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THE ELECTROMOTIVE FORCE AND FREE ENERGY OF
DILUTION OF LITHIUM CHLORIDE IN AQUEOUS
AND ALCOHOLIC SOLUTIONS.

J. N. PEARCE AND F. S. MORTIMER.

Various experimental methods may be employed for comparing the activities of solutions of electrolytes, viz., freezing point, boiling point, vapor pressure, osmotic pressure, electrical conductivity and electromotive force. Of these, the latter is generally more convenient of application; it has the advantage in that measurements are more easily made and its use is not restricted to any particular temperature interval. In solutions ranging from the moderately dilute to the very concentrated it may be applied more accurately than the conductivity method. The electromotive force method, however, has its limitations. It shares with all of the other methods the disadvantage of being inapplicable for solutions other than those of the uni-univalent electrolytes. This, coupled with the troublesome factor of the boundary potential, has limited its usefulness.

Many attempts have been made to eliminate this boundary potential. Some, following the lead of Ostwald,¹ have interposed solutions of an inert salt between the electrode vessels. Unfortunately, the electromotive forces thus measured vary considerably not only with the concentration of the interposed solution, but also with the nature of the electrolyte used. Consequently such measurements are of doubtful value.

Nernst,² Planck,³ Henderson,⁴ Cumming,⁵ and others have sought to overcome the effect due to boundary potential by introducing formulae involving the relative mobilities of the ions.

A few cells have been set up which do not involve the transference of ions from one electrode vessel to the other. Cells of this type are limited to those electrolytes for which it is possible to find electrodes reversible to both of the ions in the solution. So far the only cells thus investigated from which cal-

¹Messungen, 3d ed., p. 448.

²Theoretical Chemistry, Nernst, Translation of 6th German ed., p. 370.

³Wied. Ann., 40, 561, 1890.

⁴Zeit. phys. Chem., 59, 118, 1907.

⁵Trans. Faraday Soc., 8, 86, 1912.

culations of free energy may be made are those containing solutions of the alkali halides or of the halogen acids. From the electromotive forces of such cells it has been found possible to calculate the free energy of dilution with a high degree of accuracy.

Using potassium chloride as the electrolyte, MacInnes and Parker⁶, determined the electromotive forces of concentration cells both with and without transference. From the data thus obtained they calculated the transport numbers and the activity ratios of the ions. They found that the concentration ratios calculated from the conductivity data are invariably higher than the activity ratios determined by the electromotive force method. As the dilution increases the value of the activity ratio approaches that of the concentration ratio.

Ferguson⁷ has measured the electromotive forces of concentration cells of hydrochloric acid using electrodes reversible to both ions, in cells without transference as well as in cells directly connected. He also found that the observed activity ratios are less than the concentration ratios calculated from the conductivity data. The transport numbers for the ions of hydrogen chloride are constant in dilutions greater than thirty liters. He concludes, therefore, that conductivity measurements do give us an accurate method for calculating relative ion concentrations in the more dilute aqueous solutions of hydrogen chloride.

Ferguson and Tolman⁸ and later Ellis⁹ measured the free energy of dilution of hydrogen chloride solutions over a wide range of concentrations.

The object of the present investigation was to determine the effect of solvent on the free energy of dilution, the transport numbers of the ions and the activity ratios of lithium chloride in aqueous and alcoholic solutions.

THEORETICAL.

In his treatment of the free energy of chemical substances Lewis¹⁰ has introduced the terms activity and fugacity. Activity has the dimensions of concentration and is defined as "Such a property of a given substance that, (1) if the activity, a , for a substance is the same in any two phases, the substance will not

⁶Jour. Am. Chem. Soc., 37, 1445, 1915.

⁷Jour. Physical Chem., 20, 326, 1916.

⁸Jour. Am. Chem. Soc., 34, 232, 1912.

⁹Proc. Nat. Acad., 83, 1916.

¹⁰Jour. Am. Chem. Soc., 35, 1, 1913.

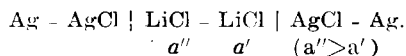
pass from one phase to the other when the two phases are brought together; (2) if a is greater in one phase than in another, the substance will tend to pass from the first phase to the second; (3) the activity of a perfect gas is equal to its concentration; (4) the activity of a solute in a perfect solution is equal to its concentration." When two phases of the same system, but of different concentrations or activities are brought together, the material in the phase of high activity will tend to escape over into the phase of lower activity.

This escaping tendency Lewis called by the term fugacity, f . It has the dimension of pressure. Activity is defined in terms of the fugacity by the equation,

$$a = f/RT$$

where R is the gas constant and T the absolute temperature.

In applying this conception of activity to a working cell, let us consider first the cell involving transference, e. g.

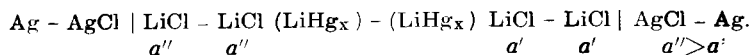


During the passage of one faraday of electricity one equivalent of chloride-ion is formed on the dilute side from the silver chloride electrode, while on the concentrated side one equivalent of chloride-ion is removed from the solution to the electrode. At the same time N_c equivalents of lithium-ion migrate into the dilute chamber and $1-N_c$ equivalents of chloride-ion migrate to the concentrated side. The total result is the transfer of N_c equivalents of lithium chloride from the concentrated to the dilute solution, or from the solution of activity a' to that of activity a'' . The free energy accompanying the transfer of one mole of the salt is given, therefore, by the relation:

$$\frac{E \cdot F}{N_c} = RT \log_e \frac{a''}{a'} \quad (1)$$

where E is the electromotive force, F the faraday (96,494 coulombs), N_c the transport number of the cation, R the gas constant (8.3160 joules), T the absolute temperature (298.09°), and a'' and a' are the activities of lithium chloride in the two solutions.

The following cell does not involve transference:



The passage of one faraday of electricity involves on the dilute

side only the formation of one equivalent of lithium chloride from the silver chloride and lithium amalgam electrodes. On the concentrated side there is transferred to the electrodes from the solution one equivalent of lithium chloride. The free energy accompanying this change is,

$$E_1 \cdot F = RT \log_e \frac{a''}{a'} \quad (2)$$

Combining equations (1) and (2) we arrive at an expression for calculating the transport number of the cation directly from the electromotive force measurements:

$$N_c = \frac{E}{E_1} \quad (3)$$

All cells on closed circuit tend to operate until the activities of the two solutions become equal. In cells without transference such an equalization by direct diffusion of the molecules and ions is impossible. The same result is obtained, however, by the formation of the salt from the electrodes on the dilute side and the simultaneous removal of the salt to the electrodes on the concentrated side. It is obvious, therefore, that the free energy of dilution of lithium chloride is equal to the sums of the free energies of dilution of the separate ions, i. e.,

$$E_1 \cdot F = RT \log_e \frac{a''(\text{LiCl})}{a'(\text{LiCl})} = RT \log_e \frac{a''_{\text{Li}} + a''_{\text{Cl}}}{a'_{\text{Li}} + a'_{\text{Cl}}}$$

Assuming that $a''_{\text{Li}} + a''_{\text{Cl}} = a''_{\text{Cl}}$ and that $a'_{\text{Li}} + a'_{\text{Cl}} = a'_{\text{Cl}}$, then for the chloride ion,

$$E_1 \cdot F = 2RT \log_e \frac{a''_{\text{Cl}}}{a'_{\text{Cl}}} = RT \log_e \frac{a''(\text{LiCl})}{a'(\text{LiCl})} \quad (4)$$

The well known relation of Nernst makes possible a calculation of the electromotive force from electrical conductivity data. For cells involving transference,

$$E = 2 N_c \frac{RT}{F} \log_e \frac{\lambda'' N''}{\lambda' N'} \quad (5)$$

and for cells without transference,

$$E_1 = 2 \frac{RT}{F} \log_e \frac{\lambda'' N''}{\lambda' N'} \quad (6)$$

The ratios of the activities of the ions and of the undissociated molecules are readily obtained from equation (4). The con-

centration ratios of the ions are calculated from the conductivity measurements by the following evident relations.

$$\frac{C''}{C} \frac{\text{Cl}^-}{\text{Cl}^-} = \frac{a' N''}{a' N'} = \frac{\lambda' N''}{\lambda' N'} \quad (7)$$

For the undissociated salt,

$$\frac{C''}{C} \frac{(\text{LiCl})}{(\text{LiCl})} = \frac{N''}{N'} \frac{(1-a'')}{(1-a')} = \frac{N''}{N'} \frac{\lambda^\infty - \lambda''}{\lambda^\infty - \lambda'} \quad (8)$$

where C'' and C' represent the concentrations of the appropriate ions or molecules, N'' and N' the salt concentrations, λ^∞ , λ'' and λ' the equivalent conductivities at infinite dilution and at the concentrations N'' and N' , respectively.

The free energy of dilution in calories per equivalent is equal to E_1 , the electromotive force, multiplied by the faraday (96,494 coulombs) and divided by the joule equivalent of the calorie, (4.182). Or,

$$E(23073) = \text{Cals.}$$

MATERIALS AND APPARATUS.

Water.—The conductivity water was prepared according to the method of Jones and Mackay.¹¹

Ethyl Alcohol.—Ordinary 95 per cent alcohol was allowed to stand over fresh quicklime for three weeks; it was then decanted and distilled. The distillate was allowed to stand over anhydrous copper sulphate for one week and then redistilled. This distillate was refluxed over metallic calcium for ten hours and again distilled. To the last distillate were added a few crystals of dry silver nitrate and it was refluxed for two hours to remove reducing agents. The distillate from this treatment was collected and preserved in dry glass-stoppered bottles, being protected from the air during distillation by calcium chloride tubes. In each distillation a fractionating column was used and only that middle portion which passed over between 77.9° and 78° (uncorr.) was used.

Methyl Alcohol.—Kahlbaum's best grade of alcohol was further purified in the same manner as the ethyl alcohol, except that the treatment with quicklime was omitted. Only that frac-

¹¹Am. Chem. Jour., 19, 83, 1897.

tion of the distillate passing over between 64.9° and 65.1° (uncorr.) was retained.

Lithium Chloride.—Kahlbaum's best grade of lithium chloride was recrystallized four times by passing pure hydrogen chloride gas into a saturated solution of the salt in conductivity water. The crystals were filtered on a Büchner funnel and sucked dry. They were then heated in a platinum dish in an electric oven in which the temperature was gradually raised to 150°. Finally, the dry salt was finely powdered in an agate mortar and transferred to porcelain boats; these were placed in a combustion tube and heated for several hours at 160° in a rapid stream of dry hydrogen chloride gas. All traces of the latter were then removed by a stream of dry hydrogen gas, after which the boats were quickly transferred to large glass-stoppered weighing tubes.

Solutions.—All of the solutions used were prepared by first dissolving an amount of the salt in excess of that desired for the highest concentration. The chloride content was then determined in at least three separate samples by the Drechsel¹² modification of the Volhard method. All of the various concentrations in any given solvent were made by the proper dilution of this solution. All measuring apparatus was certified and the solutions were made up to volume at 25°, care being taken to avoid undue exposure of the alcohols to the air.

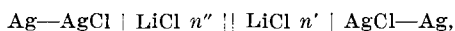
Lithium Amalgam.—This was prepared by the electrolysis of a saturated solution of lithium chloride in pyridine, using pure redistilled mercury as cathode. It was then washed in absolute alcohol, quickly dried by reduced pressure, and then filtered through a capillary tube into a sealed, glass container from which the air had previously been displaced by dry hydrogen.

Electrodes.—The silver chloride electrodes consisted of short, thick pieces of pure silver wire fused into the ends of glass tubes. To the ends within the tubes were soldered long copper wires, which were of such length that they could be bent into small mercury cups, thus making contact with the wire leads. Twelve or fifteen of the electrodes thus prepared were first grouped as cathodes about a single pure silver anode immersed in a solution of potassium-silver-cyanide. After a dense, white coating of silver had been formed they were removed, rinsed, and then inserted as anodes in a 1.0 N hydrochloric acid solution

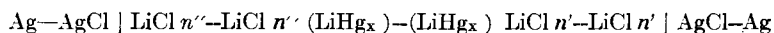
¹²Z. anal. Chem., 16, 351, 1877.

On passing the current from a single lead accumulator for one to two minutes there is formed a closely adhering, reddish brown deposit of silver chloride. For any one series of measurements, the silver chloride electrodes were always first checked against each other. This was done by grouping them in a dilute solution of hydrochloric acid and observing the potential differences between each electrode and another similar electrode taken as a standard. Only those varying by less than .05 millivolts were chosen. Two or three of these electrodes were then placed in each half-cell. After they had been in contact with their respective solutions for four or five hours, each electrode was rechecked against those in the other half-cell. Unless at least two electrodes in each half-cell differed by less than .02 millivolts, the cell was disconnected and the electrodes replated.

Form of cell.—It was desired to measure the electromotive forces of two combinations, viz., one involving transference,



the other without transference,



The form of cell adopted was such that both of these combinations could be obtained from a single set-up of the apparatus. Two half-cells, each having two side-tubes and containing solutions of the desired concentrations in contact with the silver chloride electrodes, were so arranged that from one set of side-tubes a liquid junction could be made and the first combination thus obtained. The other set of side-tubes were thus left free for liquid connection with small cells, into which dipped the amalgam electrodes, thereby forming the cell without transference. Liquid contact between the half-cells was effected by means of an inverted T-tube fitted with a three-way stop-cock. To further prevent diffusion loose plugs of cotton were inserted into the bore of these stop-cocks. Fresh liquid contacts were readily made by drawing more of each solution into the free limb of the T-tube. For cells with transference it is essential that a sharp boundary be produced between the solutions immediately before measurements are made. It was found that the electromotive force of the cells directly connected remained constant for several days when this precaution was observed.

The amalgam dropping-electrodes were similar to those used by MacInnes and Parker¹³. The amalgam was allowed to drop slowly into two small half-cells through capillary tubes connected to a common container. These capillary tubes were about one millimeter in diameter and were fitted with stop-cocks to regulate the flow. To insure good contact between the amalgam electrodes, platinum wires were fused into each of these capillary tubes just below the stop-cocks; these were then joined by a copper wire.

Numerous experiments were made to determine the most suitable concentration of the amalgam. A concentration of .002 per cent was observed to give the best results. It was found that by dropping from 20 to 30 drops per minute no appreciable bubbling occurred on the electrode. The voltage remained very constant for several minutes. The galvanometer would waver off slightly occasionally, but it would immediately return upon the formation of another drop of the amalgam.

All measurements of electromotive force were made with a Wolff potentiometer in connection with a sensitive Leeds and Northrup, "Type II," wall galvanometer. Differences of potential of .01 millivolt were easily detected in the aqueous solutions, but owing to the greater resistance in the more dilute non-aqueous solutions it was sensitive only to .05 millivolt. A Cadmium-Weston cell which had been recently standardized and occasionally rechecked against a similar element certified by the Bureau of Standards was used as the standard of reference. Although its temperature coefficient is practically negligible, this cell was kept in an insulated glass beaker, suspended in the constant temperature bath. All measurements were made at 25°. The constant temperature bath used was mechanically stirred, electrically heated and electrically controlled at 25° ± .01.

In all cases at least four cells of each combination were measured. This, together with the fact that more than one electrode was used in each solution certifies to the degree of accuracy obtained in this work.

DISCUSSION.

The experimental results obtained are to be found in the accompanying tables. Table I contains the observed and calculated electromotive forces and the transport number of the ca-

¹³Loc. cit.

tion in the solvents,—water, methyl alcohol and ethyl alcohol. A glance at these tables shows an absolute lack of agreement between the observed and calculated electromotive forces. Only in the more concentrated cells containing the aqueous solutions do the calculated results even approximate to those observed. Here the calculated values are slightly lower, while for all other cells they are higher than the observed electromotive forces, the difference between the two increasing with increasing dilution. For cells with transference both the calculated and observed electromotive forces increase with dilution, while for cells without transference the experimentally determined values decrease with increasing dilution in each of the three solvents.

TABLE I.
ELECTROMOTIVE FORCES AND TRANSPORT NUMBERS.

WATER					
ELECTROMOTIVE FORCES.					
N_1-N_2	OBSERVED		CALCULATED		TRANSPORT NUMBER CATION
	WITH TRANS.	WITHOUT TRANS.	WITH TRANS.	WITHOUT TRANS.	
1.0 —0.1	0.03192	0.11430	0.03081	0.11042	.279
	0.03195	0.11435			
	0.03195	0.11435			
0.5 —0.05	0.03501	0.10865			.322
	0.03505	0.10870	0.03589	0.11144	
	0.03503	0.10870			
0.1 —0.01	0.03581	0.10430			.343
	0.03584	0.10435	0.03886	0.11330	
	0.03585	0.10435			
0.05—0.005	0.03640	0.09950			.365
	0.03640	0.09960	0.04152	0.11376	
	0.03640	0.09960			
0.01—0.001	0.0391	0.0704			.555
	0.0391	0.0704	
	0.0391	0.0704			
METHYL ALCOHOL					
0.5 —0.05	0.03860	0.09390			.411
	0.03855	0.09385	
	0.03857	0.09385			
0.1 —0.01	0.04005	0.07980			.502
	0.04002	0.07975	
	0.04005	0.07980			
0.05—0.005	0.04105	0.07160			.573
	0.04103	0.07160	
	0.04105	0.07165			
ETHYL ALCOHOL					
0.5 —0.05	0.03322	0.08880			.374
	0.03322	0.08875	
	0.03325	0.08875			
0.1 —0.01	0.03559	0.07170			.497
	0.03560	0.07170	0.04627	0.09310	
	0.03560	0.07170			
0.05—0.005	0.03820	0.06140			.622
	0.03820	0.06145	0.05939	0.09549	
	0.03820	0.06145			

The calculated electromotive forces of cells involving transference are obtained by making the proper substitutions in equation (5); for cells without transference similar substitutions are made in equation (6). The molecular conductivities of lithium chloride which have been substituted in these equations are taken from the work of Greene¹⁴ for the aqueous solutions. Those for solutions in ethyl alcohol are taken from the work of Jones and Turner.¹⁵ No conductivity data for solutions of lithium chloride in methyl alcohol at this temperature are to be found in the literature. This is not essential, however, since the calculated electromotive forces in methyl alcohol would doubtless show results similar to those which have been found for solutions in water and ethyl alcohol.

From theoretical considerations (Equation 6) it is evident that the magnitude of the calculated electromotive force for cells without transference is dependent solely upon the ratio of the ionic concentrations as calculated from electrical conductivity. On the other hand, the observed electromotive forces for cells without transference are determined by the ratio of the activity of the solutions, and more particularly the activity of the ions, about the electrodes. For cells with transference the value of the electromotive force measured is dependent not only upon the relative activity of the ions in the two solutions, but also upon the transport numbers of these ions. The electromotive force of cells with transference is useful in this investigation only as a factor for the determination of the transport number (Equation 3). All other calculations are made from the values of the electromotive forces without transference.

The transport number of the lithium ion increases with increasing dilution in each of the solvents studied. For a given change in dilution this increase is least in the aqueous solutions and greatest for solutions in ethyl alcohol. The values of the transport numbers determined by this method are the average values between the two concentrations of the electrolyte constituting the cell. It is, therefore, difficult to make a direct comparison with other published results. Table II gives the values obtained by Kohlraush and Holborn¹⁶ for the transport number of the cation of lithium chloride in aqueous solutions at 25°.

¹⁴Trans. Chem. Soc., 93, (2) 2042, 1908.

¹⁵Am. Chem. Jour., 40, 558, 1908.

¹⁶Z. Elektrochem. u. Phys. Chem., 1, 201.

The mean values of these have been calculated and are inserted for comparison.

TABLE II.

TRANSPORT NUMBERS OF THE LITHIUM ION IN AQUEOUS SOLUTIONS.

Normality1.	—	0.1	0.5	—	.05	0.1	—	.01	.05	—	.005
Kohlraush.261	.31	.27	.33	.31	.37	.33	(.39) ¹⁷			
Calc. mean.285		.300		.340		.360				
Obs. mean.279		.322		.343		.365				

The agreement is as satisfactory as could be expected and confirms the applicability of this method of measuring the transport numbers of ions.

The transport numbers of the ions in a solution are determined by the relative mobility of these ions at the dilution in question. The mobility of an ion is in turn a function of its mass, the area and configuration of its surface and the viscosity of the solution. The variation of the transport number with the dilution of the salt in lithium chloride solutions must be caused by a change in one or more of these properties of one or both of the ions.

Jones and Getman¹⁸ have shown that, starting with a concentration of 0.24 N, the molecular lowering of the freezing-point produced by lithium chloride in aqueous solutions increased both with the concentration and with the dilution. They have also found¹⁹ that the molecular elevation of the boiling-point produced by solutions of lithium chloride in ethyl alcohol is at all concentrations greater than the values calculated on the basis of dissociation. They attribute these abnormal increases in the freezing-point lowering and boiling-point elevation with increasing concentration to "solvation."

The solvation of an ion undoubtedly increases both its mass and surface and probably also affects the viscosity of the solution. If one of the ions of an electrolyte is more highly solvated than the other, dilution will affect the two ions to a different degree. Consequently, such an electrolyte should show a difference in the relative mobility of the ions with varying dilution and therefore a corresponding change in the transport numbers. Conversely, a change in the transport numbers with dilution may be considered to be an indication of solvation. If this

¹⁷Extrapolated.

¹⁸Zeit. phys. Chem., 46, 261, 1903.

¹⁹Am. Chem. Jour., 32, 338, 1904.

change in the transport numbers with the concentration of the salt indicates solvation, then it is evident that either the ions or the molecules, or both, are solvated in each of these solvents.

The solvation of the ions or molecules of lithium chloride in these solutions should affect to some extent the activity of the solutions. The activity ratios have been calculated (Equation 4) and are to be found in Table III.

TABLE III.
ACTIVITY RATIOS AND FREE ENERGY OF DILUTION.
WATER

N_1-N_2	ACTIVITY RATIO IONS	CONC. RATIO IONS	ACTIVITY RATIO UNDISS.	CONC. RATIO UNDISS.	FREE ENERGY OF DILUTION CALCS.
1. —0.1	9.254	7.590	85.61	22.24	2638.0
.5 — .05	8.285	8.236	68.60	21.44	2506.4
.1 — .01	7.617	8.954	58.02	25.92	2407.2
.05— .005	6.942	9.049	48.18	31.43	2297.2
.01— .001	3.936	15.49	1624.4

METHYL ALCOHOL

.5 — .05	6.215	38.63	2166.
.1 — .01	4.725	22.32	1840.8
.05— .005	4.031	16.25	1652.6

ETHYL ALCOHOL

.5 — .05	5.626	31.625	2047.8
.1 — .01	4.037	6.123	16.298	17.04	1654.4
.05— .005	3.305	6.415	10.923	19.7	1417.2

The concentration ratios calculated from equation (7) have been inserted for comparison. All of these activity and concentration ratios are for solutions having a normality ratio of 10 to 1. It will be observed that the activity ratio decreases with increasing dilution in each of these solvents. Comparing similar cells in the different solvents, the activity ratio decreases as the molecular weight of the solvent increases. The activity ratio of the ions is less than the concentration ratio in all cells, except for the more concentrated aqueous solutions.

With a normality ratio of 10 to 1 it would be expected that the activity ratio of the ions should gradually increase to the value of 10 at infinite dilution. In order to determine whether the activity ratio reaches a minimum value, a cell containing aqueous solutions of higher dilutions (0.01-0.001) was measured.

No minimum is to be observed. It is, therefore, evident that lithium chloride behaves abnormally in each of these solvents. Conductivity measurements indicate that the concentration ratio of the ions approaches the value 10. Electromotive force measurements, on the other hand, indicate that the activity ratio of the ions decreases as more dilute cells are measured.

Assuming that solvation does exist in these solvents, then, according to the law of mass action, the amount of solvation per mole of solute will be greatest in the most dilute solutions. However, on account of the greater concentration of the salt, more of the active solvent will be rendered inactive in the higher concentrations. The concentration of the ions and molecules, measured on the basis of active solvent present, will be abnormally increased in the concentrated solutions. The activity of the more concentrated solution in each cell will be relatively increased and this increase will become progressively larger as more concentrated cells are used. Hence, the activity ratio should and does increase with increasing concentration.

It does not appear that the activity ratio will approach the concentration ratio at any attainable dilutions. In the calculation of the concentration ratio by the conductivity method, the assumption is made that the mobilities of the ions are the same at all concentrations, including infinite dilution. That this assumption is sometimes erroneous is shown by the results herein reported. The discrepancy between the activity and concentration ratios and between the observed and calculated electromotive forces is in all probability due to variations in the mobility of the ions.

There is, perhaps, another reason for this increase in the activity ratio with increase in the concentration of the salt. Walden²⁰ has found that the dielectric constant of salt solutions generally increases with increase in the concentration of the salt. According to the Nernst-Thompson rule this should mean a relative increase in the ionizing power of the solvent, and hence in the number of the ions present. If this is true, we should expect an increase in the activity of the ions in the more concentrated solutions. As with solvation, so should this cause the activity ratio to become progressively larger with increasing concentration.

²⁰Jour. Am. Chem. Soc., 35, 1649, 1913.

The free energy of dilution is by definition proportional to the logarithm of the activity ratio of the ions. Consequently, the free energy of dilution is found to decrease as the concentration of the salt is diminished. Comparing similar cells in the different solvents the free energy of dilution decreases as the molecular weight of the solvent increases.

This work is being continued in the higher alcohols.

SUMMARY.

The electromotive force of concentration cells containing solutions of lithium chloride in the solvents,—water, methyl alcohol and ethyl alcohol, have been measured in two combinations, viz., one involving transference of ions, the other without transference. All of the cells measured contained solutions having a normality ratio of 10 to 1. The electromotive force of cells with transference increases with the dilution, while for cells without transference it is found to decrease with increasing dilution.

The transport numbers have been determined and it has been found that for all three solvents the transport number of the lithium ion increases as the concentration of the salt is diminished.

The activity ratio of the ions in two solutions having a normality ratio of 10 to 1 decreases as more dilute solutions are used. The activity ratios of the ions have been compared with the concentration ratios calculated from electrical conductivity. The activity ratios are smaller than the concentration ratios in all cases, except in the cells containing the more concentrated aqueous solutions.

The effect of solvation and the effect of a possible increase in the dielectric constant with increasing concentration of the salt have been advanced as possible causes for the increase in the activity ratio of the ions.

The free energy of dilution decreases with increasing dilution in each of the three solvents studied.

The effect of solvent has been studied in connection with the transport numbers of the ions, the activity ratios and the free energy of dilution. For similar concentrations of solute the transport number of the lithium ion is highest in methyl al-

cohol, except in the dilute cell where it is highest in ethyl alcohol. The corresponding values in the aqueous solutions are lower than in either of the other solvents. Comparing the activity ratios and likewise the free energies of dilution for similar cells in the separate solvents, both are found to decrease as the molecular weight of the solvent increases.

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