



## XLVI. The application of the law of mass action to strong electrolytes, and the derivation of the general equation of the ionization isotherm

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XLVI. *The Application of the Law of Mass Action to Strong Electrolytes, and the derivation of the general equation of the ionization isotherm.* By WILLIAM HUGHES, B.Sc. (Oxon), M.A.\*

IF interionic forces operative in electrolytic solutions be inverse  $n_1$ th, and those causing re-formation of molecules inverse  $n_2$ th functions of the mean distance apart of the ions, then, as the author has shown (Phil. Mag. [6] xlii. p. 134),

$$(1-\alpha)^2 \bar{V} = K \sqrt{\frac{r_1^{n_1-1}}{r_2^{n_2-1}}} = K r^{\frac{n_1-n_2}{2}}, \quad \dots (1)$$

where  $\bar{V}$  is the total volume of the solution.  $r_1$  and  $r_2$  denote the same distance; therefore the assumption that the electrolyte is completely dissociated, made *loc. cit.*, is obviously unnecessary.  $\alpha$  is the fraction of the ions which are in the act of forming molecules, and if  $\bar{V}$  is the volume containing one equivalent of the electrolyte, then  $\alpha \nless 1$ .

The object of the present paper is to derive, on the above assumption of the nature of chemical force, a general relation between  $\bar{V}$  and  $\alpha$ , of which the equations of Ostwald, Rudolphi, van't Hoff, and also Partington are special cases.

Let a volume  $\delta V_1$  of solution contain one molecule of a binary electrolyte;

$\therefore N\delta V_1 = V_1$ , where  $N$  is Avogadro's Number.

$\alpha$  may be regarded either as the fraction of molecules ionized, or as what is equivalent, given by the relation

$$\frac{r_{V_1}}{r_{V_2}} = \frac{\alpha_1}{\alpha_2},$$

where every molecule is regarded as dissociated to an equal extent—i. e.,  $r$  is the same for each molecule. It follows that  $r \propto \alpha$ .

Conductivity experiments show that the ions are practically never too far apart to exert some attraction on each other until infinite dilution is reached; therefore the last relation holds at all dilutions.

Now if the ions are separated from each other to the

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maximum distance compatible with the volume of the liquid, then

$$r \propto (\delta V)^{\frac{1}{2}} \propto V^{\frac{1}{2}},$$

since  $N\delta V = V$ . This is what is meant by the term complete ionization. If they are not, then

$$\left. \begin{aligned} r &= f(V^{\frac{1}{2}}) \\ \alpha &\propto f(V^{\frac{1}{2}}) \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

Now

$$\frac{\alpha^2}{(1-\alpha)V} = K' \{f(V^{\frac{1}{2}})\}^{\frac{n_1-n_2}{2}} \text{ from (1) and (2),}$$

or

$$\frac{\alpha^2}{(1-\alpha)V\{f(V^{\frac{1}{2}})\}^{\frac{n_1-n_2}{2}}} = K'. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

This is the required general equation of the ionization isotherm.

When  $f=1$  we have complete ionization, and when  $f=\text{constant} \times$ , we have ionization proportional to  $V^{\frac{1}{2}}$ . Make  $f=\text{constant} \times$ ,  $n_1=2$  and  $n_2=5$ , then (3) becomes

$$\frac{\alpha^2}{(1-\alpha)V^{\frac{1}{2}}} = \text{const.} \quad (\text{Rudolphi.})$$

Similarly, but making  $n_2=4$ , we get

$$\begin{aligned} \frac{\alpha^2}{(1-\alpha)V^{\frac{2}{3}}} &= \frac{\alpha^{\frac{2}{3}}}{(1-\alpha)V^{\frac{1}{3}}} \times \frac{\alpha^{\frac{1}{3}}}{V^{\frac{1}{3}}} \\ &= \frac{\alpha^{\frac{2}{3}}}{(1-\alpha)V^{\frac{2}{3}}} = \text{const., from (2).} \quad (\text{van't Hoff.}) \end{aligned}$$

Similarly, but making  $n_1=n_2$ , we get

$$\frac{\alpha^2}{(1-\alpha)V} = \text{const.} \quad (\text{Ostwald.})$$

If  $\alpha$  be plotted against  $V$  in either the Rudolphi or the van't Hoff equations, it is found that  $\alpha=1$  is an asymptote, and for dilutions about  $V \int_2^\infty \alpha$  is approximately a linear function of  $V$ , the more accurately the greater  $V$ .

That is

$$r \propto \alpha \propto V + \frac{b}{m}.$$

For  $V \int_2^\infty$ ,  $b \int_{ca. 0.75}^1$ :  $\frac{b}{m}$  is a very big quantity.

Hence  $\frac{\alpha^2}{(1-\alpha)V} = \text{const.} \times \left(V + \frac{b}{m}\right)^{\frac{n_1-n_2}{2}}$  from (1) :

$$\therefore \frac{\alpha^2}{(1-\alpha)V\left(V + \frac{b}{m}\right)^{\frac{n_1-n_2}{2}}} = \text{const.} ;$$

$$\therefore \frac{\alpha^2}{(1-\alpha)V^{1+\frac{n_1-n_2}{2}}\left(1 + \frac{c}{V}\right)^{\frac{n_1-n_2}{2}}} = \text{const.} ; \quad \dots (4)$$

writing  $c$  for  $\frac{b}{m}$ .

Partington's equation,

$$\frac{\alpha^2}{(1-\alpha)(V + \rho\alpha)} = \text{const.},$$

may be written

$$\frac{\alpha^2}{(1-\alpha)V(1 + \rho\alpha/V)} = \text{const.}$$

Now putting  $n_1 = n_2$  in (4), we get

$$\frac{\alpha^2}{(1-\alpha)V\left(1 + \frac{c}{V}\right)} = \text{const.}$$

Thus, in order to derive Partington's equation, it is sufficient to show that

$$1 + \frac{\rho\alpha}{V} \propto 1 + \frac{c}{V} ;$$

or  $\rho\alpha \propto c$ , which is obviously true for dilute solutions where  $\alpha \propto c$ .

Hence our conception of the nature of chemical force fits in with Partington's equation.

### *Conclusions.*

A quantitative theoretical interpretation has been given to the equations of Rudolphi, van't Hoff, and Partington on the fundamental assumption of the nature of the chemical forces operative, described above. Complete ionization need not be assumed. This assumption is therefore highly probable, especially as it also represents quantitatively the departure of gases from Boyle's law (van der Waals' equation). The author has also shown ('Nature,' Jan. 27, 1921) that

an assumption of the same kind will enable the passivity of metals in acids to be regarded as due to a layer of anions firmly held on the surface of the metal.

The law of Mass Action holds good in the case of strong electrolytes if we represent active mass by a momentum term, as is certainly necessary in all applications of the law. Bates (J. Am. C. S. xxxvii. p. 1421, 1915) has suggested that the abnormality of strong electrolytes is due to the abnormal osmotic behaviour of the ions, and this suggestion is in entire agreement with the fundamental assumption of this investigation. Perhaps the departure of osmotic pressure from all known gas laws may be explained on a similar assumption.

Bedford Modern School,  
May 16, 1921.

## XLVII. *On Units and the Theory of Relativity.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

**I**N the January number of this Magazine, Sir George Greenhill asked for a short explanation of the statement made in some works on Relativity, that the mass of the sun is equal to 1.47 kilometres. I accordingly sent to him the following, which he suggests may be of interest to others besides himself; and I venture to forward it for publication—without wishing to express any opinion on the main problem as to the value of the Relativity theory. It gives me, however, an opportunity to say that the use of these special types of units has (almost always) led to much confusion when used by those who are not expert mathematicians.

Supposing that the earth's orbit round the sun is treated as a circle of radius  $a$ , described in periodic time  $T$ , and take the constant of gravitation to be denoted by  $\gamma$ ; then if the sun's mass is taken to be  $S$ , we have the equations

$$\gamma S/a^2 = a(2\pi/T)^2,$$

or  $\gamma ST^2 = 4\pi^2 a^3.$

Let  $c$  denote the velocity of light; then we have the result

$$\frac{\gamma S}{c^2} = \frac{4\pi^2 a^3}{(cT)^2} \cdot \cdot \cdot \cdot \cdot \quad (1)$$

On inserting the usual astronomical *data*, the value of