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T H E S I S

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Determination of Activity Coefficients and
Transport Numbers in Strong Solutions of
Zinc Chloride from Electrometric Measurements.

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INTRODUCTION.

In the electrolysis of a salt solution, the quantity of electricity carried by the cations in one direction is proportional to their speed u , and the quantity carried by the anions in the opposite direction is proportional to their speed v . Hence the total current carried is proportional to $u - v$. The fraction of the total current carried by the cation is $\frac{u}{u - v}$; this fraction is called the transference or transport number of the cation. Similarly the transport number of the anion is $\frac{v}{u - v}$. The sum of the anion and cation transport numbers is always equal to unity. There are three methods in use for the determination of transport numbers.

1. Gravimetric or Hittorf Method.

The principle of this method, devised by Hittorf, was to allow a known quantity of electricity, determined in a coulometer, to pass through a solution of known concentration after which the concentrations of the solutions round the electrodes were redetermined. From a knowledge of the change in concentration round either electrode and the quantity of current passed through the cell, the transport numbers of the ions may be calculated.

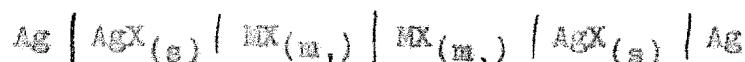
2. Moving Boundary Method.

The idea of measuring ionic velocities by observation of a moving boundary was first used by Lodge (Brit. Assoc. Repts. 1886, p. 389) who endeavoured to follow the movements of certain ions by means of their reactions with chemical indicators. Thus, the

passage through a tube, filled with a conducting gelatine, of barium and chlorine ions was followed by the faint cloudiness caused by each ion reacting with a trace of silver sulphate contained in the gelatine. Steele and Denison (Phil. Trans. A, 205 449, 1906) improved the method of observing the boundary by using the difference in refractive indices of the two solutions. Lately the method has been greatly improved by McInnes and his co-workers so that fairly accurate results are easily obtained.

3. Electromotive Force Method.

The E.M.F. of a concentration cell with transference of the type



where AgX is an insoluble silver salt and Mx a similar salt of the metal M, is given by the expression

$$E_t = n_1 \frac{Z}{Z_1} \frac{RT}{NF} \ln \frac{(a_+)_1}{(a_+)_2}$$

where

n_1 is the transport number of the ion with respect to which the extreme electrodes are non-reversible.

Z the number of ions produced by the ionization of one molecule of the salt.

Z_1 the number of ions for which the cell is non-reversible produced from one molecule of salt.

N the valence of the reversible ion.

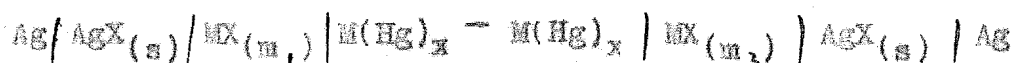
R gas constant.

T absolute temperature.

F the Faraday = 96500 coulombs.

$(a_{\pm})_1$ and $(a_{\pm})_2$ are the mean activities of the ions in the solutions of concentration m and m respectively.

For a corresponding cell without transference of the type



using the same two solutions the E.M.F. is given by the expression

$$E = \frac{Z}{Z_1} \frac{RT}{nF} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

If therefore the E.M.F. of a cell with transport is divided by E.M.F. of the corresponding cell without transference, the transport number of the non-reversible ion is obtained.

The method was at first criticised on the grounds that it gave only the mean transport number over the concentration range used in the cells and not the transport number at any particular concentration. McInnes and Beattie (Jour. Amer. Chem. Soc. 42 1127, 1920) however have overcome this difficulty and have devised a method of calculation whereby the transport number at a particular concentration may be obtained.

When the method was originally suggested by Helmholtz (Ges. Abh. I, 840, II, 979) difficulties arose in the setting up and measurement of the cells without transport. Of late years, however, the method is being used to a much greater extent since concentration cells without transport have become more common. That the method gives reliable results is shown by the following table which gives the transference numbers of lithium chloride obtained by the three methods. The first column gives the molality; the second gives the results obtained by Noyes and Falk (Jour. Amer. Chem. Soc. 33 1436,

using the Hittorf method. The third column gives the results of the moving boundary method obtained by Longworth (Jour. Amer. Chem. Soc. 54, 2741, 1932) and the fourth column those obtained by McInnes and Beattie (loc. cit.) using the E.M.F. method.

<u>m</u>	<u>Hittorf</u>	<u>Moving Boundary</u>	<u>E.M.F.</u>
.01	.332	.330	.334
.02	.328	.326	.327
.05	.320	.321	.318
.10	.313	.317	.311
.20	.304	-	.304
.30	.299	-	.299

Other workers who have used the E.M.F. method for the determination of transport numbers are:-

Jones and Dale (J.A.C.S. 51, 1073, 1929) who measured barium chloride and have deduced an equation for the variation of transference number with concentration;

Lucasse (J.A.C.S. 51, 597, 1929; 47, 743, 1925) who used cadmium chloride and bromide and the alkaline earth chlorides;

McInnes and Beattie (loc. cit.) using lithium chloride;

Carter and Lea (J.Chem. Soc. 127, 487, 1925) who measured transference numbers of concentrated hydrochloric acid.

Variation of Transport Number with Concentration.

In general the transport numbers of the ions depend on the concentration of the solution, but in most cases this dependence does not become pronounced until moderately high concentrations are

reached. This variation at high concentrations may be due to a number of different factors working singly or together.

The most important are

1. Change in Viscosity of the Solution.
2. Hydration of Ions.
3. Formation of Complex Ions.

Consideration of these Factors.

1. The change in transference number may be due to real changes in the velocities of the ions resulting in an alteration of the velocity ratios. These changes do not become pronounced until the concentration is comparatively high when the viscosity of the solution will become fairly high. The close proximity of the ions in strong solutions will also have some effect on their speeds.
2. Hydration of Ions. A number of circumstances have led to the belief that many electrolytes are hydrated in aqueous solution. The latest theory is that each solute molecule is surrounded by sheaths of solvent molecules which vary in number and proximity according to the nature of the electrolyte and the general condition of the solution concerned as regards concentration, temperature, etc..

Amongst the strongest evidence for the hydration theory is that deduced from the results of transference experiments carried out with various salt solutions in the presence of different non-electrolytic reference substances. If at the end of the experiment the ratio of solvent to reference non-electrolyte has changed at the electrodes, then it follows either that the ions have carried

solvent molecules in one direction or they have transported the non-electrolyte in the opposite direction.

Buchbock (Zeits. Phys. Chem. 55, 563, 1906) using hydrochloric acid solutions with resorcinol and mannite at widely different concentrations as the reference non-electrolyte, was the first to obtain satisfactory results in favour of the hydration theory. This was confirmed by Washburn (J.A.C.S. 31, 322, 1909) who added optically active raffinose as a reference substance and measured the optical rotation of the solutions around the electrodes before and after electrolysis. From his results he calculated the change in the amount of water round the electrodes. The formation of ion hydrates has also been supported by the work of:-

Jones and Ota (Amer. Chem. Jour. 22, 5, 1899) from freezing point data.

Jones (Zeits. Phys. Chem. 74, 325, 1910) resumé of general results.

Reisenfeld and Rheinhold (Zeits. Phys. Chem. 66, 672, 1909) by a comparison of ionic volume and ionic mobility.

Washburn (loc. cit.) from transference observations.

Remy (Trans. Farad. Soc. 23, 381, 1927) who calculated the number of water sheaths associated with each ion.

The result of such hydration would be to increase the size of the ion and consequently reduce its mobility. As the cation and anion need not necessarily be hydrated to the same extent the velocity ratios will be changed. In concentrated solutions, owing to the large numbers of ions present, the relative hydration of the ions will decrease, hence a variation in the transference number is to be expected.

3. **Complex Formation.** The suggestion that the abnormal behaviour of certain salts in solution might be attributed to the formation of complex ions was first put forward by Hittorf. In the course of his study on migration he found that the migration ratio of the anion in solutions of many double salts and certain single ones increased rapidly with increase in concentration, and at high concentration became greater than unity. He suggested that this was due to the formation of complex ions which dissociated on dilution.

Various workers have obtained evidence of the formation of complex ions in solutions of zinc salts.

Künseher (Zeit. Anorg. Chem. 41, 337, 1904) investigated solutions of zinc oxalate in ammonium and potassium oxalates, and of zinc hydroxide in sodium hydroxide. In the former case the complex anions $\text{Zn}(\text{C}_2\text{O}_4)_3$ and $\text{Zn}(\text{C}_2\text{O}_4)_2$ were found while the alkaline solutions of zinc hydroxide were shown to contain the zincate ion ZnO_2 .

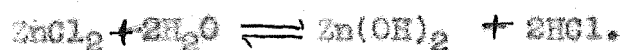
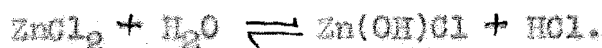
Künne (Ann. Phys. Chem. 64, 655, 1898) showed that zinc sulphate probably contained a complex anion $\text{Zn}(\text{SO}_4)_2$.

Drücker (Zeit. Electrochem. 79, 236, 1912) showed by conductivity, transport number and electromotive force measurements that even in concentrations less than 0.1M. an aqueous solution of zinc chloride contains a complex cation, probably ZnCl .

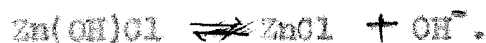
W. Hittorf (Zeits. Phys. Chem. 43, 249, 1903) measured the transport number of zinc chloride and found that of the anion to be 1.241 at a concentration of 4.035 M.. He attributes this high value as being due to complex formation.

It is seen therefore that zinc in aqueous solutions of its salts shows a tendency to form complex ions.

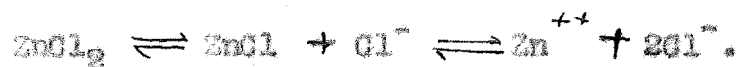
The hydrolysis of zinc chloride may be formulated in two stages. Denham (J. Chem. Soc. 93, 41, 1908)



The oxychloride may then ionize to give the complex cation mentioned by Druker.



The same complex ion would be formed by the first stage ionization of the zinc chloride molecule.



There is a good deal of evidence for the formation of auto-complexes in strong solutions of zinc salts.

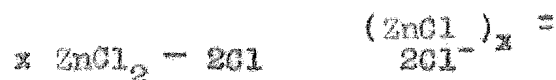
Donnan and Bassett (J. Chem. Soc. 81, 939, 1902) show that in strong solutions of cobalt chloride an auto-complex is formed according to the equation



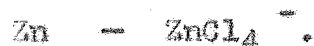
Denham (Zeits. Phys. Chem. 65, 641, 1909) showed from transference number measurements that copper in aqueous and alcoholic solutions of its chloride gave rise to an autocomplex, the formula probably being $\text{Cu}_2\text{Cl}_6^{--}$.

McBain (Zeit. Electrochem. 11, 222, 1905) showed that cadmium iodide contained the complex CdI_3^- .

Hence in strong solutions of zinc chloride the possibility of the formation of an autocomplex must be considered.



If there is a large excess of zinc chloride the following reaction involving the oxychloride may take place.



The formation of such complex anions would tend to decrease the cation transport number until it finally became negative.

ACTIVITY COEFFICIENTS.

In recent years, the attempt to interpret the properties of solutions of strong electrolytes in terms of the degree of dissociation as measured by the conductivity ratio, has been abandoned and instead much effort is being devoted to the exact determination of thermodynamic properties of solutions. Lewis introduced the term "fugacity", which is closely related to vapour pressure and represents the tendency of a species to escape from solution. It is equal to the vapour pressure if the vapour obeys the perfect gas laws. The "activity" (a), of a substance in a given state is the ratio of its fugacity to the fugacity in some state which is chosen as a standard. In the standard state the activity equals unity and for ideal solutions the activity equals the concentration. The fraction $\frac{a}{m}$, where m is the molality, is called the "activity coefficient", of the solution; it may be

regarded as a measure of the extent to which an ion or molecule departs from ideal behaviour.

Activity coefficients were at first only determinable by empirical methods and so appeared to have no special value. Recently, however, Debye and Hückel have found it possible to calculate them on purely theoretical grounds; hence these quantities are beginning to acquire a definite physical significance. Various methods may be used for the determination of activity coefficients such as freezing-point lowering, vapour-pressure lowering, solubility, distribution ratio and electromotive-force measurements. Results obtained from these methods approximate fairly closely to each other. In recent years the electromotive force method has been used very frequently and is now considered to give very accurate results.

The recent hypothesis that strong electrolytes are completely ionized in all concentrations which may be regarded as dilute, has tended to throw some doubt on the question of activity. Noyes (J.A.C.S. 46, 1086, 1924) states that this view of complete ionization will be confirmed if the deviations from ideal behaviour of the ions from that of a perfect solute are accounted for by the treatment of Milner and Debye and Hückel. Their basic idea is that owing to the electrical attraction between oppositely charged ions there are on the average in the neighbourhood of any ion, more ions of unlike than like sign; hence when the solution is diluted, the separation of the ions involves doing work against the electrical attraction and a corresponding increase in the energy content of the solution.

Bray (J.A.C.S. 49, 2372, 1927) compared the activity coefficients of zinc sulphate as derived from the inter-ionic attraction theory of Debye and Huckel with those obtained from E.M.F. data. He found that in extremely dilute solutions the results were in excellent agreement but at higher concentrations the error was much greater than experimental.

Scatchard and Tefft (J.A.C.S. 52, 2272, 1930) measured the activity coefficients of zinc chloride over a concentration range (.01 - 1.4 M) and found marked deviations from the Debye-Huckel theory. They attribute this to incomplete dissociation of the primary ion ZnCl .

One of the most characteristic features of the behaviour of strong salt solutions is the fact that the activity coefficients, decreasing with increasing concentration in the dilute range, pass at higher concentrations through a minimum and thereafter increase rapidly, in some cases to a value greater than unity. The assumption of hydration of the ions has presented itself as the immediate and most plausible explanation of this phenomenon. In a solution of increasing salt concentration the hydration has a double effect, firstly to increase the salt concentration calculated as the mol-fraction by removing the water molecules; then to liberate free ions the activity of which are under consideration, as a result of the increasing dehydrating effect of the salt solution.

Several other possible explanations have been advanced but to all these the same objection applies, namely, that the phenomena observed are certainly of a more complex nature than any one theory assumes.

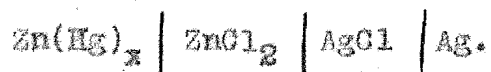
Brönsted (Trans. Farad. Soc. 23, 430, 1927) says that "when hydration, electric Debye-Hückel effects, ionic association, change in dielectric constant etc. unite as they certainly do in influencing the behaviour of ions, any theory, which can explain the observations on a basis of a few or one of these influences, cannot possibly be trusted as a sound solution to the problem."

AIM OF WORK.

The object of the investigation was to determine to what extent complex formation occurred in zinc chloride solutions and the effect on it of concentration and temperature. Also to determine if possible the nature of the complex ions present.

METHOD.

The method of attack was to measure the electromotive forces of two types of cells - with and without liquid junction. In the cell without liquid junction each half cell was measured separately, i.e. measurements were made on the cell

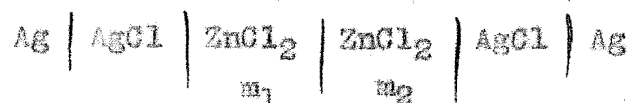


The E.M.F. of the complete cell



was obtained by subtracting the E.M.F.'s of the appropriate half-cells.

Measurements on the following cell with transport were made.



EXPERIMENTAL SECTION.

Preparation of Solutions.

Sticks of AR. zinc chloride were dissolved in water and the precipitate of oxychloride formed was dissolved by the addition of hydrochloric acid. The solution so formed was analysed for both zinc and chlorine content and if these were not equivalent to the formula ZnCl_2 , sufficient hydrochloric acid or zinc oxide was added to make them so. This stock solution did not precipitate oxychloride on dilution and consequently each dilution was analysed for zinc only.

Method of Analysis.

The zinc concentration was determined by titration against standard potassium ferrocyanide solution by the method of Cone and Gady (J.A.C.S. 49, 356, 1927). These workers have shown that the usual external indicator, uranium nitrate, can be replaced by an internal indicator made by dissolving one gram of diphenylbenzidine in 100 c.c. concentrated sulphuric acid. This method was found to give a sharper end point and concordant results.

The chloride concentration was obtained by adding a measured excess of standard silver nitrate and back titrating the excess with standard potassium thiocyanate. All concentrations are expressed as mols. of zinc chloride per 1000 grams water.

ELECTROMOTIVE-FORCE MEASUREMENTS.

Apparatus - General.

The E.M.F.'s of the concentration cells (described below) were measured by the Poggendorf potentiometer method. The cells were

contained in a water thermostat controlled by a mercury-toluene gas regulator. The thermostat kept its temperature to $25^{\circ}\text{C.} \pm 0.1^{\circ}$.

The E.M.F.'s of the concentration cells were compared with that of a standard cadmium cell. The potentiometer was a Leeds and Northrup student potentiometer with a Leeds and Northrup mirror galvanometer to determine the balance point.

DETAILS OF APPARATUS.

Standard Cell.

This was a saturated cadmium cell made up according to the directions given by Spencer ("Phys. Chem." Vol.II p.106) and frequently tested against the laboratory standard (Effley Lab. Newport U.S.A. No. 16723.)

Silver-Silver Chloride Electrodes.

These were prepared according to the directions of Allmand and Hunter (Trans. Farad. Soc. 24, 300, 1928). Squares of platinum gauze 1 cm. side were cathodically coated with silver from a solution containing 7 grams AgNO_3 and 10 grams KCN in 200 c.c. distilled water. A rod of pure silver was used as the anode. The electrolysis was carried out for 24 hours at a current of .01 amps, six electrodes being in parallel. These were washed in boiling distilled water for ten minutes and then chloridized anodically in a .1 N hydrochloric acid solution for half an hour at a current of 7 milliamps per electrode. The final electrode was a dark brown colour.

Before use the six electrodes were measured against one another in a solution of zinc chloride and if any one differed appreciably from the rest it was discarded. These electrodes could be taken from a solution of one concentration and after thorough washing could

be put into another of different concentration without affecting them in any way. After a certain time, however, it was found necessary to remake the electrodes.

Zinc Electrodes.

These consisted of amalgamated zinc rods prepared according to Spencer ("Phys. Chem." Vol. II p. 127). Before use the electrodes were washed with distilled water, amalgamated under dilute sulphuric acid, washed again and dried. These were also measured against each other before use and any differing at all from the rest were discarded.

According to Richards and Dunham (J.A.C.S. 44 678 1922) zinc forms no solid amalgam and hence the potential of the pure zinc should be that of the saturated liquid amalgam. They find this to be nearly the case. Cohen (Zeits. Phys. Chem. 34, 612, 1900) found a difference of .0006 volts.

Cells with Transference.

The type of cell used was a slightly modified form of that used by Lucasse (loc. cit.) and is shown in Fig. 1. In the Lucasse cell the tube D was straight and it was found that it was extremely easy for the solution in B to run into C thus changing the concentration round the electrodes. The tube D was therefore bent downwards, making it more difficult for the solutions to mix.

To make a measurement the tubes A and E were filled with the dilute solution and the electrode put in place. The tube C and the connecting tube D were then filled with the more concentrated solution and the electrode inserted. The mid-vessel B was filled with an approximately one to one mixture of the two solutions

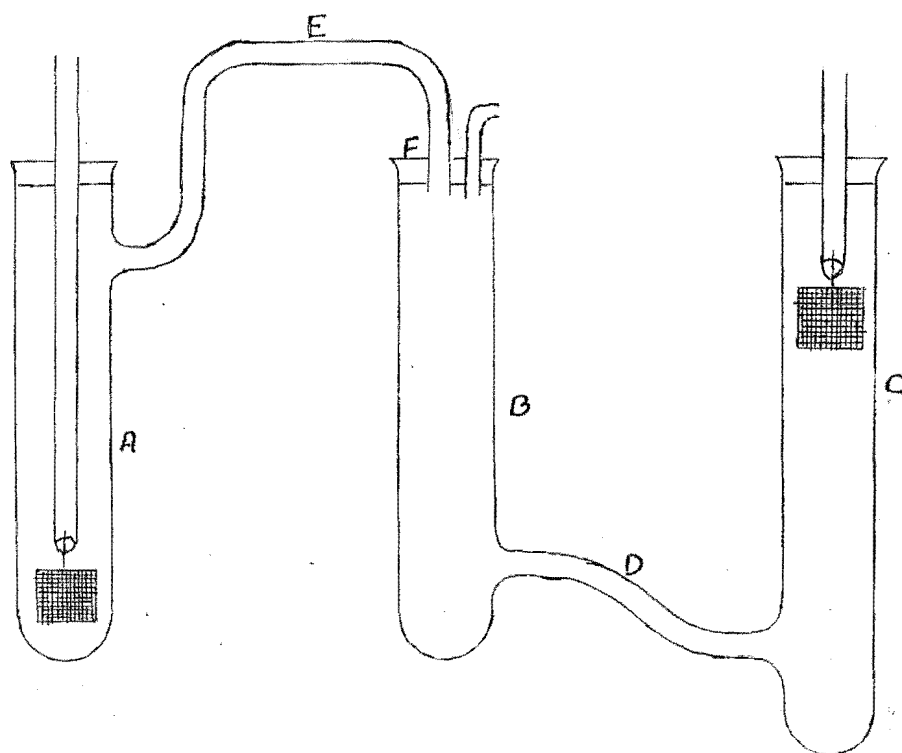
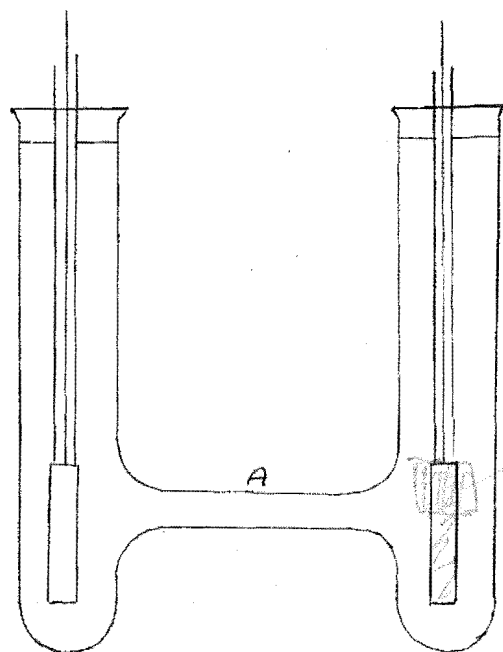


Fig I



same electrode

Fig II

surrounding the electrodes and the two half-cells connected by a stopper at F.

The whole cell was then immersed in the thermostat and left for three hours in order to reach equilibrium after which time six readings were taken at half-hour intervals. The mean of these was accepted as the E.M.F. of the cell. Two such cells were measured on each solution using different electrodes in each. They were found never to differ by more than .2 millivolt.

Cells Without Transport.

The measurement of the half cell



was carried out in the vessel shown in Fig. II. After the electrodes were placed in position the cell was immersed in the thermostat and the same procedure adopted as for the cell with transport.

As dissolved silver chloride is known to affect certain amalgam electrodes it was decided to investigate its effect on zinc amalgam. A tap was inserted at A (Fig. II) in order to keep the solution surrounding the zinc electrode separate from that round the silver - silver chloride electrode. This was kept closed the whole time a measurement was being made. Although measurements were made at several concentrations no measurable difference could be detected from those in which there was no tap. There is conflicting evidence as to the solubility of AgCl in zinc chloride; some workers report it entirely insoluble, while others give it varying degrees of solubility (Mellor, "Inorg. Chem." Vol. III p.397). From the above results it was concluded that if it is soluble, it is

not present in sufficient quantity to have any effect on the zinc electrode.

Dissolved oxygen is also known to affect certain amalgam electrodes in solutions of low concentration, but whether it affected the zinc electrode at the higher concentrations does not appear to have been tested. A series of solutions were made up with boiled distilled water cooled in an atmosphere of nitrogen. Before the zinc electrode was inserted in the cell nitrogen was bubbled through the solution for 2 to 3 hours and then for a further half hour after the electrode had been placed in the solution. Cells prepared in this way showed no difference in E.M.F. from those in which no precautions against oxygen were taken. Hence it was concluded that over the concentration range used, dissolved oxygen had no effect on the zinc electrode.

METHODS OF CALCULATION.

Activity Coefficients.

For a complete concentration cell without transference containing a solution of a bi-univalent electrolyte, the E.M.F., concentration, and activity coefficient are related according to the equation

$$E = \frac{3RT}{2F} \ln \frac{m_1 \gamma_1}{m_2 \gamma_2}$$

Thus if the value of the activity coefficient at one concentration is known from some other measurements the value at the various concentrations can be calculated from E.M.F. data.

Scatchard and Telford (J.A.C.S. 52, 2272, 1930) have determined the activity coefficients of zinc chloride at 25°C. from E.M.F. measurements and give a value .325 for a 1 M solution. This value

was used in the present work and when introduced in the above equation the activity coefficient is given by

$$\log \gamma = 11.27 E - \log m - .4881.$$

No value for the activity coefficient at 35°C. could be found. As it changes very little with temperature in this region (cf. McBain and White, J.A.C.S. 48, 2517, 1926, and Foxton and Shutt, Trans. Farad. Soc. 23, 480, 1927) it was assumed that the value at 35° for a 1 M solution was the same as at 25°, i.e. .325.

The equation for activity coefficients at 35° therefore reduces to

$$\log \gamma = 10.89 E - \log m - .4881.$$

Transference Numbers.

The E.M.F. of a cell with transport of the type measured is given by

$$E_t = n_c \frac{3RT}{2F} \ln \frac{m_1 \gamma_1}{m_2 \gamma_2}$$

where n_c is the zinc ion transport number. This equation, combined with that for a corresponding cell without transport, viz.

$$E = \frac{3RT}{2F} \ln \frac{m_1 \gamma_1}{m_2 \gamma_2}$$

results in the equation

$$n_c = \frac{Et}{E} \dots \dots \dots (1)$$

thus allowing the direct calculation of transport numbers.

Equation (1) however was not used in the calculation as it involves the assumption of a constant transport number over the concentration range used in the cells. The exact equation is $\frac{dEt}{dE}$ (McInnes and Beattie, loc. cit.), where the E.M.F., dE , is measured for an

infinitesimal concentration change, and may be used as follows. Let a curve be drawn such that each point on it has an abscissa which is the E.M.F. of a cell without transport and an ordinate which is the E.M.F. of a cell with transport for the same pair of concentrations. All E.M.F.'s are to be such as would be measured between a solution of one reference concentration and a solution of any other concentration. Each E.M.F. corresponds to a concentration and therefore the transport number at any particular concentration may be found as the slope of the curve at that point. This slope was obtained by determining an equation expressing E_t as a function of E . This on differentiating gave $\frac{dE_t}{dE}$, the transport number.

TABLE II.Activity Coefficients at 25°C.

m	log m	E	E - E _m	γ
.0922	2.9647	1.0848	- .0768	.480
.3334	7.523	1.0425	- .0345	.398
.5476	7.7385	1.0251	- .0171	.381
.7206	7.888	1.0170	- .0090	.356
.8024	7.9064	1.0139	- .0059	.349
.833	7.921	1.0130	- .0050	.343
.9951	7.998	1.0081	- .0001	.326
(1.000)		(1.0080)	(0)	(.325)
1.191	0.076	1.0029	.0051	.312
1.408	0.1485	.9982	.0098	.298
1.792	.253	.9914	.0166	.279
2.065	.315	.9861	.0219	.278
2.584	.412	.9785	.0295	.270
2.738	.434	.9756	.0324	.275
3.136	.496	.9704	.0376	.275
3.463	.540	.9660	.0420	.279
3.563	.552	.9647	.0433	.281
4.174	.621	.9555	.0525	.304
5.007	.700	.9449	.0631	.334
5.102	.708	.9419	.0661	.354
6.230	.795	.9284	.0796	.413
6.577	.818	.9245	.0835	.454
7.560	.879	.9124	.0956	.511
8.912	.950	.8972	.1108	.646

.514

TABLE II (continued)

m		E	E - E _m	γ
10.33	1.014	.8818	.1262	.831
11.20	1.049	.8749	.1331	.916
12.48	1.0962	.8628	.1452	1.127

TABLE III.Activity Coefficients at 35°C.

m	Log m	E	E - E _m	γ
.3273	T.515	1.0385	- .0317	.449
.7553	T.878	1.0160	- .0092	.342
.9917	T.996	1.0069	- .0001	.326
(1.000)		(1.0068)	(0)	(.325)
1.748	0.243	.9914	.0154	.259
2.993	0.476	.9713	.0355	.268
3.987	0.601	.9562	.0506	.290
4.989	0.698	.9425	.0643	.327
5.899	0.771	.9276	.0792	.402
6.884	0.838	.9175	.0893	.444
7.739	0.889	.9046	.1022	.546
9.307	0.969	.8873	.1195	.702

Fig III

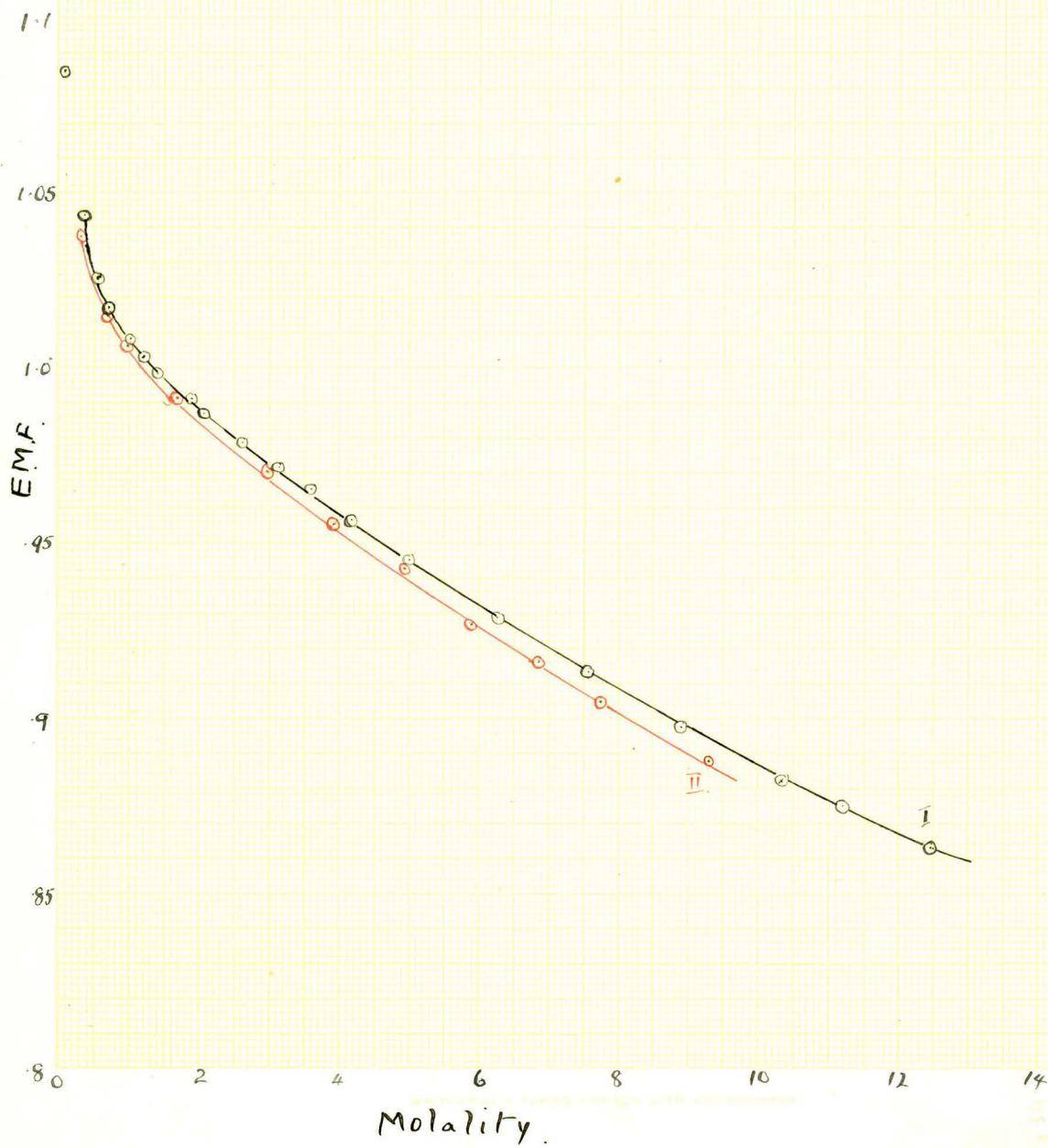
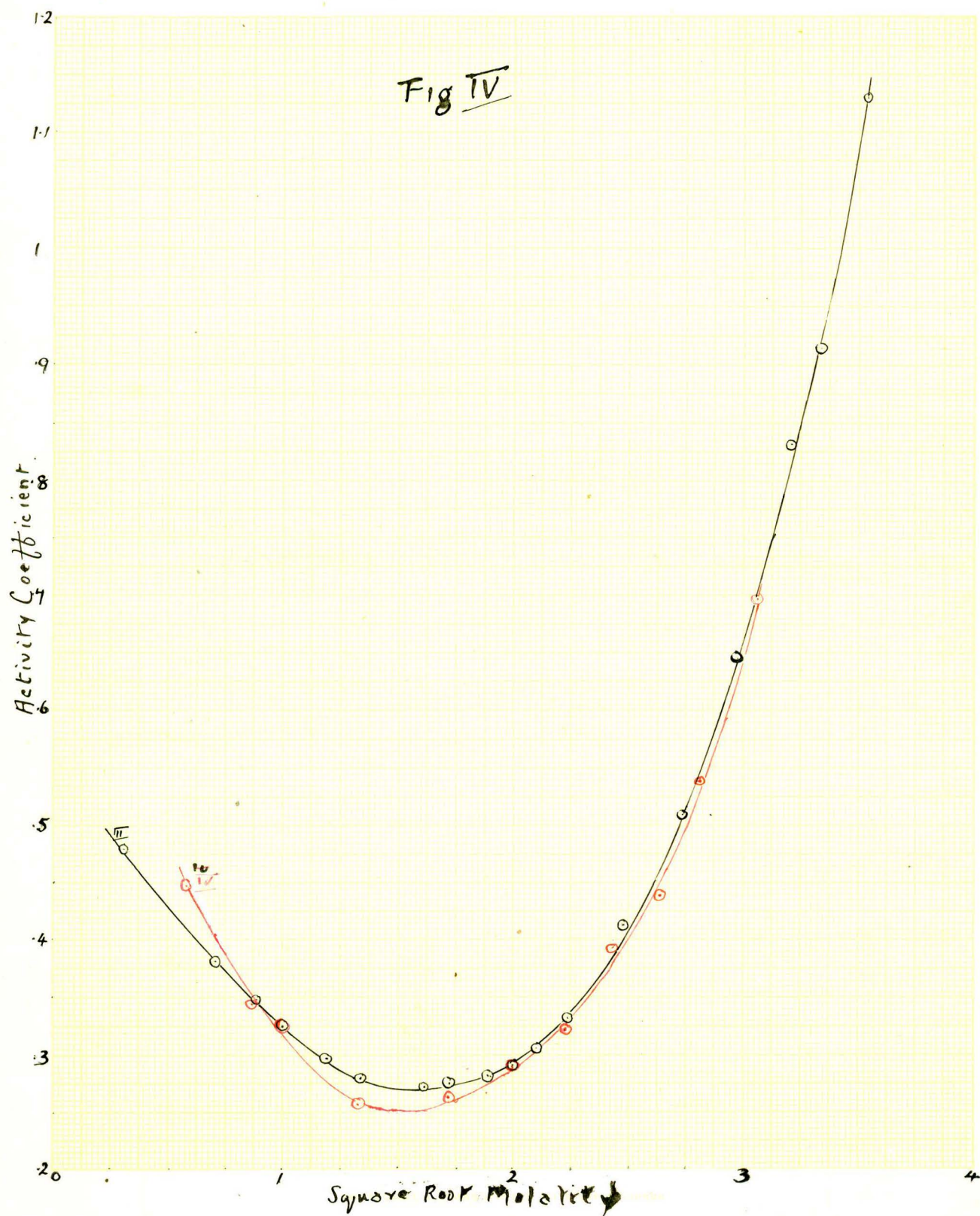


Fig IV



RESULTS.

Cells without Transference and Activity Coefficients.

The results of measurements on cells without transport at 25°C. are given in table II. The first column gives the molality of the solutions and the second gives the E.M.F. of the half-cell Zn | ZnCl₂ | AgCl | Ag. The third column gives the E.M.F. of the complete cell without transference



from which the activity coefficients in the fourth column were calculated. Table III gives a similar set of figures at 35°C.

These results are shown graphically in Figs. III and IV. Graphs I and II (Fig. III) are the E.M.F.'s of half cells plotted against molality at 25° and 35° respectively. Graphs III and IV (Fig. IV) show the variation in activity coefficient with concentration at 25° and 35° respectively.

It will be seen from Graphs III and IV that the activity coefficients first decrease with increasing concentration until at a concentration of about 2.75 M at 25°C. and 2.5 M at 35°C the values pass through a minimum and thereafter increase rapidly with concentration. Foxton and Shutt (loc. cit.) measured the activity coefficients at 60° and 80° and found the minimum at about 2.75 M.

The values on the whole are less than would be expected on the assumption of the similarity with BaCl₂ which acts as a typical strong electrolyte. Scatchard and Tefft (loc.cit.) give a value of .425 for a 1.5 M solution of BaCl₂ while that for ZnCl₂ was found to be .285. However, Lucasse (J.A.C.S. 51, 2597, 1929) found the

value for CdCl_2 in a 2 M solution to be only .048. He states, "that if cadmium chloride behaves like a typical strong electrolyte at all, it is only at extremely dilute solutions. At moderate and high concentrations its behaviour becomes such as to preclude it unquestionably from consideration as completely dissociated."

It would appear therefore that zinc chloride is intermediate between typical strong electrolytes such as BaCl_2 which are in agreement with the total ionization theory of Debye and Hückel, and substances like CdCl_2 . Scatchard and Tefft have fitted the activity coefficients with the Debye-Hückel theory by assuming incomplete dissociation of the primary ion ZnCl .

It is seen that the curve at 35° crosses that at 25° in two places. From the most dilute solution measured to about 1 M the activity coefficient increases with temperature. This increase cannot be due to increased complex formation which is promoted by rise in temperature, as it would cause a decrease in the number of active ions in the solution, and so decrease the activity coefficient. The effect of a rise in temperature on hydration cannot be definitely stated but it is to be expected that it would favour the dissociation of the ion hydrates



Such a dissociation would increase the number of active ions in solution and so increase the activity coefficient.

From 1 M to about 7 M the activity coefficient decreases with temperature which points to increased complex formation predominating over the hydration effect. At higher concentrations than 7 M it seems that the activity coefficients at 35° are slightly above those

at 25°. This points to the fact that complex formation has either reached a maximum or that the hydration effects predominate over the effect of increasing complex formation. Another possibility is that ionic association takes place in a different way from that in weaker solutions.

However these are only a few of the facts which may influence the activity coefficients and as mentioned in the introduction any one theory is insufficient to account for their behaviour at higher concentrations.

Cells with Transport and Transport Numbers.

Table IV gives the results of cells with transport at 25°C. The first column gives the molality of the reference solution and the second gives the molality of the variable solution. The third and fourth columns give the E.M.F.'s of the cells without and with transport respectively. Table V gives the similar results at 35°.

TABLE IV.
Transference Numbers at 25°C.

m	m ₁	log m	$\bar{t} = (E_m - E_m')$	E_t	n_0
.3334	.3334	7.523	0	0	.391
"	.5467	7.738	.0174	.0061	.286
"	.8024	7.904	.0286	.0078	.193
"	.8597	7.934	.0296	.0098	.179
"	1.191	0.076	.0395	.0103	.112
"	2.584	0.412	.0640	.0115	-.092
"	3.136	0.496	.0715	.0104	-.151
"	3.463	0.540	.0765	.0090	-.194
"	4.174	0.621	.0870	.0069	-.274
"	5.007	0.700	.0976	.0032	-.349
"	6.230	0.785	.1141	-.0031	-.448
"	6.577	0.818	.1180	-.0049	-.468
"	7.560	0.879	.1301	-.0110	-.517
"	8.912	0.930	.1453	-.0179	-.551
"	10.33	1.014	.1607	-.0268	-.545
"	11.20	1.049	.1676	-.0310	-.534
"	12.48	1.096	.1797	-.0373	-.485

TABLE V.
Transference Numbers at 35°C.

m	m_1	$(E_m - E_m) = E.$	E_t	n_c
.3273	.3273	1.515 0	0	.423
"	.7553	1.898 .0225	.0069	.266
"	.9917	1.896 .0316	.0090	.196
"	1.748	0.243 .0471	.0109	.038
"	2.993	0.616 .0672	.0096	- .156
"	3.987	0.601 .0823	.0064	- .287
"	4.989	0.698 .0960	.0019	- .399
"	5.899	0.771 .1109	- .0040	- .463
"	6.884	0.838 .1210	- .0094	- .489
"	7.739	0.889 .1339	- .0156	- .485
"	9.307	0.969 .1512	- .0237	- .404

Fig V.

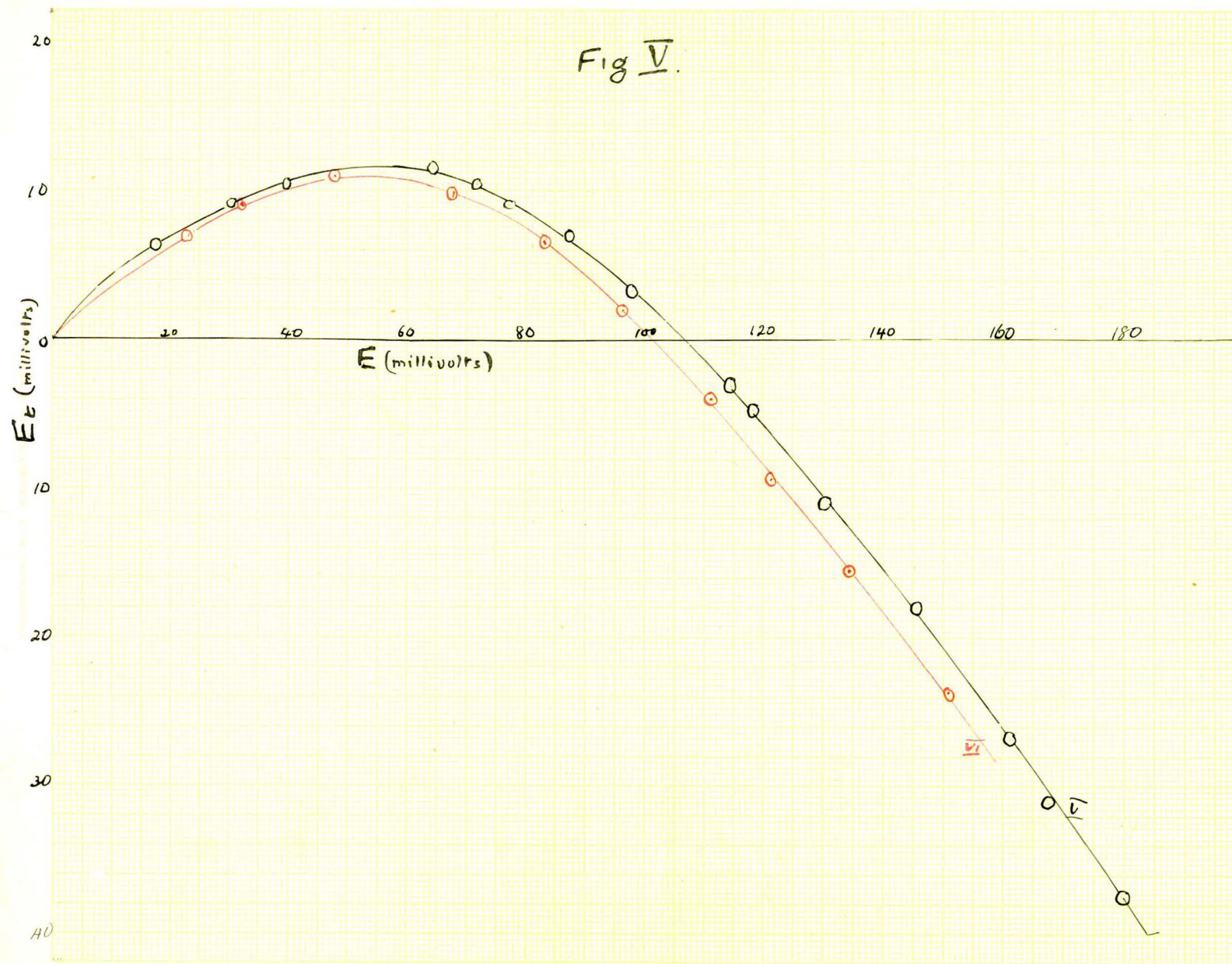
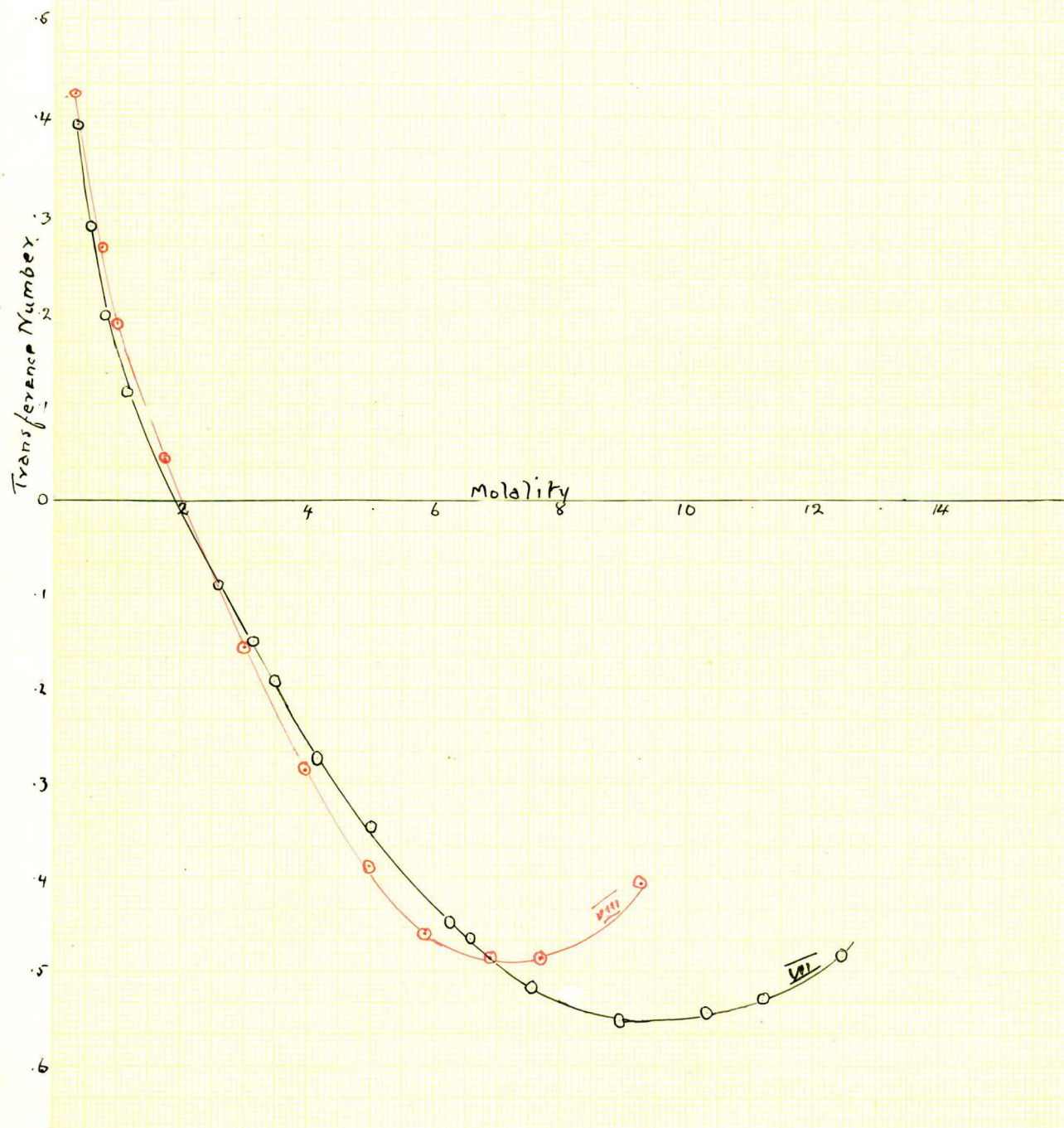


Fig VI



The E.M.F.'s of the cells without transport were plotted against the E.M.F.'s of the corresponding cells with transport giving the curves shown in Fig. V - graph V at 25°C. and VI at 35°C. It will be noticed that the values of E_t starting from zero E.M.F., increase to a maximum and then decrease to negative values. The negative values are from cells in which the concentrated solution was more positive than the dilute. The curve at 35° is similar to that at 25° and lies slightly below it.

In order to calculate the transport numbers equation were found for these curves in the following way. From appearance the curves were thought to resemble parabolas and attempts were made, by the method of averages (Lipka, "Graphical and Mechanical Computations", p.) to fit the curve with an equation of the type $E_t = a E^2$, "a" being a constant. It was found, however, that a value of "a" could only be obtained which fitted the curve for values of E up to about 100 m.v. after which the theoretical values were too low. A correction factor was therefore found which disappeared at values of E lower than 100 but which had to be taken into account at higher values. The following equations were determined for the two curves, all E.M.F.'s being expressed in millivolts..

$$\text{At } 25^\circ\text{C. } (E_t - 11.8) = - .0042(E - 53)^2 + 7.12 \times 10^{-8}(E - 53)^4 \quad \text{..... (1)}$$

$$\text{and at } 35^\circ\text{C. } (E_t - 11) = - .005(E - 51)^2 + 1.54 \times 10^{-7}(E - 51)^4 \quad \text{..... (2)}$$

These on differentiating with respect to E gave

$$\text{at } 25^{\circ} \quad \frac{dS_t}{dE} = - .0084 (E - 53) - 2.848 \times 10^{-7} (E - 53)^3$$

$$\text{and at } 35^{\circ} \quad \frac{dS_t}{dE} = - .01 (E - 51) - 6.16 \times 10^{-7} (E - 51)^3$$

Substitution of values of E in these equations gave the transport numbers given in the fifth columns of tables IV and V and are shown graphically in Fig. VI - graph VII at 25° and VIII at 35° .

The only other values that could be found for the transport number at 25° were those of Hittorf (Zeits. Phys. Chem. 43, 249, 1903) who determined the anion transport number by the gravimetric method. This results are given below in the second column; the third column gives those obtained in the present work.

Molality	n_c (Hittorf)	n_c (E.M.F.)
4.035	- .241	- .256
2.64	- .08	- .085

The results are in fair agreement.

Foxton and Shutt (loc. cit.) determined the E.M.F.'s of cells with and without transport containing zinc chloride solutions at 60° and 80° but did not calculate transport numbers. Their results were graphed and the mean transport number over various concentration ranges were calculated. These are given in the following table.

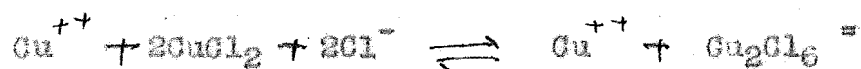
4.035 1.5 2.64 2.776 H₂O

TABLE V.

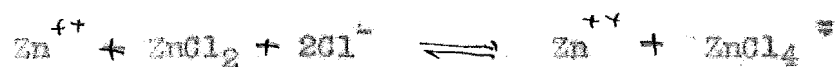
m_1	m_2	n_a (Mean).
2.39	.867	.904
4.24	.177	.905
4.94	.079	.928
4.94	.926	1.176
12.4	4.622	1.495
12.47	4.637	1.483
23.87	4.814	1.461
24.99	4.839	1.452

From these results it is obvious that a large proportion of the zinc travels to the anode as complex anions probably of the formula $(ZnCl_4)^{-}$ or $(Zn_2Cl_6)^{-}$.

Denham (loc. cit.) has shown that copper in strong solutions of its chloride tends to form autocomplexes probably according to the formulae



A similar effect may happen to zinc chloride in concentrated solutions



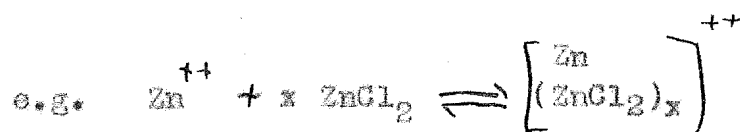
If the equilibria represented above lie almost wholly to the right the cation transport number would be less than zero.

The presence of a minimum in the transport number suggests that there are two or more factors, which influence the transport number, working against one another. As was stated in the introduction there are three main factors which influence the transport number and these will now be discussed in regard to the minimum. Before the minimum is reached the factor which has the greatest influence is the increasing formation of complex anions. At the minimum either the formation of complex anions has reached a maximum or there is some other factor which has a greater influence on the transport number in the opposite direction. The possible factors influencing the transport number at the minimum are:-

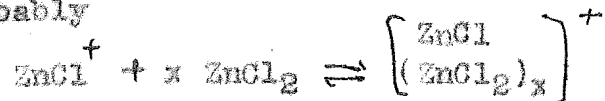
(1) Formation of complex cations; (2) change in hydration of ions; and (3) changes in the relative ionic velocities brought about by changes in viscosity.

Discussion of these factors.

1. At such high concentrations the possibility of another form of ionic association must be taken into account. There are present in the solution zinc ions, chlorine ions and presumably various forms of complex ions as well as undissociated molecules of zinc chloride and probably oxychloride. Thus not only may zinc chloride combine with the anions present to form complex anions but the possibility of the zinc chloride associating with the cations to form complex cations appears at least feasible.



or more probably



It is quite probable that in such strong solutions the dissociation of the zinc chloride only proceeds as far as the primary stage giving rise to a complex cation



Also the oxychloride which is quite soluble in strong solutions of zinc chloride may dissociate to give a complex cation



As more zinc chloride is added to the solution there will be more of these various complex cations formed which will oppose the effect of complex anions and consequently the cation transference number will increase thereby causing the minimum.

The effect of a rise of temperature on these ions would presumably be the same as the effect on the complex anions, that is, to increase the number formed. If there can only be a certain number of complex anions present before the complex cations,

Zn ZnCl_2 ZnCl etc., are formed to any extent, a rise of temperature will shift the minimum to a lower concentration. This was found to be the case.

Also if a rise of temperature promotes the formation of complex cations then after the minimum point has been reached, the transport number should increase more rapidly at the higher temperature than at the lower. This also agrees with experimental results.

2. Hydration.

If each ion in the solution has a definite hydration value, that is, has a definite number of water molecules associated with it, then, as the concentration is increased there will be a particular concentration at which it is possible that all the molecules of water present are taken up to form ion-hydrates. On further increasing the concentration some of the ionhydrates may partially dissociate and the free water molecules so produced taken up by the new ions. In this way ions with fewer water molecules associated with them are produced. In short with increasing concentration it is to be expected that the average hydration per ion will fall off - a direct consequence of the application of the Law of Mass Action. These ions will have a smaller diameter than the fully hydrated ones and consequently their mobilities will be increased.

If the hydrates of the anions and cations are dissociated relatively to the same extent their velocities will be increased in the same ratio and consequently there will be no change in the transport number. If, on the other hand, the degree of hydration of the cations is decreased to a greater extent than that of the anions, the velocity of the cations will be increased more than that of the anions. This will increase the cation transport number and consequently the curve will tend to show a minimum. In such strong solutions, however, the increased attraction of the ions for one another due to their closer proximity may counteract the increase in velocity mentioned above.

The effect of a rise of temperature on the ion-hydrates will be to dissociate them which will give the ions greater freedom. As before if the hydrates of the cations are dissociated to a greater extent than those of the anions there will be a corresponding increase in the cation transport number. This was found to be the case.

3. Viscosity.

The viscosity of the solution will tend to have a greater retarding effect on the large complex ions than on the smaller single one. It is possible therefore that at the minimum the viscosity becomes so great as to prevent to a certain extent the migration of the large complex ions and yet still allow the smaller ones to move fairly freely. This will tend to increase the cation transport number. The objection to this is that by their greater hydration (Glasstone "Electrochem. of Solutions" p. 43-52) the smaller ions may have a radius approaching that of the complexes and consequently would be retarded to much the same extent.

Also the viscosity decreases with increasing temperature. If it is assumed that in the region of the minimum point there is no formation of complex cations, and that the minimum is caused by some other factor, a decrease in viscosity will give the complex cations, which are undoubtedly present, greater freedom. Hence with rise in temperature the transport number of the cation would decrease. This is contrary to experimental fact.

If, on the other hand, the minimum is caused by the formation of complex cations a decrease in viscosity with rise of temperature

would increase the cation transport number by giving the complex cations greater freedom. This is in agreement with experimental results and so gives support to the theory that the minimum is caused by the formation of complex cations.

Summing up it would appear, therefore, that the minimum in the transport number can be attributed mainly to the formation of complex cations at higher concentrations. Changes in hydration values also fit in with experimental results although this would probably have only a small effect on the transport number. However the system is so complex, especially in concentrated solutions, that no definite conclusions can be reached as to the exact nature of the ions in solution, or of the factors operating to increase the migration number in the neighbourhood of the minimum.

SUMMARY OF WORK.

1. Electromotive force measurements were made on the cells



and



at the two temperatures 25° and 35°C.

2. The mean activity coefficients of the ions have been calculated at the two temperatures.
3. The activity coefficient - molality curve shows a minimum in the region of 2.5 M.

4. From results of measurements of cells with and without transport, the transference numbers of the cation have been calculated.
5. The cation transport number shows a minimum in the region of 9.5 M. at 25°C. and 7 M. at 35°C.
6. Attempts were made to explain the minimum as being due to the formation of complex cations and to a lesser extent to changes in the hydration values.
7. In concentrated zinc chloride a large number of the ions are in the form of complexes.

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