

the work necessary to overcome the forces of electrical attraction in this case can be easily calculated. Milner (*Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 747) has already developed a method for calculating the virial of solutions of univalent binary electrolytes, and has shown that the Clausius theorem agrees well with experimental results. No relation between the activity coefficient $\frac{\mu_v}{\mu_\alpha}$ and the osmotic pressure of salt solutions has, however, yet been established on the basis of complete ionisation at all dilutions. We have seen that the molecular conductivity is proportional to the number of free ions, $n \cdot N \cdot e^{-\frac{A}{nRT}}$. Since at infinite dilution $A = 0$,

$$\frac{\mu_v}{\mu_\alpha} = e^{-\frac{A}{nRT}},$$

or

$$A = nRT \log_e \frac{\mu_\alpha}{\mu_v} \dots \dots \dots (2)$$

which holds good for all types of salt solutions. Here A , of course, is the virial, and PV thus becomes equal to

$$\begin{aligned} nRT - \frac{1}{3}nRT \log_e \frac{\mu_\alpha}{\mu_v}, \\ = nRT \left\{ 1 - \frac{1}{3} \log_e \frac{1}{\alpha} \right\}, \end{aligned}$$

or

$$i = n \cdot \left\{ 1 - \frac{1}{3} \log_e \frac{1}{\alpha} \right\} \dots \dots \dots (3)$$

According to Arrhenius, on the view that in a solution we have an equilibrium between ions and undissociated molecules,

$$i = 1 + (n-1)\alpha \dots \dots \dots (4)$$

At infinite dilution, equations (3) and (4) lead to the same limiting value of $i = n$. At other dilutions, the two equations give different results. In this paper it is proposed to examine which of these equations agrees best with actual observations.

Determination of α for Univalent Binary Electrolytes at Various Dilutions.

It has already been shown that the variation of activity-coefficient with dilution for univalent binary electrolytes is given by the equation

$$\frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\alpha}{\mu_v} = 2RT \log_e \frac{1}{\alpha}.$$

The agreement with the observed values is quite satisfactory for dilutions of 10 litres and upwards (Part I). This coincidence becomes, however, less perfect as the concentration increases. This is certainly due to the fact, suggested by Washburn (*J. Amer. Chem. Soc.*, 1911, **33**, 1464), and later emphasised by Noyes and Falk (*ibid.*, 1912, **34**, 458), that the ratio $\frac{\mu_v}{\mu_\alpha}$ is not a true measure of the activity-coefficient. A correction for change in ionic mobility, due to the change in the viscosity of solutions with dilution, is necessary; the ratio $\frac{\mu_v \eta_v}{\mu_\alpha \eta_\alpha}$, furnishes a much closer approximation to the true values of the activity-coefficient than the ratio $\frac{\mu_v}{\mu_\alpha}$. Taking into account this correction for viscosity, the equation for univalent binary electrolytes becomes

$$A = \frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\alpha \eta_\alpha}{\mu_v \eta_v} = 2RT \log_e \frac{1}{a} \quad (5)$$

From table I it will be evident that, with this modification, the above equation can be very well applied to concentrations up to 0.5*N*. In the table, the values of μ_v and η_v have been taken from the paper of Noyes and Falk (*loc. cit.*). The striking regularity brought to notice by these investigators, that salts of analogous constitution have the same activity-coefficient at the same dilution, is, of course, a necessary deduction of the above equation. Above 0.5*N*, the volume actually occupied by the solute molecules is not negligible.

TABLE I. T = 18°.

Salt.	Extra- polation value of $\mu_\alpha \eta_\alpha$.	Calc. value of $\mu_\alpha \eta_\alpha$ from $\mu_{10} \eta_{10}$.	$v =$				
			2.	5.	10.	20.	
1. NaCl	108.9	109.8	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	82.3 84.2	88.8 89.1	92.7 92.7	96.1 96.1
			$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	99.2 101.3	107.0 107.5	111.8 111.8	115.8 115.6
3. LiCl	98.8	99.0	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	74.2 75.5	80.0 80.2	83.6 83.6	86.7 86.6
			$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	101.0 101.3	108.6 109.1	113.5 113.5	117.6 117.4
4. KBr	132.2	134.5	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	100.1 101.4	— —	112.9 112.9	116.9 116.7
			$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	100.1 101.4	— —	112.9 112.9	116.9 116.7

It will be observed that the difference between the calculated value of $\mu_\alpha \eta_\alpha$ and the extrapolation value, obtained by means of empirical equations, is within 2 per cent.

TABLE II.

	V=2.	5.	10.	20.	50.	100.
Theoretical value of α for all univalent binary electrolytes according to equation 5. Per cent.....	74.8	80.8	84.4	87.5	90.6	92.4

Variation of α with Dilution for Ternary Electrolytes.

For ternary electrolytes, the variation of activity-coefficient with dilution is very satisfactorily represented by the equation

$$\frac{6N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{3 \cdot \sqrt[3]{V}}} = 3RT \log_e \frac{\mu_{\alpha}}{\mu_{\nu}} = 3RT \log_e \frac{1}{\alpha}$$

In table III, the percentage values of α , calculated from the above equation for various dilutions, are given.

TABLE III.

$v =$	10.	20.	40.	50.	100
$\alpha =$	67.8	73.5	78.3	79.7	84.0

Determination of the Value of i for Univalent Binary Electrolytes.

The method of determining i with sufficient exactness is based on observations on the lowering of the freezing point of salt solutions. Attempts were made to determine i from the diminution of the vapour pressure of solutions (compare Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 231), but until the recent work of Lovelace, Frazer, and Miller (*J. Amer. Chem. Soc.*, 1916, **38**, 515) the methods were not sufficiently accurate. These investigators have succeeded in improving the technique of the method to such an extent that the temperature of the bath can be kept constant within 0.001° for more than twelve hours, and a pressure of 0.0001 mm. can be exactly measured. The results obtained by them are rather peculiar, inasmuch as the molecular lowering of the vapour pressure of a solution of potassium chloride remains constant as the concentration changes from $2N$ to $0.2N$. Any opinion on these results must at present be suspended, as the work is still in progress.

The method based on the lowering of the freezing point has been well investigated, and all the observations, with the exception of those of Ponsot (*Ann. Chim. Phys.*, 1897, [vii], **10**, 79; 1899, **16**, 162), go to show that i continually increases until the limiting

value n is reached. Noyes and Falk, in their valuable paper on the properties of salt solutions (*J. Amer. Chem. Soc.*, 1910, **32**, 1020), have given a fairly complete account of the investigations on the lowering of the freezing point up to that time. They have not attached the same weight to the data obtained by different investigators, and hence their mean value of i is somewhat arbitrary. In table IV I have recalculated the mean value of the molecular lowering of the freezing point on the simpler, but still arbitrary, basis that the probable error of the various investigators is approximately the same. The value of i is obtained by dividing the mean molecular lowering of the freezing point by 1.858. In the footnote are given the references to the work of the investigators whose data have been utilised in calculating the mean value of i .

The weighted mean of the "molecular number i " for salts of the uni-univalent type, obtained by Noyes and Falk (*loc. cit.*, p. 1027), is included in table VIII for the sake of comparison. It should be noted that this mean was obtained by excluding the data on the molecular numbers of lithium chloride and sodium bromide. The values of i for these salts, as will be seen from table IV, are always higher than the mean. For ternary electrolytes, Noyes and Falk do not give any weighted mean, but observe that "the values of the molecular numbers are of similar magnitude, the range being 2.57 to 2.68 at dilution 10 and 2.71 to 2.77 at dilution 50."

TABLE IV.

Salt.	$V=2.$	5.	10.	20.	50.	100.
KCl ¹	1.800	1.833	1.862	1.886	1.922	1.947
NaCl ²	1.824	1.850	1.880	1.897	1.928	1.945
LiCl ³	—	—	1.901	1.912	1.928	1.937
CsCl ⁴	1.780	—	1.878	1.892	1.930	—
NaBr ⁵	—	1.871	1.891	1.911	—	—
KBr ⁶	1.813	1.841	1.870	1.910	1.929	—

¹ Jones, *Zeitsch. physikal. Chem.*, 1893, **11**, 110; **12**, 639. Loomis, *Ann. Phys. Chem.*, 1894, [iii], **51**, 500; 1896, **57**, 495; 1897, **60**, 523; *Zeitsch. physikal. Chem.*, 1900, **32**, 578; 1901, **37**, 406. Lewis, *ibid.*, 1894, **15**, 365. Abegg and Nernst, *ibid.*, 1894, **15**, 681; 1896, **20**, 207. Whetham, *ibid.*, 1900, **33**, 344. Raoult, *ibid.*, 1898, **27**, 617. Jahn, *ibid.*, 1905, **50**, 129; 1907, **59**, 31. Richards, *ibid.*, 1903, **44**, 563. Ponsot, *loc. cit.* Bedford, *Proc. Roy. Soc.*, 1910, [A], **83**, 454.

² Jones, Loomis, Raoult, Ponsot, Abegg, Jahn, Hausrath, *Ann. Physik*, 1902, [iv], **9**, 522. Osaka, *Zeitsch. physikal. Chem.*, 1902, **41**, 560.

³ Loomis, Jahn.

⁴ Jahn, Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 185.

⁵ Jahn.

⁶ Jahn, Biltz.

TABLE V.

Mean value of i for univalent binary electrolytes at various dilutions.

$v =$	2.	5.	10.	20.	50.	100.
$i =$	1.805	1.849	1.880	1.900	1.935	1.942

Determination of i for Ternary Electrolytes at Various Dilutions.

In calculating the value of i , the method described before has been followed. Table VI contains the mean value of i for some well-investigated ternary electrolytes at various dilutions.

TABLE VI.

Salt.	Mean value of i .			
	$v = 10.$	20.	50.	
CaCl_2^1	$i = 2.624$	2.685	2.789	
MgCl_2^2	$i = 2.677$	2.708	2.763	
SrCl_2^3	$i = 2.629$	2.673	2.781	
BaCl_2^4	$i = 2.580$	2.640	2.712	
ZnCl_2^5	$i = 2.579$	2.666	2.771	
$\text{CO}(\text{NO}_3)^6$...	$i = 2.700$	2.760	—	
$\text{Cu}(\text{NO}_3)^7$...	$i = 2.630$	2.730	—	
$\text{Ni}(\text{NO}_3)_2^8$...	$i = 2.600$	2.670	2.810	

¹ Loomis, Ponsot, Jones and Pearce. ² Loomis. ³ Loomis, Jones and Pearce. ⁴ Bedford, Loomis, Jones, Ponsot, Whetham. ⁵ Jones. ⁶ Jones and Pearce. ⁷ Jones and Pearce. ⁸ Jones and Pearce.

TABLE VII.

Mean value of i for ternary electrolytes at various dilutions.

$v =$	10.	20.	50.
$i =$	2.620	2.691	2.771

The Validity of the Clausius Theorem.

TABLE VIII.

	$v = 2.$	5.	10.	20.	50.	100.
i According to Noyes and Falk	1.804	1.837	1.865	1.887	1.925	1.937
i Observed for univalent binary salts	1.805	1.849	1.880	1.900	1.935	1.942
i According to equation 3	1.806	1.859	1.887	1.910	1.934	1.947
i According to equation 4	1.748	1.808	1.844	1.875	1.906	1.924

TABLE IX.

	$v = 10.$	20.	50.
i Observed for ternary salts	2.620	2.691	2.771
i According to equation 3	2.616	2.695	2.773
i According to equation 4	2.356	2.470	2.594

It is evident that the equation

$$i = n \left\{ 1 - \frac{1}{3} \log_e \frac{\mu_x}{\mu_v} \right\},$$

based on the Clausius theorem, agrees best with the experimental results. The Arrhenius equation fails conspicuously in the case of ternary electrolytes. Jones attempted to explain this anomaly by his hydrate theory. The high value of i according to him, is due to the fact that the solvent combines with the solute, the ratio of solute to solvent molecules increases, and hence i becomes abnormally large. His theory may be correct for concentrated solutions. There is, however, some inherent improbability in the fact that in dilute solutions about 150 water molecules must be made to combine with an ion in order that the difference between the observed value of i and that calculated from Arrhenius's equation may be explained. The hydrate theory of dilute solutions becomes simply unnecessary in view of the complete validity of the Clausius theorem as applied to salt solutions.

Activity-coefficient of Salts in Mixed Solutions.

Here we have the following empirical rule: "The conductivity and the freezing-point lowering of a mixture of salts having one ion in common are those calculated under the assumption that the degree of ionisation (activity-coefficient) of each salt is that which it would have if it were present alone at such an equivalent concentration, that the concentration of either of its ions is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture" (A. A. Noyes, *Tech. Quart.*, 1904, 17, 301).

Let there be two solutions of sodium chloride and potassium chloride, and let their equivalent dilutions be V and V' respectively. If X and Y are their respective activity-coefficients, then

$$\log \frac{1}{x} = k \left(\frac{1}{V} \right)^{\frac{1}{2}},$$

and

$$\log \frac{1}{y} = k \left(\frac{1}{V'} \right)^{\frac{1}{2}}.$$

If the two solutions are mixed together, the total volume = $V + V'$. But, on mixing, there is a distribution of arrangement until the entire solution is uniform. Since there are only ions in a solution, and since the arrangement in sodium chloride and potassium chloride solutions is identical, the distance between the sodium and chlorine ions in an electric doublet is the same as it would have

been if the dilution were $\frac{V+V'}{1+1}$. The result is that the activity-coefficient of sodium chloride in the mixture corresponds with that of the pure solution at dilution $\frac{V+V'}{2}$, which is the equivalent dilution of the common ion. The same is true for potassium chloride. On mixing, therefore,

$$\log \frac{1}{x'} = k \left(\frac{2}{V+V'} \right)^{\frac{1}{2}},$$

$$\log \frac{1}{y'} = k \left(\frac{2}{V+V'} \right)^{\frac{1}{2}}.$$

where x' and y' are the respective activity-coefficients of the salts in the mixture.

Therefore $X'=Y'$, or the activity-coefficient of each of the salts is the same and corresponds with that of a solution the equivalent concentration of which is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture.

If $V=V'$, that is, if the initial concentration of both solutions is the same,

$$\frac{1}{V} = \frac{1}{V'} = \frac{1+1}{V+V'},$$

therefore $X=Y=X'=Y'$. That is, the activity-coefficient does not change when two salt solutions having the same equivalent concentration are mixed. This is the condition for isohydry.

Conclusions.

In this series of papers on the abnormality of strong electrolytes, I have proceeded on the following assumptions:

(1) A salt solution is always completely ionised, the force of attraction between ions being governed by the law of inverse squares.

(2) The arrangement of ions in a univalent binary electrolyte corresponds with a simple cubic lattice, whilst in a solution of a ternary electrolyte the arrangement corresponds with a fluorspar lattice.

The following equations have been derived:

I. $A = \frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{V}} = 2RT \log_e \frac{\mu_\alpha}{\mu_\nu} \dots$ for universal binary salts.

II. $A = \frac{6N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} = 3RT \log_e \frac{\mu_\alpha}{\mu_\nu} \dots$ for ternary salts.

III. $i = n \left\{ 1 - \frac{1}{3} \log_e \frac{\mu_\alpha}{\mu_\nu} \right\}$

The validity of these fundamental equations has been completely demonstrated both in aqueous and non-aqueous solutions. The variation of the activity-coefficient with temperature has been successfully calculated, and the conditions for isohydry have been determined. In fact, a complete theory of dilute salt solutions has been propounded.

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