CLIX.—*Equilibrium in Electrolyte Solutions and the Reaction-velocity Equation.*

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OBJECTIONS have been raised (Wynne-Jones, preceding paper) to the interpretation of the results obtained for the rate of interaction of hydrochloric acid and a chloroamine (J., 1927, 2761) on two grounds—(*a*) the condition of equilibrium in an electrolytic solution, and (*b*) the nature of the reaction-velocity equation.

The condition of equilibrium in a system containing hydrogen chloride and its ions was given (*loc. cit.*, p. 2766) as

$$- dF_{\mathrm{HCl}} + dF_{\mathrm{H}^{\cdot}} + dF_{\mathrm{Cl}'} + dF_{\mathrm{medium}} = 0$$

where the dF's refer to the changes in the partial free energies of the various species and dF_{medium} has a finite value.* Wynne-

* An erroneous value for dF_{medium} was employed in *J. Physical Chem.*, 1928, **32**, 67, and the conclusions there reached are withdrawn.

Jones asserts that, since the number of solvent molecules is unchanged by the slight displacement,

$$dF_{\text{medium}}\ (i.e.,\ \partial F/\partial n_{\text{medium}}\cdot dn_{\text{medium}}) = 0.$$

The point of view is dependent on one's conception of an ion. It is legitimate to regard the ion as an unhydrated particle and to evaluate its partial free energy on this assumption. It would also be legitimate to evaluate the partial free energy of, say, sodium in water by additions of metallic sodium to an aqueous sodium hydroxide solution, but this partial free energy would not be equal, or even proportional, to that of the sodium hydroxide which is actually present. From the reaction-velocity standpoint, it is obviously desirable to deal as far as possible with the ions actually existing, *i.e.*, with the hydrated complexes. On this view, a slight displacement of the equilibrium HCl $\longrightarrow$ $H^{\cdot} + Cl'$ involves a change in the number of free solvent molecules and in the free energy of the medium, a fact which should be allowed for in the condition for equilibrium. The activity of hydrogen chloride measured electrometrically is therefore only proportional to the activity of the ions if they are unhydrated. It is, however, proportional to the activity of the un-ionised hydrogen chloride, as was stated.

The same conclusions may be reached more directly by writing the ionic equilibrium as follows :

$$\mathrm{HCl} + (x + y)\,\mathrm{H_2O} \rightleftharpoons \mathrm{H}^{\cdot},x\mathrm{H_2O} + \mathrm{Cl}',y\mathrm{H_2O}$$

which necessitates that

$$a_{\mathrm{H}^{\cdot}x\mathrm{H_2O}}\, a_{\mathrm{Cl}'y\mathrm{H_2O}}/a_{\mathrm{HCl}}\, a_{\mathrm{H_2O}}^{x+y} = K$$

i.e., the activities of the ions involve the variable activity of the solvent.

The evaluation of the free energy change of the medium (*J. Physical Chem.*, 1928, **32**, 67) as $nz^2\varepsilon^2\kappa/6D$ is incorrect. It should be amended to $z^2\varepsilon^2\kappa n_1 dn_0/n_0$, where dn_0 is the number of solvent molecules bound by dn_1 ions, and n_1 and n_0 are the number of ions and solvent molecules per c.c. This term cannot at present be evaluated, and, if it is neglected, the free electrical energy of an ion to be used in determining the critical increment of an ionic reaction is $-z^2\varepsilon^2\kappa/2D$ (*J. Physical Chem.*, 1927, **31**, 1790). The reaction-velocity equation for ions then reduces to

$$\log k = C + 1{\cdot}00 z_A z_B \sqrt{\mu}$$

which is the form used by Brønsted (Brønsted and Livingston, *J. Amer. Chem. Soc.*, 1927, **49**, 435).

It may be noted, however, that the assumptions underlying the derivation of this equation in the two cases are different. That derived by the author assumes that the energy of activation is sensibly constant in aqueous solution and is made up of energy given by a Maxwell distribution and of potential energy possessed by the reacting ions due to their charges. In the Brønsted equation the activity coefficient of the critical complex, f_x (which is also a measure of the critical increment; Brønsted, *Z. physikal. Chem.*, 1925, **115**, 343), is assumed to vary with the ionic strength as would any other ion of the same valency. A differentiation between the equations would appear to be possible here. Secondly, the similarity in the form of the equations depends on the reagents being electrically charged.

The rate of interaction of hydrogen chloride and a chloroamine was found to be directly proportional to the activities of the reagents measured in the presence of each other. There was no appearance of deviation indicating the necessity of an f_x term for neutral molecules, although the electrolyte concentration was varied from 0·1 to 1·5 M.

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