CLVIII.—*Equilibrium in Solutions.   A Note on " The Activity Theory of Reaction Velocity."*

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IN a recent paper (J., 1927, 2761), Soper and Pryde, in discussing the velocity of reaction in solution, have considered the equilibrium in a system containing, for example, hydrogen chloride and its ions $HCl \rightleftharpoons H^{\cdot} + Cl'$, for which process they advance as the criterion of equilibrium

$$- dF_{HCl} + dF_{H^{\cdot}} + dF_{Cl'} + dF_{medium} = 0 . \quad . \quad . \quad (1)$$

where the dF's refer to changes in the partial free energies of the various species.

On the basis of this equation Soper, both in the paper mentioned and elsewhere (*J. Physical Chem.*, 1927, **31**, 1790; 1928, **32**, 67), has discussed in detail the thermodynamic properties of electrolytic solutions. The chief results of this discussion are the derivation of a new activity relationship for ions involved in equilibria with neutral molecules, and the deduction of a modified equation for the velocity of ionic reactions.

So far as the activity relations are concerned, Soper asserts that wherever one is considering the transfer of ions from one concentration to another the activities of these ions are related to their partial free energies; if, however, an equilibrium be considered, the activities are determined by the total free energy of the solution. Applying these conceptions, he has derived, on the basis of the Debye–Hückel theory, the two following equations connecting the activity coefficient with the ionic strength for aqueous solutions at $25°$: $\log f = -0{\cdot}505z^2\sqrt{\mu}$, where the partial free energies are concerned, and $\log f = -0{\cdot}33z^2\sqrt{\mu}$, where the total free energy enters.

In the velocity of ionic reactions, Soper considers the second equation to determine the activity coefficients of the ions and consequently deduces for a bimolecular reaction between ions

$$v = kc_A c_B f_A f_B / f_{AB}$$

where

$$f_A f_B / f_{AB} = 0{\cdot}66 z_A z_B \sqrt{\mu}.$$

This equation is the form to which the general reaction velocity equation of Brønsted reduces for the special case of an ionic reaction. In Brønsted's equation, however, the kinetic activity factor is given by

$$f_A f_B / f_{AB} = 1{\cdot}00 z_A z_B \sqrt{\mu}.$$

It is evident that, if Soper's contentions are valid, he has derived relationships of great significance, and has, in fact, revolutionised the thermodynamic treatment of electrolytic solutions. Consequently, it is of importance to examine his fundamental postulates and to see how far they are in accord with thermodynamics.

In the first place, it must be pointed out that it is not very logical to restrict the application of a thermodynamic equation, such as (1), to ions, and to employ another equation for neutral molecules. Soper attempts to justify this by the argument that the magnitude of the term $dF_{med.}$ is greater for ions than for neutral molecules; but such a difference in magnitude is not a difference in principle such as to justify the employment of two different equilibrium equations. Further, the assignment of two values to a potential

function under the same conditions seems in serious conflict with thermodynamics.

Leaving aside such general considerations, let us take a reaction such as $A + B + \ldots \rightleftharpoons P + Q + \ldots$. The free energy of such a system will, at constant temperature and pressure, be a function of the number of molecules of each species present; hence $dF = (\partial F/\partial n_A)dn_A + (\partial F/\partial n_B)dn_B + \ldots + (\partial F/\partial n_{\text{med.}})dn_{\text{med.}}$, where $n_A, n_B, \ldots n_{\text{med.}}$ refer to A, B, etc., and the medium. Employing G. N. Lewis's notation $\overline{F} = (\partial F/\partial n)$ for the partial molar free energy of any species, we have

$$dF = \overline{F}_A . dn_A + \overline{F}_B . dn_B + \ldots + \overline{F}_{\text{med.}} . dn_{\text{med.}}.$$

Since at equilibrium a small displacement is unattended by a change in the free energy of the system, $dF = 0$, i.e.,

$$0 = \overline{F}_A . dn_A + \overline{F}_B . dn_B + \ldots \overline{F}_{\text{med.}} . dn_{\text{med.}} \qquad (2)$$

On comparing (2) with (1), it is noticeable that (1) contains no terms for the change in the number of molecules, and this omission is the crucial error for the further development of the equilibrium criterion; for when we are considering a reaction in solution, the solvent does not occur on one side only of the reaction scheme, and consequently a small displacement of the equilibrium does not involve any change in the number of solvent molecules; therefore the equilibrium condition is

$$0 = \overline{F}_A . dn_A + \overline{F}_B . dn_B + \ldots + 0 . \overline{F}_{\text{med.}}.$$

Thus, by reproducing the thermodynamic derivation, we are able to see that the classical expression which omits the term for the free energy of the solvent is completely valid even for ionic equilibria.

However, in order to make the matter still clearer and more tangible, we may examine the method employed by Soper in the deduction of his formula for reaction velocity. He states : " The total free electrical energy of a solution of n ions found by charging them reversibly is $\frac{1}{3}nz\varepsilon\psi$, where ψ is the potential at one of these ions due to the surrounding ' ion-atmosphere.' Part of this electrical free energy resides in the medium, but change in the partial free electrical energy of the ions is attended simultaneously by a change in the electrical free energy of the medium. The total potential energy possessed by an ion in virtue of its charge is thus $\frac{1}{3}z\varepsilon\psi$ . . . ."

Soper is fully aware that the term $\frac{1}{3}nz\varepsilon\psi$ is the total electrical free energy of the solution, but he seems to think that the potential energy of an ion within this solution may be obtained by dividing this term by the number of ions. The true value of the potential energy of a single ion is, however, the work obtained by discharging

the ion reversibly ; this is given by $W = \int_0^\epsilon z\psi d\epsilon = \frac{1}{2}z\epsilon\psi$ as shown by Güntelberg. If now we substitute this term wherever Soper uses $\frac{1}{3}z\epsilon\psi$, the spurious factor $2/3$ disappears and the ordinary activity relations, as well as the original form of Brønsted's velocity equation, are obtained. It must therefore be concluded that the various modifications proposed are all alike without foundation in thermodynamics.

So far as the particular question of reaction velocity in solution is concerned, the agreement with experiment obtained by Soper for his expression is a consequence of the operation of the linear terms in the Debye–Hückel equation for activity coefficients, *viz.*, $- \log f = Ac^{\frac{1}{2}} + Bc$. The introduction of these terms will, in the range 0.04—$1.0N$, lower the kinetic activity factor to approximately two-thirds of its limiting value.

In conclusion, it may be stated that the Brønsted formula has proved entirely satisfactory wherever it is applied within the region for which it was originally developed. When it is remembered that the formula is successful in predicting salt effects of the most varied type and magnitude, for which previous theories have been entirely unable to account, it will be realised that the formula represents a very marked step in advance, and may, so far as the region of dilute solutions is concerned, be considered a solution of the problem.

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