48. *Activity Coefficients of Zinc Chloride, Bromide and Iodide from Electromotive Forces.*

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The E.M.F.'s of the double cells

$Zn^+|M_2'\text{-}ZnCl_2,\ Hg_2Cl_2|Hg—Hg|Hg_2Cl_2,\ M_2\text{-}ZnCl_2|Zn^-$
$Zn^+|M_2'\text{-}ZnBr_2,\ Hg_2Br_2|Hg—Hg|Hg_2Br_2,\ M_2\text{-}ZnBr_2|Zn^-$
$Zn^+|M_2'\text{-}ZnI_2,\ Hg_2I_2|Hg—Hg|Hg_2I_2,\ M_2\text{-}ZnI_2|Zn^-$,

were measured at 25° and 35° over a range of molarity 0·5—0·001 for zinc chloride, 0·36—0·001 for zinc bromide, and 0·25—0·002 for zinc iodide. The activity coefficients were calculated by using a graphical extrapolation method, and also by correlating E.M.F.'s with the La Mer equation. The results obtained indicate that the chloride and bromide behave as typical strong electrolytes in the concentration range studied, but with the iodide there is evidence of the formation of complex ions.

The activity coefficients of zinc chloride usually quoted are those of Scatchard and Tefft (*J. Amer. Chem. Soc.*, 1930, **52**, 2272) and occasionally those calculated from Horsch's measurements (*ibid.*, 1919, **41**, 1787) by Getman (*J. Physical Chem.*, 1931, **35**, 2749). In both cases E.M.F.'s were used but the results are not in good agreement, as can be seen from Table VII. The only available data for the activity coefficients of zinc bromide are those of Baxter (M.Sc. Thesis, London University, 1939), and for those of zinc iodide Bates's data (*J. Amer. Chem. Soc.*, 1938, **60**, 2983).

Helmholtz (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1882, i, 825; Ostwald's "Klassiker," No. 124, 37) used the cell $Zn^+|M_1\text{-}ZnCl_2,\ Hg_2Cl_2|Hg\text{–}Hg|Hg_2Cl_2,\ M_2\text{-}ZnCl_2|Zn^-$ and calculated the work done in transferring an amount of water from the dilute to the concentrated solution. The value of the E.M.F. *e* found by equating the osmotic work to the electrical work was in satisfactory agreement with the observed E.M.F.

The cell $Zn^-|ZnCl_2,\ AgCl|Ag^+$ is a modification of that used by De la Rue and Müller (J., 1868, **21**, 488; *Compt. rend.*, 1868, **67**, 794) and was used by several investigators to test the Gibbs–Helmholtz equation. Preliminary measurements by Braun (*Ann. Physik*, 1882, **17**, 593) and Czapski (*ibid.*, 1884, **21**, 209) showed that the cell emits heat. Jahn (*ibid.*, 1886, **28**, 21; 1893, **50**, 188) used zinc chloride solutions between 0·556 and 2·22 molal and found E.M.F.'s in satisfactory agreement with those calculated from the Gibbs–Helmholtz equation. These results were confirmed by Lévay (*ibid.*, 1891, **42**, 103). The temperature coefficients of the cells $Zn^{-}|ZnCl_2, AgCl|Ag^{+}$ and $Zn^{-}|$N-$ZnCl_2|$N/2-$ZnCl_2, Hg_2Cl_2|Hg^{+}$ were measured by Gockel (*ibid.*, 1890, **40**, 450). Goodwin (*Z. physikal. Chem.*, 1890, **13**, 577) measured the E.M.F.'s of the double cells :

$$Zn^{+}|\text{M}_1\text{-}ZnCl_2, Hg_2Cl_2|Hg\text{–}Hg|Hg_2Cl_2, \text{M}_2\text{-}ZnCl_2|Zn^{-}$$
$$Zn^{+}|\text{M}_1\text{-}ZnCl_2, AgCl|Ag\text{–}Ag|AgCl, \text{M}_2\text{-}ZnCl_2|Zn^{-},$$

and the corresponding cells with zinc bromide, over a concentration range 0·2—0·001 mole/l., and compared them with those calculated from the equation $e = (3\boldsymbol{R}T/2\boldsymbol{F}) \ln (\kappa_1/\kappa_2)$, where κ_1, κ_2 are the specific conductivities of the solutions. Satisfactory agreement was obtained. Horsch (*loc. cit.*) used the cell $Zn^{-}|ZnCl_2, AgCl|Ag^{+}$ over a range of molality 0·0003—0·01*m*, the electrodes being finely divided metal. The conductivity ratio was again used, and the standard potential of $Zn|Zn^{++}$ was calculated as $0{\cdot}7582 \pm 0{\cdot}002$ volt. The use of the conductivity ratio cannot be considered as satisfactory in the light of modern theory. Foxton and Shutt (*Trans. Faraday Soc.*, 1927, **23**, 480) measured the activity coefficients of zinc chloride in concentrated solutions (0·074—25*m*) by using the cells $Zn^{-}|ZnCl_2|Cl_2|Pt^{+}$ and $Zn^{+}|m_1\text{-}ZnCl_2|m_2\text{-}ZnCl_2|Zn^{-}$. They assumed that the activity coefficient of 1·0*m*-zinc chloride is equal to that of 1·0*m*-barium chloride, and thence found that the activity coefficients of zinc chloride were considerably greater than those of barium chloride in concentrated solutions. Abnormal transport numbers were found with the cell with transport, and there is evidence for the presence of complex ions in concentrated solutions. Labendzinski (*Z. Electrochem.*, 1904, **10**, 77) used the cell $Zn^{-}\text{–}Hg|0{\cdot}5$N-$ZnCl_2$, 1·0N-KCl, $Hg_2Cl_2|Hg^{+}$ and found little evidence of complex ions at this concentration.

Scatchard and Tefft (*loc. cit.*) measured the E.M.F. of the cell $Hg^{-}\text{–}Zn|ZnCl_2, AgCl|Ag^{+}$ at 25° with solutions 1·48—0·003*m*. The zinc amalgam was prepared by electrolysis of zinc chloride solution with a zinc anode and mercury cathode. The zinc chloride solution was saturated with zinc oxide (to prevent hydrolysis) and a correction (less than 0·1 mv.) applied. (This addition of zinc oxide was mentioned by Helmholtz.) The E.M.F. is given by

$$e = e_0 - 2{\cdot}303(3\boldsymbol{R}T/2\boldsymbol{F}) \log (m_{\pm}\gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the activity coefficient on the molal scale (moles per kg. of solvent) ; $2{\cdot}303 \times 3\boldsymbol{R}T/2\boldsymbol{F} = 0{\cdot}088725$ and $m_{\pm}$, the mean molality (defined as $[(\nu_{+}\, m)^{\nu_{+}}(\nu_{-}m)^{\nu_{-}}]^{1/\nu}$ where ν_{+}, ν_{-} are the number of ions produced from one mole), is used instead of the molality m (in this case $m_{\pm} = \sqrt[3]{4}m$). Since the E.M.F. is used with an extended form of the Debye–Hückel equation, the concentrations must be on the molar scale (M, moles/l. of solution) and the equation $\log \gamma = \log f - \log (1 + 0{\cdot}054m)$ gives f, the activity coefficient on the molar scale (Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098). Hence the following equation was obtained :

$$e_0 - 0{\cdot}088725 \log f_{\pm} = e + 0{\cdot}088725\,[\log m - \log (1 + 0{\cdot}054m)] + 0{\cdot}01781 = e_0'' \quad . \quad . \quad . \quad (2)$$

Hitchcock (*ibid.*, 1928, **50**, 2076) found that an extended Debye–Hückel equation, $-\log f = 0{\cdot}5\sqrt{I} - BI$, where $I = \frac{1}{2}(\Sigma c_i z_i^2)$ is the ionic strength, c_i = concentration, and z_i the valency of an ion, accounted for the behaviour of hydrochloric acid in solutions up to 0·02*m*. Scatchard and Tefft used the corresponding equation for zinc chloride, $-\log f = 2 \times 0{\cdot}5\sqrt{3}\sqrt{c} - 3cB$, and correlated it with (2), obtaining the equation $e_0 + 0{\cdot}266175Bc = e_0'' - 0{\cdot}155\sqrt{c} = e_{\text{D}}$, and e_{D} was plotted against $\sqrt{c}$. If the Debye–Hückel equation holds at small concentrations the plot should approach a straight line asymptotically at zero concentration. Scatchard and Tefft found evidence of an inflexion at high dilutions, which they attributed to incomplete dissociation, and they showed that inflexion is more pronounced the smaller the ionisation constant. The value of e_{D} obtained by graphical extrapolation to infinite dilution gave $e_0 = 0{\cdot}9834$ v. Cohen (*Z. physikal. Chem.*, 1900, **34**, 612) found that the difference in standard potential between zinc and the two-phase zinc amalgam was 0·0006 v., and by taking this into account the standard potential $Zn|Zn^{++}$ was found to be 0·7616 v. When e_0 was known γ could be calculated from equation (1) for each value of e. La Mer, Gronwall, and Greiff (*J. Physical Chem.*, 1931, **35**, 2245, 3103, 3692 ; cf. Partington and Stonehill, *Phil. Mag.*, 1936, **22**, 857) calculated " a," the mean ionic diameter of zinc chloride, from Scatchard and Tefft's measurements as 3·8 A. They obtained an equation containing the activity coefficient f and " a " by a method described below, and by substituting various values of " a " the corresponding values of f were found. The equation for the E.M.F. of the cell $Zn^{-}|\text{M}_2\text{-}ZnCl_2, AgCl|Ag^{+}$ is $e = e_0 - (3\boldsymbol{R}T/2\boldsymbol{F}) \ln \text{M}_2 f_2$, and the value " a " = 3·8 A., which gave the most constant value of e_0, was taken as correct. Getman (*loc. cit.*) used both a single zinc crystal and polycrystalline 99·999% pure zinc electrodes in the cell $Zn^{-}|ZnCl_2, Hg_2Cl_2|Hg^{+}$. No mention is made of the electrodes having been annealed. He found that the difference between the E.M.F.'s with the two types of electrodes was of the order of the experimental error. The E.M.F. is $e = e_0 - 0{\cdot}08873 \log (1{\cdot}588\, m\gamma)$. e_0 and the standard potential $Zn|Zn^{++}$ were found by three methods : (1) The values of γ were determined from Horsch's measurements by the method of Randall (*Trans. Faraday Soc.*, 1927, **23**, 505), and substituted in the equation for the E.M.F. The mean value of e_0 was 1·0278 v., and if the standard potential of the mercury–mercurous chloride electrode, $Hg|Hg_2Cl_2, Cl^{-}$, is 0·2676 v., the standard potential $Zn|Zn^{++}$ is 0·760 v. (2) The activity coefficients found by Scatchard and Tefft, used similarly, gave the standard potential $Zn|Zn^{++} = 0{\cdot}762$ v. (3) In a method similar to Hitchcock's, $e_0 - 0{\cdot}155\sqrt{c}$ was plotted against $\sqrt{c}$. The graph was a straight line in the region of low concentration and by linear extrapolation to infinite dilution e_0 was found to be 1·0300 v. and the standard potential $Zn|Zn^{++} = 0{\cdot}7624$ v. No indication was found of an inflexion in the region of high dilution such as was reported by Scatchard and Tefft.

Jahn, Horsch, and Scatchard and Tefft all used the cell $\mathrm{Zn^-|ZnCl_2, AgCl|Ag^+}$. The E.M.F.'s found by Jahn are higher than those of Scatchard and Tefft. Horsch made measurements from 0·0003 to 0·01*m*, and between 0·002 and 0·01*m* the results agree with those of Scatchard and Tefft; but in very dilute solutions they are less accurate, and it was in this region that Getman carried out the extrapolation of Horsch's measurements.

Bates (*loc. cit.*) measured the E.M.F. of the cell $\mathrm{Zn^-{-}Hg|ZnI_2, AgI|Ag^+}$, over a range 0·8—0·002*m* at intervals of 5° between 5° and 40°. Air was carefully excluded by keeping the solutions under hydrogen. Iodide was determined by Volhard's method, but no mention is made of the determination of the zinc content. The zinc electrodes were 5% amalgam, which according to Clayton and Vosburgh (*J. Amer. Chem. Soc.*, 1936, **58**, 2093; cf. Cohen, *loc. cit.*) has the same potential as pure zinc. Bates found the standard potential by the Hitchcock extrapolation, using the same method as Scatchard and Tefft for zinc chloride, and from the results he concluded that zinc iodide is practically completely ionised. He then applied a Hückel equation $-\log\gamma = u\sqrt{Id}/(1 + A\sqrt{Id}) + BId$, where d is the density of the solution, and u, A, and B are constants, to the equation for the E.M.F. $e = e_0 - k\log 4m^3\gamma^3$, and obtained the equation $e_0' = e_0 + 3kBId = e + k\log 4 + 3k\log m - 3k\sqrt{Id}/(1 + A\sqrt{Id})$. The Hitchcock extrapolation was carried out and the standard potential $\mathrm{Zn|Zn^{++}}$ found to be 0·7627 at 25°. When e_0 is known, γ is given by the equation $e = e_0 - k\log 4m^3\gamma^3$ and the activity coefficients below 0·2*m* were found to be those of a typical strong electrolyte, though in higher concentrations γ increased slightly with concentration.

We have determined the activity coefficients of zinc chloride, bromide, and iodide by a slightly different method, and the results found for the chloride and bromide are in satisfactory agreement with those of Scatchard and Tefft and of Baxter (*op. cit.*), respectively. The results of Baxter, Bates, and the authors for zinc iodide are in fair agreement below 0·045M. In more concentrated solutions Bates's results are typical of a normal bi-univalent type electrolyte, whereas ours and those of Baxter give abnormally high activity coefficients. This points to complex-ion formation in the more concentrated solutions, which is also indicated by measurements of transport numbers (Hittorf, *Ann. Physik*, 1859, **106**, 543; Kummel, *ibid.*, 1898, **64**, 665) and conductivity (Jäger, *Monatsh.*, 1887, **8**, 772).

In this research the concentrations of the solutions are all expressed on the molar scale (M), since this has a theoretical significance with reference to the Debye–Hückel theory (cf. Kingerley and La Mer, *J. Amer. Chem. Soc.*, 1941, **62**, 3260). Molarities may be converted into molalities (m) by the formula $m = 1000\mathrm{M}/(1000d - w\mathrm{M})$, where d is the density of a solution of molarity M, and w is the molecular weight of the solute. The difference between the two scales is negligible below 0·1M for zinc chloride, 0·08M for the bromide, and 0·048M for the iodide. All solutions were made up and standardised at 25°.

The Helmholtz double cell,

$$\begin{array}{l}\mathrm{Zn^+|M_2'\text{-}ZnCl_2,\ Hg_2Cl_2|Hg{-}Hg|Hg_2Cl_2,\ M_2\text{-}ZnCl_2|Zn^-}\\ \mathrm{Zn^+|M_2'\text{-}ZnBr_2,\ Hg_2Br_2|Hg{-}Hg|Hg_2Br_2,\ M_2\text{-}ZnBr_2|Zn^-}\\ \mathrm{Zn^+|M_2'\text{-}ZnI_2,\ Hg_2I_2|Hg{-}Hg|Hg_2I_2,\ M_2\text{-}ZnI_2|Zn^-}\end{array}$$

was used, the E.M.F. of which is given by $e = (3\boldsymbol{R}T/2\boldsymbol{F})\ln(a_\pm)_2'/(a_\pm)_2$ where $a_\pm$, the mean ion activity is equal to $[(a_+^{\nu_+})(a_-^{\nu_-})]^{1/\nu}$, a_+ and a_- are the ion activities, ν_+, ν_- the number of ions produced from one mole, and $\nu = \nu_+ + \nu_-$. The factor $3\boldsymbol{R}T \times 2{\cdot}303/2\boldsymbol{F}$ is 0·0887 at 25° and 0·0917 at 35°. At 25°,

$$e = 0{\cdot}0887\log(a_\pm)_2' - 0{\cdot}0887\log(a_\pm)_2 \qquad (3)$$

In measurements, one molarity M_2' is kept constant and the other M_2 is varied; M_2' is greater than M_2, and the zinc electrode in contact with the solution M_2' is positive. The cell reactions are, *e.g.*, $\mathrm{Zn + Hg_2Cl_2 = ZnCl_2 + 2Hg}$ in the dilute solution M_2, and $\mathrm{ZnCl_2 + 2Hg = Hg_2Cl_2 + Zn}$ in the concentrated solution M_2'. The net effect is the transfer of 1 mole of zinc halide, or 3 moles of ions, from the concentrated to the dilute solution, for every $2\boldsymbol{F}$ passing through the cell. Addition of $0{\cdot}0887\log(\mathrm{M}_\pm)_2$, where $\mathrm{M}_\pm$ is the mean molarity, to each side of equation (3) and rearrangement gives $e + 0{\cdot}0887\log(\mathrm{M}_\pm)_2 - 0{\cdot}0887\log(a_\pm)_2' = -0{\cdot}0887\log(a_\pm)_2 + 0{\cdot}0887\log(\mathrm{M}_\pm)_2 = -0{\cdot}0887\log f_2$, since $f = a_\pm/\mathrm{M}_\pm$. For a uni-bivalent salt such as zinc chloride, $\mathrm{M}_\pm = \sqrt[3]{\mathrm{M}.4\mathrm{M}^2} = \mathrm{M}\sqrt[3]{4}$, hence

$$e + 0{\cdot}0887\log\mathrm{M}_2 + 0{\cdot}01780 - 0{\cdot}0887\log(a_\pm)'_2 = -0{\cdot}0887\log f_2 \qquad (4)$$

When $\mathrm{M}_2 = 0$, then $f_2 = 1$ and

$$e + 0{\cdot}0887\log\mathrm{M}_2 = 0{\cdot}0887\log(a_\pm)_2' - 0{\cdot}01780 \qquad (5)$$

To find $(a_\pm)_2'$ we measured the E.M.F.'s of a series of double cells in which M'_2 was kept constant and M_2 varied, and $e' = e + 0{\cdot}0887\log\mathrm{M}_2$ was plotted as ordinate against $\sqrt{\mathrm{M}_2}$. The curve was extrapolated to $\mathrm{M}_2 = 0$, and the limiting extrapolated value from equation (5) is then $0{\cdot}0887\log(a_\pm)_2' - 0{\cdot}01780 = e'_{\text{ex.}}$. From this the activity coefficients of various molarities were calculated from equation (4) which may be written as $e' - e'_{\text{ex.}} = -0{\cdot}0887\log f_2$. A similar procedure was adopted at 35°.

EXPERIMENTAL.

Zinc chloride. Pure hydrochloric acid was prepared by absorbing the gas in conductivity water, A.R. zinc oxide was added until no more dissolved and the acid reaction to litmus was slight. The formation of basic salts was avoided by adding the zinc oxide slowly and keeping the solution cool towards the end. The solution was filtered from the slight excess of zinc oxide and diluted with conductivity water.

Zinc bromide. Pure hydrobromic acid was prepared from purified bromine by Scott's method (J., 1900, **77**, 648), and the constant-boiling solution treated as above.

Zinc iodide. To a constant-boiling solution of hydriodic acid prepared according to Mellor (" Treatise," etc., Vol. 2, p. 170) and distilled, zinc oxide was added to saturation, excess being filtered off on a sintered-glass crucible; the resulting solution was stored in a bottle kept full of liquid.

The chloride, bromide and iodide concentrations were determined gravimetrically as silver halide, and the zinc gravimetrically as zinc oxide and zinc ammonium phosphate.

Mercurous chloride and bromide. These were prepared electrolytically from pure mercury as the anode in pure N-hydrochloric or hydrobromic acid. The mixture of finely divided mercury and mercurous halide obtained was washed with water, dried at 80°, and stored in a vacuum desiccator.

Mercurous iodide. This was prepared by slowly adding a solution of potassium iodide to a mechanically stirred solution of mercurous nitrate. The precipitate was filtered off, washed with water, and dried at 80°. The mercury was determined gravimetrically as metal, and the iodide by fusion with sodium carbonate and subsequent gravimetric determination as silver iodide.

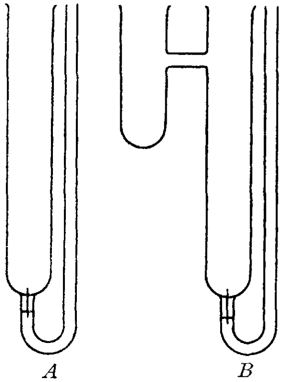
Mercury. Redistilled mercury was passed several times through a solution of mercurous nitrate and 5% nitric acid, filtered through a capillary tube, washed with water, and dried.

Conductivity water was used for all the stock solutions and for the analysis.

Electrodes. In the earlier part of the work (Baxter, *op. cit.*) rods of pure electrolyte zinc were used. In our experiments 99·99% zinc purified by distillation was used, and we are greatly indebted to Dr. W. H. Vernon of the Chemical Research Laboratory, Teddington, for a supply of this metal, made by the National Smelting Company, Avonmouth. The sheet metal was used in strips and also cast into rods in charcoal moulds. The strip electrodes gave the more constant E.M.F.'s. The literature on the allotropy of zinc is still conflicting, but very pure zinc occurs in one form only (Mellor, *op. cit.*, Vol. 4, p. 430; Gmelin, " Handbuch," 1924, **10**, 13). In order to eliminate surface strains, the metal was annealed at 300° (in the region of a supposed $\beta \longrightarrow \gamma$ transformation) for several hours, and cooled slowly (12 hrs.) to room temperature. Several types of zinc electrodes were prepared and tested by Baxter (*op. cit.*), and of these we have used amalgamated zinc electrodes. Zinc strips were mechanically cleaned with powdered ignited alumina, washed, and immersed in dilute mercurous nitrate solution containing a little nitric acid. After ½ hr. they had become well amalgamated. Pairs of electrodes were short-circuited in dilute zinc chloride solution for 24 hrs. With electrodes in a cell containing zinc chloride solutions of the same concentration on each side, all types except the amalgamated electrodes gave unsatisfactory results, the E.M.F. with these being less than 0·00001 v. A cell set up with one amalgamated and one unamalgamated electrode showed an E.M.F. of less than 0·00001 v., hence the amalgamated strip had the same potential as pure zinc. Cohen (*loc. cit.*) found a difference of 0·0006 v.

FIG. 1.

The Cells.



Cells. Two types of cell were used (see Fig. 1). The bent narrow-bore tubing formed a mercury contact with a sealed-in platinum wire. Two of these cells were connected by an amalgamated copper wire dipping in the mercury contact tubes. In *B* the shorter limb carried the zinc electrode and this cell was used for the more concentrated solutions.

Two methods were used in filling the cells. In the first, mercury was put in and mercurous halide which had been washed six times with cell solution was added as a suspension in the cell solution. The cells were corked and sealed with collodion. After the suspension had settled, the electrodes were fitted and the cells sealed as before. In the second method mercurous halide was added to the mercury, and the cell solution run in. The electrodes were fitted, and the cells sealed. Both methods gave the same E.M.F., but cells filled by the second method reached equilibrium in an hour, whereas those filled by the first method required 2—3 hrs.

The cells were in thermostats at 25° and 35°, the control being to ±0·02°. The temperature was measured by a standardised mercury thermometer immersed in a vessel of similar shape to the cell, but containing water. E.M.F.'s were measured by a three-range Tinsley Ionisation Potentiometer, a moving-coil galvanometer, and a standard Weston cell, readings being made to 0·01 mv. The cells, potentiometer, and accessories stood on an equipotential surface of tin-foil (White, *J. Amer. Chem. Soc.*, 1914, **36**, 2011). At 35° more time was required to reach equilibrium. The best procedure was to take a reading at 25°, place the cell in a thermostat at 35°, and leave it for 3 hrs. before taking a reading.

Results.—Baxter's (*op. cit.*) results are shown in Tables I, II (marked *), III and IV, and graphically in Figs. 2, 3, and 4. In the case of zinc chloride at 25° ($M_2' = 0{\cdot}4984$) calculations were made from the activity coefficients found by

TABLE I.

Zinc Chloride.

M_2.	$e_{25°}$.	$e'_{25°}$.	$f_{25°}$.	M_2.	$e_{25°}$.	$e'_{25°}$.	$f_{25°}$.
$M_2' = 0{\cdot}4984$ (Baxter).							
0·4984	0	—0·0268	0·383	0·0182	0·1081	—0·0463	0·635
0·4153	0·0064	—0·0275	0·389	0·0138	0·1169	—0·0481	0·665
0·2988	0·0166	—0·0299	0·415	0·0122	0·1203	—0·0495	0·690
0·2124	0·0272	—0·0325	0·443	0·0081	0·1346	—0·0510	0·717
0·1003	0·0517	—0·0369	0·493	0·0047	0·1516	—0·0550	0·796
0·0529	0·0735	—0·0398	0·536				
$M_2' = 0{\cdot}4942$ (Authors) : $e'_{ex.} = -0{\cdot}0642$.							
0·4942	0	—0·02714	0·382	0·0092	0·12910	—0·05151	0·719
0·4317	0·00473	—0·02763	0·387	0·0083	0·13264	—0·05196	0·728
0·2886	0·01734	—0·03053	0·417	0·0070	0·13840	—0·05270	0·742
0·1992	0·02865	—0·03350	0·451	0·0058	0·14495	—0·05345	0·751
0·1162	0·04665	—0·03625	0·484	0·0050	0·14990	—0·05420	0·771
0·0800	0·05852	—0·03879	0·517	0·0047	0·15225	—0·05425	0·773
0·0500	0·07357	—0·04173	0·558	0·0035	0·16260	—0·05530	0·794
0·0200	0·10375	—0·04695	0·639	0·0023	0·17710	—0·05690	0·827
0·0116	0·12125	—0·05045	0·700	0·0012	0·20010	—0·05898	0·873

Baxter, and the results are represented on the 25° graph ($M_2' = 0·4942$). Where the values of e' did not lie exactly on the e'–$\sqrt{M}$ curve, Baxter took the values of e' indicated by the curve.

TABLE II.

Zinc chloride. $M_2' = 0·3606$: $e'_{ex.} = -0·07445$ at 25°, $-0·07991$ at 35°.

M_2.	$e_{25°}$.	$e'_{25°}$.	$f_{25°}$.	$e_{35°}$.	$e'_{35°}$.	$f_{35°}$.
0·3606	0	−0·03929	0·401	0	−0·04062	0·373
0·3014 *	—	—	—	0·00580	−0·04196	0·386
0·2886	0·00710	−0·04077	0·417	0·00699	−0·04251	0·391
0·2048 *	—	—	—	0·01830	−0·04486	0·415
0·1992	0·01868	−0·04347	0·447	0·01885	−0·04540	0·421
0·1524 *	—	—	—	0·02810	−0·04684	0·436
0·1162	0·03637	−0·04651	0·484	0·03674	−0·04896	0·460
0·1020 *	—	—	—	0·04140	−0·04960	0·467
0·0800	0·04841	−0·04890	0·515	0·04937	−0·05133	0·488
0·0757 *	—	—	—	0·05140	−0·05150	0·490
0·0500	0·06326	−0·05204	0·559	0·06511	−0·05419	0·524
0·0488 *	—	—	—	0·06540	−0·05470	0·531
0·0254 *	—	—	—	0·08650	−0·05980	0·604
0·0200	0·09335	−0·05745	0·643	0·09471	−0·06119	0·625
0·0183 *	—	—	—	0·09770	−0·06170	0·633
0·0116	0·11098	−0·06072	0·700	0·11286	−0·06464	0·682
0·0106 *	—	—	—	0·11610	−0·06520	0·691
0·0083	0·12236	−0·06224	0·728	0·12382	−0·06698	0·723
0·0081 *	—	—	—	0·12500	−0·06710	0·725
0·0070	0·12821	−0·06289	0·741	0·12995	−0·06765	0·735
0·0058	0·13478	−0·06362	0·755	0·13656	−0·06854	0·752
0·0052 *	—	—	—	0·14060	−0·06920	0·764
0·0050	0·13962	−0·06448	0·772	0·14159	−0·06941	0·768
0·0038 *	—	—	—	0·15150	−0·07050	0·790
0·0035	0·15222	−0·06568	0·796	0·15461	−0·07069	0·793
0·0023	0·16683	−0·06717	0·828	0·16969	−0·07221	0·824
0·0012	0·18972	−0·06928	0·874	0·19347	−0·07443	0·872

* Indicates measurements made by Baxter.

TABLE III.

Zinc bromide.

M_2.	$e_{25°}$.	$e'_{25°}$.	$f_{25°}$.	$e_{35°}$.	$e'_{35°}$.	$f_{35°}$.
$M_2' = 0·3782$ (Baxter).						
0·3787	0	−0·0375	0·505	0	−0·0387	0·498
0·3118	0·0072	−0·0377	0·508	0·0076	−0·0388	0·499
0·1999	0·0238	−0·0382	0·515	0·0242	−0·0399	0·515
0·1388	0·0364	−0·0397	0·535	0·0377	−0·0410	0·527
0·0959	0·0487	−0·0416	0·562	0·0502	−0·0431	0·556
0·0804	0·0549	−0·0422	0·571	0·0563	−0·0441	0·570
0·0474	0·0724	−0·0450	0·614	0·0743	−0·0471	0·614
0·0224	0·0984	−0·0479	0·662	0·1013	−0·0500	0·661
0·0125	0·1182	−0·0507	0·712	0·1217	−0·0529	0·711
0·0090	0·1292	−0·0522	0·740	0·1327	−0·0549	0·747
0·0071 *	0·1375	−0·0530	0·756	0·1419	−0·0552	0·753
0·0050 *	0·1496	−0·0545	0·786	0·1543	−0·0567	0·782
0·0031	0·1660	−0·0565	0·827	0·1711	−0·0589	0·826
0·0017	0·1880	−0·0577	0·854	0·1941	−0·0599	0·847
0·0010 *	0·2069	−0·0592	0·887	0·2134	−0·0617	0·886
* Readings taken in present research to verify extrapolation.						
$M_2' = 0·3819$ (Authors) $e'_{ex.} = -0·06345$ at 25°, $-0·06645$ at 35°.						
0·3819	0	−0·03709	0·504	0	−0·03834	0·494
0·3112	0·00764	−0·03732	0·508	0·00803	−0·03846	0·495
0·2086	0·02275	−0·03762	0·511	0·02315	−0·03926	0·505
0·1401	0·03666	−0·03904	0·531	0·03796	−0·04031	0·519
0·1000	0·04782	−0·04088	0·557	0·04934	−0·04236	0·546
0·0788	0·05562	−0·04226	0·577	0·05712	−0·04408	0·570
0·0626	0·06339	−0·04341	0·594	0·06510	−0·04530	0·588
0·0500	0·07101	−0·04429	0·608	0·07292	−0·04638	0·604
0·0325	0·08568	0·04632	0·641	0·08820	−0·04830	0·634
0·0209	0·10102	−0·04798	0·669	0·10399	−0·05000	0·662
0·0187	0·10461	−0·04859	0·680	0·10779	−0·05070	0·673
0·0098	0·12698	−0·05112	0·726	0·13070	−0·05350	0·722
0·0088	0·13075	−0·05165	0·736	0·13462	−0·05398	0·731
0·0078	0·13474	−0·05216	0·746	0·13878	−0·05452	0·741
0·0071	0·13787	−0·05263	0·755	0·14207	−0·05503	0·751
0·0063	0·14202	−0·05818	0·766	0·14621	−0·05559	0·761
0·0050	0·15010	−0·05400	0·783	0·15453	−0·05647	0·778
0·0041	0·15682	−0·05488	0·801	0·16160	−0·05740	0·797
0·0031	0·16665	−0·05585	0·821	0·17158	−0·05842	0·818
0·0019	0·18408	−0·05732	0·853	0·18962	−0·05998	0·850
0·0010	0·20730	−0·05800	0·886	0·21356	−0·06154	0·884

TABLE IV.

Zinc iodide.

$M_2' = 0{\cdot}2499$ (Baxter).

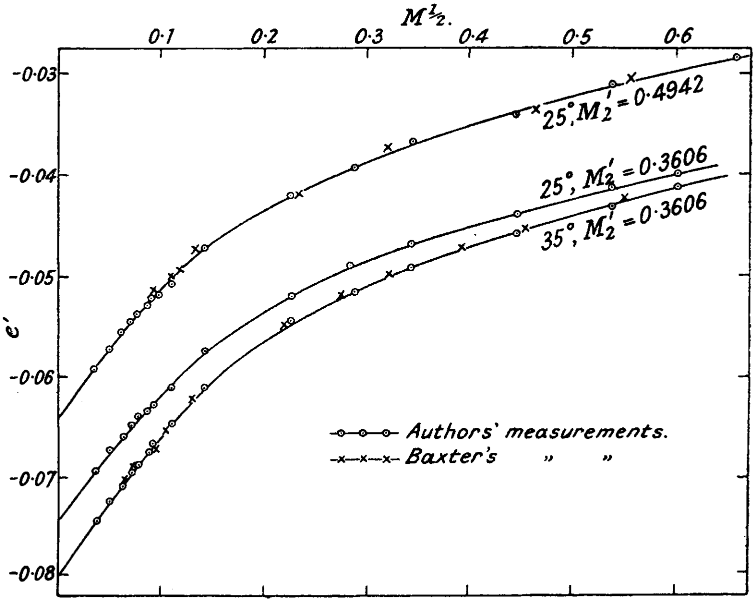
M_2.	$e_{25°}$.	$e'_{25°}$.	$f_{25°}$.	M_2.	$e_{25°}$.	$e'_{25°}$.	$f_{25°}$.
0·2499	0	—0·0534	1·995	0·0470	0·1095	—0·0082	0·618
0·1938	0·0222	—0·0410	1·446	0·0249	0·1307	—0·0109	0·674
0·1318	0·0462	—0·0319	1·142	0·0166	0·1448	—0·0130	0·700
0·1210	0·0508	—0·0306	1·104	0·0114	0·1570	—0·0154	0·743
0·0986	0·0634	—0·0258	0·973	0·0081	0·1680	—0·0135	0·783
0·0765	0·0798	—0·0198	0·817	0·0051	0·1848	—0·0190	0·808

$M_2' = 0{\cdot}02631$ (Authors) : $e'_{ex.} = -0{\cdot}02320$ at 25°, $-0{\cdot}0243$ at 35°.

M_2.	$e_{25°}$.	$e'_{25°}$.	$f_{25°}$.	$e_{35°}$.	$e'_{35°}$.	$f_{35°}$.
0·2631	0	—0·05144	2·082	0	—0·05319	2·067
0·2216	0·01270	—0·04535	1·777	0·01311	—0·04691	1·764
0·1943	0·02246	—0·04067	1·573	0·02322	—0·04205	1·562
0·1678	0·03198	—0·03678	1·422	0·03308	—0·03801	1·411
0·1339	0·04718	—0·03027	1·201	0·04881	—0·03126	1·191
0·1220	0·05296	—0·02808	1·135	0·05476	—0·02903	1·127
0·1002	0·06544	—0·02319	1·002	1·06770	—0·02394	0·9910
0·0822	0·07839	—0·01786	0·871	0·08124	—0·01827	0·859
0·0687	0·08966	—0·01344	0·776	0·09296	—0·01374	0·767
0·0484	0·11092	—0·00578	0·636	0·11489	—0·00571	0·627
0·0265	0·13131	—0·00849	0·683	0·13593	—0·00867	0·675
0·0169	0·14652	—0·01058	0·721	0·15158	—0·01092	0·716
0·0123	0·15761	—0·01169	0·742	0·16225	—0·01235	0·741
0·0100	0·16480	—0·01260	0·760	0·17016	—0·01324	0·758
0·0082	0·17164	—0·01336	0·775	0·17738	—0·01402	0·773
0·0075	0·17475	—0·01375	0·783	0·18036	—0·01444	0·781
0·0068	0·17818	—0·01412	0·790	0·18398	—0·01482	0·788
0·0059	0·18301	—0·01469	0·802	0·18898	—0·01542	0·800
0·0050	0·18881	—0·01529	0·814	0·19497	—0·01603	0·813
0·0042	0·19493	—0·01587	0·827	0·20002	—0·01662	0·825
0·0034	0·20243	—0·01657	0·842	0·20718	—0·01736	0·840
0·0022	0·21788	—0·01782	0·870	0·22290	—0·01867	0·868

FIG. 2.

Zinc Choride.



In the extrapolation method described above, measurements in very dilute solutions, where the experimental accuracy is least, have most weight, and to obtain accurate extrapolation we made a large number of readings between 0·001 and 0·01M. Consistent results could not be obtained with more dilute solutions, the E.M.F. falling off rapidly with time. The results are given in the tables and Figs. 2, 3 and 4. The extrapolation was carried out on a large-scale graph. The activity coefficients below 0·001M were calculated from the simple Debye–Hückel equation : $\log f = 0{\cdot}50 z_+ z_- \sqrt{I}$; where z_+, z_- are the valencies of the ions with correct sign, and I is the ionic strength. From the extrapolated value of e' the value of e' for each concentration was calculated and the points were found tô lie increasingly well on the extrapolated curve as infinite dilution was approached. The activity coefficients are given correct to three decimal places.

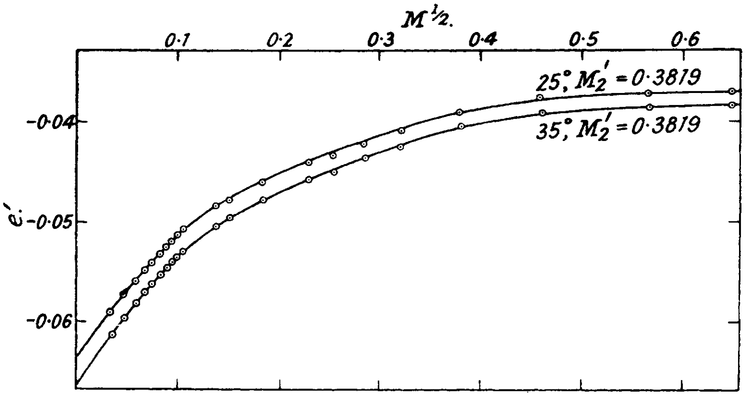


FIG. 3.
Zinc Bromide.

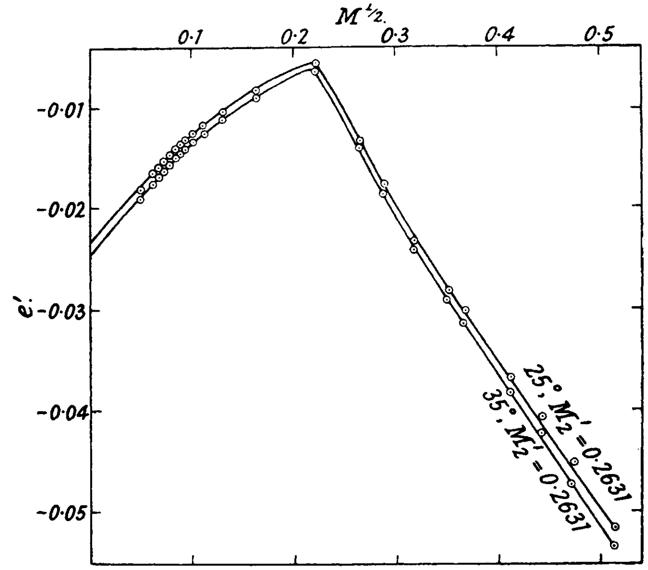


FIG. 4.
Zinc Iodide.

DISCUSSION.

The simple Debye–Hückel equation

$$\log f = A z_+ z_- \sqrt{I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where A is a constant depending on the solvent and temperature, does not give satisfactory results at concentrations greater than 0·001M. A more accurate equation includes a parameter " a," the distance of closest approach of the ions :

$$\log f = z_+ z_- A\sqrt{I}/(1 + \mathrm{a}B\sqrt{I}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

A and B being constants for a given solvent and temperature. At 25° in water :

$$\log f = 0{\cdot}50\, z_+ z_- \sqrt{I}/(1 + 0{\cdot}328\ 10^8 \mathrm{a}\sqrt{I}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From the activity coefficients found by the extrapolation method values of " a " can be calculated from (8), and these should be reasonable (about 10^{-8} cm.) and remain constant over a fair concentration range. The following values of " a " were found :

Zinc chloride.

M	0·0182	0·0138	0·0123	0·0116	0·0081	0·0070	0·0058	0·005	0·0047	0·0035	0·0012
a, A.	2·41	2·13	3·04	2·28	1·54	2·38	2·25	2·14	5·22	0·81	0·86

Zinc bromide.

M	0·0125	0·0098	0·0090	0·0078	0·0063	0·0041	0·0031	0·0017	0·0010
a, A.	4·78	4·14	4·60	4·02	5·52	4·13	3·56	1·88	2·31

Zinc iodide.

M	0·0123	0·0100	0·0082	0·0075	0·0068	0·0059	0·0050	0·0042	0·0034	0·0022
a, A.	8·76	8·22	7·60	7·49	7·26	7·12	6·87	6·61	6·49	5·71

These vary rapidly with concentration even in dilute solutions, and it is known that the activity coefficients of some bi-univalent type electrolytes may give negative values of " a " in dilute solutions (Partington and Stonehill, *loc. cit.*). Several attempts have been made to improve the agreement between the Debye–Hückel theory and the experimental results. Hückel introduced a semi-empirical constant C to take into account the supposed variation in dielectric constant of the solution with concentration :

$$\log f = z_+z_-A\sqrt{I}/(1 + aB\sqrt{I}) - CI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This equation has been successfully used with alkali chlorides and hydrogen chloride (MacInnes and Brown, *J. Amer. Chem. Soc.*, **1935**, **57**, **1356**; Harned and Ehlers, *ibid.*, **1933**, **35**, 2149), but we find that it does not hold for zinc chloride. The equation was tested by plotting $\delta = \log f$ (obs.) $-\log f$ [calc. from (8)] against I with values of " a " from 0 to 5 A. If (9) is correct, the plot for some value of " a " should be a straight line of slope C passing through the origin. The curves obtained were not linear for any positive value of " a." A correction term $C\sqrt{I}$ was also found by Baxter to give unsatisfactory results. La Mer, Gronwall, and Sandved (*Physikal. Z.*, 1928, **29**, 358; cf. *Nature*, **1931**, **128**, 499) attributed the disagreement between experiment and the simple Debye–Hückel theory to the use of a linear extrapolation to an exponential function in the determination of (7). A more complete solution of the Poisson–Boltzman equation for the case of symmetrical electrolytes gave an equation which agrees very well with the experimental results. La Mer, Gronwall, and Greiff (*loc. cit.*) extended the theory to unsymmetrical electrolytes, *i.e.*, electrolytes having ions of different valencies, and obtained the equation :

$$\ln f = z_+z_-\Big[\frac{1}{10^8\mathrm{a}}\mathrm{B}_1(x) + \frac{1}{(10^8\mathrm{a})^2}10^2(z_+ + z_-)^2\mathrm{B}_2(x) - \frac{1}{(10^8\mathrm{a})^3}10^3$$

$$(z_+^2 + z_+z_- + z_-^2)(z_+ + z_-)^2\mathrm{B}_3{}^*(x) - \frac{1}{(10^8\mathrm{a})^3}\cdot 10^3(z_+^2 + z_+z_- + z_-^2)\,.\,\mathrm{B}_3(x)\Big] \quad . \quad (10)$$

$$\text{where } \mathrm{B}_1(x) = \frac{10^8\boldsymbol{e}^2}{D\boldsymbol{k}T}\frac{1}{2}\cdot\frac{x}{1 + x}$$

$$\mathrm{B}_2(x) = \left(\frac{10^8\boldsymbol{e}^2}{D\boldsymbol{k}T}\right)^2\cdot 10^2[\tfrac{1}{2}\mathrm{X}_2(x) - \mathrm{Y}_2(x)]$$

$$\mathrm{B}_3{}^*(x) = \left(\frac{10^8\boldsymbol{e}^2}{D\boldsymbol{k}T}\right)^3\cdot 10^3[\tfrac{1}{2}\mathrm{X}_3{}^*(x) - 2\mathrm{Y}_3{}^*(x)]$$

$$\mathrm{B}_3(x) = \left(\frac{10^8\boldsymbol{e}^2}{D\boldsymbol{k}T}\right)^3\cdot 10^3[\tfrac{1}{2}\mathrm{X}_3(x) - 2\mathrm{Y}_3(x)]$$

$x = \kappa$ " a " where $1/\kappa$ is the " radius of the ion atmosphere," as in the Debye–Hückel theory. With the values of the constants $\boldsymbol{N} = 6{\cdot}061 \times 10^{23}$, $\boldsymbol{k} = 1{\cdot}372 \times 10^{-16}$, $\boldsymbol{e} = 4{\cdot}774 \times 10^{-10}$, and Wyman's (*Physical Rev.*, 1930, **35**, 623) value of D, the dielectric constant of water : $D_{t^\circ} = 78{\cdot}54\,[1 - 0{\cdot}00460\,(t - 25) + 0{\cdot}0000088\,(t - 25)^2]$, equation (10) after conversion into common logarithms reduces to

$$-\log f = 2[A\frac{1}{10^8\mathrm{a}}\cdot\frac{x}{1 + x} + B\frac{1{\cdot}10^2}{(10^8\mathrm{a})^2}\cdot[\tfrac{1}{2}\mathrm{X}_2(x) - \mathrm{Y}_2(x)]$$

$$- C\frac{3}{(10^8\mathrm{a})^3}\cdot 10^3[\tfrac{1}{2}\mathrm{X}_3{}^*(x) - 2\mathrm{Y}_3{}^*(x)] - \frac{C9}{(10^8\mathrm{a})^3}\cdot 10^3[\tfrac{1}{2}\mathrm{X}_3(x) - 2\mathrm{Y}_3(x)] \quad . \quad (11)$$

The values of the constants are (Baxter, *loc. cit.*) :

Temp.	*A.*	*B.*	*C.*	$\kappa \times 10^8$.
25°	1·5407	0·21862	0·15511	0·3287
35	1·5621	0·22470	0·16162	0·33097

The values of the functions $10^2[\frac{1}{2}\mathrm{X}_2(x) - \mathrm{Y}_2(x)]$ and $10^3[\frac{1}{2}\mathrm{X}_3(x) - 2\mathrm{Y}_3(x)]$ are tabulated for various values of x by La Mer, Gronwall, and Sandved (*loc. cit.*), and those of $10^3[\frac{1}{2}\mathrm{X}_3{}^*(x) - 2\mathrm{Y}_3{}^*(x)]$ by La Mer, Gronwall, and Greiff (*loc. cit.*). This equation was applied to the E.M.F. measurements as follows, the method being similar to that used by La Mer, Gronwall, and Greiff, La Mer and Cowperthwaite (*J. Amer. Chem. Soc.*, **1931**, **53**, **4333**), and La Mer and Parks (*ibid.*, p. 2040).

The E.M.F. is given by $e = C'$ ($\log \mathrm{M}_2'f_2' - \log \mathrm{M}_2f_2$) where $C' = 2{\cdot}303 \times 3\boldsymbol{R}T/2\boldsymbol{F}$ and hence

$$e/C' + \log \mathrm{M}_2 + \log f_2 = \log \mathrm{M}_2'f_2' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

A likely value of " a " was assumed, and $\log f_2$ calculated from (11) for each molarity within the range of validity of the equation (up to $\sqrt{I} = 0{\cdot}1$). The values of f_2 for " a " = 3·7A. are given in Table VI, col. 4. The values of f_2 and e for each molarity were substituted in equation (12) and a series of values of $\mathrm{M}_2'f_2'$ were found. In the case of zinc chloride the process was repeated with " a " equal to 3·5, 3·6, 3·7, 3·8 and 3·9 A., and the value of " a " which gave the most constant value of $\mathrm{M}_2'f_2'$ was taken as correct. A graphical method was used to find this constant value of $\mathrm{M}_2'f_2'$. The mean value of $\mathrm{M}_2'f_2'$ was found for each value of " a," and the total deviation, irrespective of sign, was plotted against the corresponding " a " value. The graph consisted of two intersecting straight lines, and the abscissa of the point of intersection gave 3·7 A. as the most probable value of " a." The values of f_2 and M_2'/f_2' for various values of " a " are in Table V.

TABLE V.

Zinc chloride : E.M.F.'s from Table I and various values of " a " being used.

	a = 3·5 A.			a = 3·6 A.		
M.	f_2, calc.	M_2'/f_2'.	$\delta \times 10^4$.	f_2, calc.	M_2'/f_2'.	$\delta \times 10^4$.
0·0083	0·7201	0·1873	13	0·7224	0·1879	11
0·0070	0·7369	0·1877	9	0·7387	0·1887	3
0·0058	0·7551	0·1886	0	0·7561	0·1888	2
0·0050	0·7691	0·1884	2	0·7702	0·1887	3
0·0047	0·7731	0·1890	4	0·7750	0·1894	4
0·0035	0·7982	0·1901	15	0·7995	0·1905	15
0·0023	0·8305	0·1892	6	0·8314	0·1894	4
0·0012	0·8724	0·1888	2	0·8730	0·1889	1

a = 3·5 A.: Average $M_2'/f_2' = 0·1886$. Total $\delta = 0·0051$.

a = 3·6 A.: Average $M_2'/f_2' = 0·1890$. Total $\delta = 0·0043$.

	a = 3·7 A.			a = 3·8 A.			a = 3·9 A.		
M.	f_2, calc.	M_2'/f_2'.	$\delta \times 10^4$.	f_2, calc.	M_2'/f_2'.	$\delta \times 10^4$.	f_2, calc.	M_2'/f_2'.	$\delta \times 10^4$.
0·0083	0·7244	0·1884	8	0·7265	0·1890	5	0·7285	0·1894	4
0·0070	0·7406	0·1887	5	0·7425	0·1895	0	0·7442	0·1895	3
0·0058	0·7578	0·1892	0	0·7597	0·1897	2	0·7612	0·1896	2
0·0050	0·7722	0·1892	0	0·7725	0·1892	3	0·7739	0·1895	3
0·0047	0·7749	0·1893	1	0·7778	0·1890	5	0·7791	0·1904	6
0·0035	0·8005	0·1904 *	12	0·8204	0·1912	17	0·8032	0·1915	17
0·0023	0·8326	0·1897	5	0·8332	0·1899	4	0·8341	0·1901	3
0·0012	0·8736	0·1890	2	0·8740	0·1891	4	0·8746	0·1892	6

a = 3·7 A.: Average $M_2'/f_2' = 0·1892$. Total $\delta = 0·0033$.

a = 3·8 A.: Average $M_2'/f_2' = 0·1895$. Total $\delta = 0·0040$.

a = 3·9 A.: Average $M_2'/f_2' = 0·1899$. Total $\delta = 0·0044$.

* If this value is omitted the average becomes 0·1891.

The mean value of M_2'/f_2' for " a " = 3·7 A. was used in equation (12) to calculate the activity coefficients over the whole concentration range, and the results are given in Table VII, col. 5.

The results for zinc bromide and iodide were treated in the same way. The La Mer equation was also applied to the measurements at 35°. The following values of " a " were found : zinc chloride 3·7 A., zinc bromide 4·8 A., zinc iodide 6·1 A.

This method is considerably more accurate than the graphical extrapolation method (see p. 162) since it uses results over a greater concentration range. As we had paid much attention to solutions between 0·01 and 0·001 M, a large number of measurements were available. For purpose of comparison with previous work, the activity coefficients of zinc chloride at 25° were expressed on the molal scale, and the values at round molalities are given in Table VII together with those of Scatchard and Tefft and those calculated by Getman from Horsch's measurements.

TABLE VI.

Activity coefficients of zinc chloride at 25°.

	f_{25° from extrapolation method.		f_{25° calc. from La Mer's equation and
M.	$M_2' = 0·4942$.	$M_2' = 0·3606$.	E.M.F.'s.
0·4942	0·382	—	0·383
0·4317	0·387	—	0·388
0·2886	0·417	0·417	0·418
0·1992	0·451	0·447	0·451
0·1162	0·484	0·484	0·485
0·0800	0·517	0·515	0·517
0·0500	0·558	0·559	0·560
0·0200	0·639	0·642	0·641
0·0116	0·700	0·700	0·701

	f_{25° from extrapolation method.			f_{25° calc. from La Mer's equation and
M.	$M_2' = 0·4942$.	$M_2' = 0·3606$.	f_{25° calc. from (12).	E.M.F.'s.
0·0083	0·728	0·728	0·724	0·727
0·0070	0·742	0·741	0·751	0·742
0·0058	0·756	0·757	0·758	0·757
0·0050	0·771	0·772	0·772	0·772
0·0047	0·773	—	0·775	0·774
0·0035	0·794	0·794	0·800	0·794
0·0023	0·827	0·827	0·830	0·830
0·0012	0·873	0·872	0·874	0·874

At 35°

m.	*f*, extrapn. method.	*f*, calc. from La Mer's equation and E.M.F.'s.	*m.*	*f*, extrapn. method.	*f*, calc. from (11).	*f*, calc. from La Mer's equation and E.M.F.'s.	*m.*	*f*, extrapn. method.	*f*, calc. from (11).	*f*, calc. from La Mer's equation and E.M.F.'s.
0·3606	0·373	—	0·0757 *	0·490	—	0·490	0·0081 *	0·725	0·722	0·721
0·3014 *	0·386	0·387	0·0500	0·524	—	0·526	0·0070	0·735	0·736	0·737
0·2886	0·381	0·392	0·0488 *	0·531	—	0·535	0·0058	0·752	0·753	0·754
0·2048 *	0·415	0·416	0·0254 *	0·604	—	0·605	0·0052 *	0·764	0·764	0·760
0·1992	0·421	0·422	0·0200	0·625	—	0·626	0·0050	0·768	0·767	0·770
0·1524 *	0·436	0·437	0·0183 *	0·633	—	0·634	0·0038 *	0·790	0·790	0·791
0·1162	0·460	0·461	0·0116	0·682	—	0·684	0·0035	0·793	0·797	0·794
0·1020 *	0·467	0·467	0·0106 *	0·691	—	0·689	0·0023	0·824	0·829	0·828
0·0800	0·488	0·488	0·0083	0·723	0·719	0·725	0·0012	0·873	0·871	0·872

TABLE VII.

Zinc chloride.

At 25°.

m.	γ(Horsch, calc. by Getman).	γ(Scatchard and Tefft).	γ(Baxter).	γ(Authors).	*m.*	γ(Horsch, calc. by Getman).	γ(Scatchard and Tefft).	γ(Baxter).	γ(Authors).
0·5	—	0·376	0·382	0·378	0·02	0·619	0·642	0·636	0·641
0·4	—	0·393	0·396	0·391	0·01	0·680	0·708	0·709	0·710
0·3	—	0·415	0·417	0·413	0·005	0·723	0·767	—	0·772
0·2	—	0·448	0·447	0·449	0·002	0·797	0·838	—	0·835
0·1	0·486	0·502	0·495	0·499	0·001	0·857	0·881	—	0·883
0·05	0·533	0·556	0·547	0·559	0·0005	0·880	—	—	—

TABLE VIII.

Zinc bromide.

	f from extrapn. method.		*f* calc. from La Mer's equation and E.M.F.'s.			*f* from extrapn. method.		*f* calc. from (11).	*f* calc. from La Mer's equation and E.M.F.'s.	
M.	Baxter.	Authors.	Baxter.	Authors.	M.	Baxter.	Authors.		Baxter.	Authors.
					At 25°.					
0·3819	—	0·504	—	0·504	0·0200	—	—	—	0·670	—
0·3118	0·508	—	—	—	0·0187	—	0·680	—	—	0·681
0·3112	—	0·508	—	0·508	0·0125	0·712	—	—	—	—
0·2086	—	0·511	—	0·511	0·0100	—	—	—	0·727	—
0·1999	0·515	—	—	—	0·0098	—	0·726	0·728	—	0·729
0·1401	—	0·531	—	0·531	0·0090	0·740	—	—	—	—
0·1388	0·535	—	—	—	0·0088	—	0·736	0·737	—	0·735
0·1000	—	0·557	0·553	0·557	0·0078	—	0·746	0·748	—	0·747
0·0959	0·562	—	—	—	0·0071	0·756	0·755	0·756	—	0·756
0·0804	0·571	—	—	—	0·0063	—	0·766	0·766	—	0·766
0·0788	—	0·577	—	0·577	0·0050	0·786	0·783	0·785	0·771	0·783
0·0626	—	0·594	—	0·593	0·0041	—	0·801	0·800	—	0·802
0·0500	—	0·608	0·610	0·610	0·0031	0·827	0·821	0·820	—	0·823
0·0474	0·614	—	—	—	0·0020	—	—	—	0·843	—
0·0325	—	0·641	—	0·641	0·0019	—	0·853	0·852	—	0·853
0·0224	0·662	—	—	—	0·0017	0·854	—	—	—	—
0·0209	—	0·669	—	0·669	0·0010	0·887	0·886	0·888	—	0·887
					At 35°					
0·3819	—	0·494	—	0·494	0·0200	—	—	—	0·661	—
0·3118	0·499	—	—	—	0·0187	—	0·673	—	—	0·673
0·3112	—	0·495	—	0·496	0·0125	0·711	—	—	—	—
0·2086	—	0·505	—	0·506	0·0100	—	—	—	0·721	—
0·1999	0·515	—	—	—	0·0098	—	0·722	0·723	—	0·724
0·1401	—	0·519	—	0·519	0·0090	0·747	—	—	—	—
0·1388	0·527	—	—	—	0·0088	—	0·731	0·733	—	0·730
0·1000	—	0·546	0·544	0·547	0·0078	—	0·741	0·743	—	0·741
0·0959	0·556	—	—	—	0·0071	0·753	0·751	0·751	—	0·751
0·0804	0·570	—	—	—	0·0063	—	0·761	0·762	—	0·763
0·0788	—	0·570	—	0·571	0·0050	0·782	0·778	0·780	0·766	0·779
0·0626	—	0·588	—	0·588	0·0041	—	0·797	0·796	—	0·796
0·0500	—	0·604	0·603	0·605	0·0031	0·826	0·818	0·817	—	0·819
0·0474	0·614	—	—	—	0·0020	—	—	—	0·836	—
0·0325	—	0·634	—	0·634	0·0019	—	0·850	0·849	—	0·851
0·0224	0·661	—	—	—	0·0017	0·847	—	—	—	—
0·0209	—	0·662	—	0·663	0·0010	0·886	0·884	0·885	—	0·885

No data of the activity coefficients of zinc chloride at 35° are available, but the values now found, together with those of zinc bromide and iodide, are in good agreement with Baxter's figures. The results for the iodide agree with Bates's below 0·02 M.

The La Mer equation, which has been successfully applied to a number of strong electrolytes, gives good agreement with experimental results for zinc chloride and bromide, and hence we infer that these salts behave as typical strong electrolytes in the range of molarity studied. No assumption of incomplete dissociation is necessary. Zinc iodide, however, has activity coefficients higher than those calculated by the equation, but the difference becomes smaller as infinite dilution is approached. This would be explained if zinc iodide is not completely dissociated except in rather dilute solutions. This is borne out by the high values of the activity coefficients at higher concentrations. The results may be explained by the formation of a complex ion $(ZnI_3)^-$ or $(ZnI_4)^=$. The complex ion of cadmium iodide was shown to be $(CdI_3)^-$ (Bates and Vosburgh, *J. Amer. Chem. Soc.*, 1938, **60**, 137). The existence of this type of ionisation would account for the shape of the graph of *e* against $-\log$ M (Fig. 5).

FIG. 5.

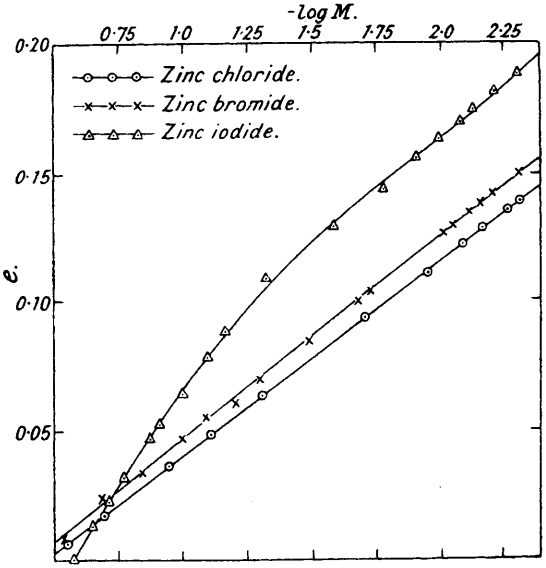


TABLE IX.

Zinc iodide.

At 25°.

M.	*f* by extrapn. Baxter.	*f* by extrapn. Authors.	*f* calc. from La Mer's equation and E.M.F.'s.	*f* (Bates).
0·2631	—	2·082	2·034	—
0·2499	1·995	—	—	—
0·2216	—	1·777	1·736	—
0·1988	—	—	—	0·567
0·1943	—	1·573	1·537	—
0·1938	1·446	—	—	—
0·1678	—	1·422	1·390	—
0·1339	—	1·201	1·173	—
0·1318	1·142	—	—	—
0·1220	—	1·135	1·161	—
0·1210	1·104	—	—	—
0·1002	—	1·002	0·976	—
0·0995	—	—	—	0·580
0·0986	0·973	—	—	—
0·0822	—	0·871	0·850	—
0·0765	0·817	—	—	—
0·0687	—	0·776	0·759	—
0·0500	—	—	—	0·621
0·0484	—	0·636	0·619	—
0·0470	0·618	—	—	—
0·0300	—	—	—	0·659

M.	*f* by extrapn. Baxter.	*f* by extrapn. Authors.	*f* calc. by (11).	*f* calc. from La. Mer's equation and E.M.F.'s.	*f* (Bates).
0·0265	—	0·683	—	0·669	—
0·0249	0·674	—	—	—	—
0·0200	—	—	—	—	0·690
0·0169	—	0·721	—	0·705	—
0·0166	0·700	—	—	—	—
0·0123	—	0·742	0·725	0·727	—
0·0114	0·743	—	—	—	—
0·0100	—	0·760	0·742	0·742	0·746
0·0082	—	0·775	0·758	0·758	—
0·0080	—	—	—	—	0·761
0·0075	—	0·783	0·765	0·764	—
0·0068	—	0·790	0·773	0·771	—
0·0059	—	0·802	0·783	0·784	—
0·0051	0·808	—	—	—	—
0·0050	—	0·814	0·795	0·796	0·799
0·0042	—	0·827	0·808	0·808	—
0·0034	—	0·842	0·822	0·822	—
0·0030	—	—	—	—	0·833
0·0022	—	0·870	0·850	0·850	—
0·0020	—	—	—	—	0·851

At 35°.

M.	*f* by extrapn. (Authors).	*f* calc. from La Mer's equation and E.M.F.'s.	*f* (Bates).
0·2631	2·067	2·012	—
0·2216	1·764	1·719	—
0·1988	—	—	0·558
0·1943	1·562	1·521	—
0·1678	1·411	1·375	—
0·1339	1·191	1·161	—
0·1220	1·127	1·097	—
0·1002	0·991	0·966	—
0·0995	—	—	0·572
0·0822	0·859	0·838	—
0·0687	0·767	0·746	—
0·0500	—	—	0·613
0·0484	0·627	0·611	—
0·0300	—	—	0·652
0·0265	0·675	0·659	—

M.	*f* by extrapn. (Authors).	*f* calc. from (11).	*f* calc. from La Mer's equation and E.M.F.'s.	*f* (Bates).
0·0200	—	—	—	0·687
0·0169	0·716	—	0·697	—
0·0123	0·741	0·721	0·721	—
0·0100	0·758	0·738	0·738	0·741
0·0082	0·773	0·753	0·751	—
0·0080	—	—	—	0·757
0·0075	0·781	0·761	0·762	—
0·0070	—	—	—	0·768
0·0068	0·788	0·769	0·767	—
0·0059	0·800	0·779	0·780	—
0·0050	0·813	0·792	0·792	0·796
0·0042	0·825	0·804	0·803	—
0·0034	0·840	0·819	0·821	—
0·0022	0·868	0·847	0·848	—

If the iodide dissociated normally, the slope of this curve should be 0·0887. The slope of the iodide curve is about 0·08 over the range from 0·025 M to the highest dilution. The form of the curve can also be accounted for by assuming incomplete dissociation.

Evidence as to the nature of the complex ions formed could be obtained by a determination of the transport numbers, experiments on which are nearing completion. If the ions Zn^{++} and $(ZnI_3)^-$ are present, on electrolysis zinc is transported into and out of the anode compartment. At high concentrations there may be a gain in the zinc concentration and hence a negative value of the cation transport number. An unstable complex ion will ionise as the concentration decreases and the cation transport number will attain the value expected for a solution containing simple ions. Hence if the ion $(ZnI_3)^-$ is present the cation transport number will increase as the concentration falls. If there is incomplete dissociation, the ion ZnI^+ on migration will carry some iodine into the cathode compartment while free iodide ions will be transported out. The transport number of the anion, measured by the loss of electrolyte in the cathode compartment, will be small, and the cation transport number large. In this case, when the $(ZnI)^+$ ion dissociates on dilution the cation transport number will decrease. As far as is known, no recent measurements have been made of the transport numbers of zinc iodide.

The following results were found by Hittorf (*loc. cit.*) and Kummell (*loc. cit.*) :

Hittorf.			
m	4·725	1·277	0·647
n_c	—0·157	0·273	0·325

Kummell.			
m	0·01952	0·00976	0·00496
n_c	0·398	0·414	0·421

These results, though not very numerous, show that the cation transport number increases as the concentration decreases. This is in agreement with the existence of a complex anion such as $(ZnI_3)^-$ or $(ZnI_4)^=$.

Attention is directed to the simplicity in practical application of the La Mer equation, and it is suggested that apparently anomalous results found by the use of the Debye-Hückel equation in regions of concentration where it is known to fail, cannot give any convincing evidence for incomplete ionisation. Special emphasis is laid on the failure of the extended Debye–Hückel equation (7) or obvious simplifications of it (*e.g.*, $aB \simeq 1$) in quite low concentration ranges.

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