that of all the complexes with the same distance of approach would depend upon forces of much shorter range than that between two ionic charges, and that such a variation would therefore not affect this term. It is only for this case of the effect of electrolytes on reactions between ions that the term proportional to the square root of the concentration is other than zero. For the higher terms the difficulties of all kinds increase: the variation of the average concentration at a given distance depends upon specific properties whose effect is more difficult to calculate; it is less certain that any one of these is so important that the others may be neglected; and the chances are greater that factors other than the distance may be effective. Therefore in all the cases that follow the answer is not only less sharp, it is also less certain. Nevertheless the answer is worth seeking.

From equation 4 we may also obtain the effect of changing solvent on a reaction between two ions in so far as that effect is due to changing dielectric constant and in so far as the solvent may be treated as a homogeneous medium of uniform dielectric constant. If the dielectric constant in the state in question is D, and in the standard state D_0,

$$\ln \frac{f_A f_B}{f_X} = \ln \frac{C_X^0}{C_A^0 C_B^0} - \ln \left(\frac{C_X^0}{C_A^0 C_B^0} \right)_0 = \frac{\epsilon^2 z_A z_B}{D k T r} \left(\frac{1}{D_0} - \frac{1}{D} \right) \tag{9}$$

If the two ions have the same sign, an increase in the dielectric constant increases the reaction rate; if they have opposite signs,

the rate decreases with increasing dielectric constant.   If the ions may be regarded as rigid spheres of radius b,

$$r = b_A + b_B$$

and

$$\ln \frac{f_A f_B}{f_X} : \ln f_A : \ln f_B = \frac{z_A z_B}{b_A + b_B} : \frac{z_A^2}{2 b_A} : \frac{z_B^2}{2 b_B} \tag{10}$$

If the two ions have the same size the factor in the expression of the reaction rate is, neglecting its sign, the mean of the activity coefficients of the ions.

Reaction between an ion and a non-electrolyte

For the reaction between an ion and a non-electrolyte we cannot use the theory of Debye and MacAulay (13) which gives a fair approximation of the activity coefficient of the ion or of the non-electrolyte by treating all non-electrolytes as part of a homogeneous medium of uniform dielectric constant.   We may, however, follow Gross (8) and calculate the effect of adding electrolyte from Debye's second treatment of activity coefficients (14), a treatment which is limited to solutions very dilute both in ions and in non-electrolyte reactant.   If we assume that the effect of an A ion disappears at a great distance from the ion, the activity of the non-electrolyte B is equal to its concentration at an infinite distance C_∞, and the activity coefficient is the ratio C_∞ / C_B, where C_B is, as before, the average concentration.   By the Debye theory the concentration of B molecules at a distance r from the ion is given by

$$C_r = C_\infty \, e^{-\frac{R^4}{r^4}} \tag{11}$$

$$R^4 = \frac{\epsilon^2 z_A^2 \beta_B}{8 \pi N k T D_0} = \frac{\epsilon^2 z_A^2 \delta_B}{8 \pi N k T D_0^2}$$

where N is the Avogadro number, and β_B and δ_B are given[2] by

$$D = D_0 (1 - \beta_B C_B) = D_0 - \delta_B C_B \tag{13}$$

[2] This equation differs somewhat from that of Debye, in whose paper C is the mole fraction and not the volume concentration.   The present form is somewhat simpler to apply and extrapolates to $+20$ instead of -275 for the dielectric constant of ether.   Its use makes no difference in the calculation of the salting out.

Since R is independent of the electrolyte concentration we may write

$$C_X = K'C_A C_r = K'C_A C_\infty \, e^{-\frac{R^4}{r^4}} = KC_A C_\infty = KC_A C_B \, f_B \qquad (14)$$

The change in rate of a reaction between an ion and an uncharged molecule caused by the addition of an electrolyte is equal to the change in activity coefficient of the uncharged molecule. Debye's treatment gives an expression for $\ln f_B$ which is a complicated function of the radius of the ion, D_0 and δ, but which is proportional to the salt concentration and is positive if the non-electrolyte decreases the dielectric constant, negative if it increases it. This calculation of the effect on the reaction rate is probably only a first approximation even for that part of the effect which it pretends to represent. The assumption that the field strength around an ion, and therefore R, is independent of the electrolyte concentration is equivalent to the assumption that the activity coefficient of the complex is equal to that of the simple ion.

We may also use this result of Debye to calculate the effect of changing solvent on the rate of a reaction between an ion and a neutral molecule when both the reactants are at very small concentrations. In this case the concentration of B at an infinite distance from an A ion may be taken as equal to the average concentration, $C_\infty = C_B$, but R is not independent of the medium. From the first two equalities in equation 14 we obtain

$$\ln \frac{f_A \, f_B}{f_X} = \ln \frac{C_X}{C_A C_B} - \ln \frac{C_X^0}{C_A^0 C_B^0} = \frac{1}{r^4} \, (R_0{}^4 - R^4)$$

$$= \frac{\epsilon^2 \, z_A^2}{8\pi NkTr^4} \left(\frac{\delta_0}{D_0{}^2} - \frac{\delta}{D^2} \right) \qquad (15)$$

To use equation 15 we must know δ as a function of D. If the dielectric constants are all additive, that is, if equation 13 holds over the whole range with all the solvents

$$\frac{\delta}{D^2} = \frac{V_B}{D} \left(1 - \frac{D_B}{D} \right) \qquad (16)$$

where V_B is the molal volume of B. When D is less than $2D_B$, increasing the dielectric constant decreases the rate; for larger

values of D the rate increases with increasing dielectric constant. However, if it is the reciprocals of the dielectric constants which are additive,

$$\frac{\delta}{D^2} = -\frac{V_B}{D} \qquad (17)$$

and the rate always decreases with increasing dielectric constant, although less rapidly the larger the dielectric constant. If it is the polarizations which are additive, the relation is more complicated and depends upon the absolute value of D_B as well as upon the ratio D_B/D:

$$\frac{\delta}{D^2} = \frac{V_B}{3 D^2}\left[(D-1)(D+2) - \frac{D_B - 1}{D_B + 2}(D+2)^2\right] \qquad (18)$$

When $D_B = 1$, there is a minimum in the rate for $D = 2D_B$ as in equation 16; but as D_B increases this minimum shifts very rapidly to higher D's and is reached only at $D = \infty$ when $D_B = 2$. For all values of D_B that are probable in liquid solutions the rate always decreases with increasing dielectric constant.

Although the effect of changing dielectric constant on the reaction rate in this case depends so much on the form of the functional relation of dielectric constant to concentration that we cannot generalize about it, the relation of δ to D is measurable in any particular case and equation 15 may then be applied. This equation is limited to the case of uniform dielectric constant and so applies to changes from one pure solvent to another, but not strictly to mixed solvents. From a qualitative study of the more general equations given by Debye (14), we should expect that small amounts of a substance that lowers the dielectric constant would have a smaller effect on the rate than that calculated by equation 15 from its effect on the dielectric constant, because the concentration around the ions would be less than the average concentration. Larger quantities should have more nearly the calculated effect. Similarly, small quantities of a substance that increases the dielectric constant should have a larger effect than calculated. If the difference in dielectric constant is large, the first additions should have a relatively enormous effect and might

practically inhibit the reaction, for most of them would congregate in the immediate neighborhood of the ions.   The effect might in this case depend upon the ratio of the concentration of added molecules to that of the ions rather than upon the concentration of added molecules alone.

Reaction between two uncharged molecules

The effect of electrolytes on reactions between two uncharged molecules, in so far as it depends only on the distance of approach and in so far as the medium may be assumed to have a uniform dielectric constant, should be calculable by the method used by Debye (14) for the salting out effect, integrating over all the solution the product of two concentrations rather than a single concentration.   We can say offhand that the rate of a reaction between two molecules both of which are salted out should be increased, and roughly as the mean of their activity coefficients; if one is salted out and the other salted in, the rate of reaction should decrease; if both are salted in, the effect of the orientation around the ion should be important.   It might enormously increase the increased rate due to the concentration effect, or it might counteract it; the answer is therefore indefinite.   If the solvent is one of the two reactants, the effect of electrolytes should be very small unless the other reactant is very strongly salted in, in which case there should be a retarding action.   In all cases the logarithm of the reaction rate should vary as an approximately linear function of the electrolyte concentration.

The application of statistical mechanics to the effect of adding non-electrolytes on the rate of reaction between two uncharged molecules must await the development of the theory of non-electrolyte solutions.   We may be sure that here the variation of the orientation with changing medium is an important factor and the variation of the deformation may be.   Beyond that we can at present only make a few qualitative predictions in special cases (11).

For reactions more complicated than bimolecular, the author can see no method of approach other than to assume that the probability of a ternary collision is the product of the probabilities

of the three binary collisions involved, and similarly for more complicated reactions. As with our previous assumptions, this one should have its greatest validity for long range forces, that is, for the electrolyte effect on reactions between ions. For the limiting law, or for less dilute solutions with rigid ions all of the same size which must touch to react, this requires only the replacement of $z_A z_B$ in equation 7 or 8 by the sum of all the cross products of the valences, agreeing as it should with Brönsted's method of approach (11).

SUMMARY

The relation of statistical mechanics to the theory of reaction rates in solution, and particularly to Brönsted's theory, has been reviewed, and it has been shown that the function of statistical mechanics is not to establish this theory, but to assist in its application. A discussion has also been given of the application of Debye's theories to various types of reactions.

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