

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE
UNIVERSITY OF IOWA.]

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

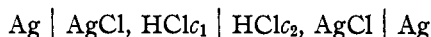
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The study of the electromotive forces in aqueous solutions of electrolytes has always presented an attractive field for research. One has but to scan the literature¹ of the last twenty-five years to be convinced of the enormous amount of work which has been done in this field alone. It is only in more recent years that attempts have been made to extend electrometric measurements with the view of correlating the results of the measurements of electromotive force of concentration cells with other colligative properties of solutions.

Dolezalek² has determined the electromotive forces at 30° of hydrogen-chlorine cells, using hydrochloric acid for the electrolyte and in concentrations ranging from 4.98 *N* to 12.25 *N*. His results are sufficiently accurate to permit the calculation of the free energy of transference of hydrochloric acid for the various concentrations used.

Using concentration cells of the type



Jahn³ determined with great accuracy the electromotive forces for concentrations ranging from 0.033 *N* to 0.00167 *N*. Similar cells were made using correspondingly dilute solutions of the chlorides of sodium and potassium. From the results obtained he concluded: (1) that the mobility of the ions is dependent to a high degree upon their concentration, increasing with increasing concentration, (2) that the conductivity of an electrolyte is not a true measure of its dissociation.

Tolman and Ferguson⁴ determined the electromotive forces for concentration cells of the type $\text{Hg} \mid \text{HgCl}, \text{HCl} \mid \text{HCl}, \text{H}_2 \mid \text{Pt}$ at 18° and combined so as to eliminate transference. From these they calculated the free energy of dilution of hydrochloric acid, and the ratios of the fugacities of the ions and of the molecules. They found that for strong electrolytes, even in dilute solutions, the fugacity, or activity, of the ions is not strictly proportional to the concentration, while that of the undissociated electrolyte is very far from proportional to its concentration.

¹ For a complete summary see Abegg-Auerbach and Luther, "Messungen elektromotorischer Kräfte."

² *Z. physik. Chem.*, **26**, 321 (1898).

³ *Ibid.*, **33**, 545 (1900).

⁴ *THIS JOURNAL*, **34**, 232 (1912).

McInnes and Parker¹ have extended the electrometric measurement of the free energy of dilution to aqueous solutions of potassium chloride. Using silver chloride and amalgam electrodes, they determined the electromotive force of cells both with and without transference. From their data they were able to calculate the transport numbers and the activity ratios of the ions. They found that the concentration ratios calculated from conductivity are invariably higher than the activity ratios determined by the electromotive-force method; further, that the activity ratio approaches the value of the concentration ratio as the dilution increases.

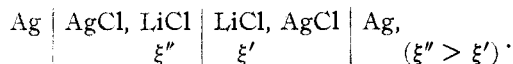
Ferguson² also has worked with concentration cells containing hydrochloric acid, using electrodes reversible to both ions in cells with and without transference. He also found that the activity ratios are less than the concentration ratios.

Somewhat similar results were obtained by Ellis³ for hydrochloric acid solutions in concentrations ranging from 0.00167 *N* to 4.484 *N*. Assuming provisionally that the activity coefficient of the most dilute solution is substantially equal to the ionization coefficient derived from the conductance ratio, he calculated a series of absolute activity coefficients for the remaining concentrations. Beginning with the most dilute solution, the activity coefficients, thus calculated, decrease with increasing concentration, pass through a minimum at 0.5 *N* and then increase with further increase in concentration. The conductance-viscosity ratio $\lambda\eta/\lambda_0\eta_0$ decreases throughout with increase in the concentration of the acid.

Thus far water has been the only solvent used in investigations of this nature. It was thought worth while therefore, to make a systematic comparative study of the influence of the solvent upon the electromotive forces, the transport numbers, the activity ratios of the ions and molecules, and the free energy of dilution of electrolytes in water and organic solvents.

The concentration cells chosen for this work consist of solutions of lithium chloride in water and in the five lower alcohols of the paraffin series.

In such a study it is necessary to make use of two types of concentration cells. Let us consider first the cell involving transference, *e. g.*,



During the passage of one faraday of electricity, one equivalent of the chloride ion is formed on the dilute side from the silver chloride electrode, while on the concentrated side one equivalent of the chloride ion is removed from the solution to the electrode. At the same time N_c equivalents of the lithium ion migrate into the dilute chamber and $(1 - N_c)$ equivalents of the chloride ion migrate to the concentrated side. The total result is

¹ THIS JOURNAL, 37, 1445 (1915).

² *J. Phys. Chem.*, 20, 326 (1916).

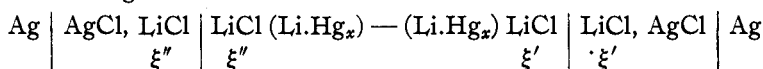
³ THIS JOURNAL, 38, 737 (1916).

the transfer of N_c equivalents of lithium chloride from the concentrated to the dilute solution, or from the solution of activity ξ'' to that of ξ' . The free energy accompanying the transfer of one mole of the salt is given by the relation

$$-\Delta F = \frac{E.F}{N_c} = RT \log_e \frac{\xi''}{\xi'}, \quad (1)$$

where E is the electromotive force, F the faraday (96494 coulombs), N_c the transport number of the cation, R the gas constant (8.316 j.), T the absolute temperature (298.09°).

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 the 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

$$-\Delta F_1 = E_1.F = RT \log_e \frac{\xi''}{\xi'}. \quad (2)$$

Combining Equations 1 and 2 we arrive at an expression for calculating the transport number of the cation directly from electromotive-force measurements, *viz.*,

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

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 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 energy of dilution of the separate ions, *i. e.*,

$$-\Delta F_1 = E_1.F = RT \log_e \frac{\xi''(\text{LiCl})}{\xi'(\text{LiCl})} = RT \log_e \frac{\xi''_{\text{Li}^+} \cdot \xi''_{\text{Cl}^-}}{\xi'_{\text{Li}^+} \cdot \xi'_{\text{Cl}^-}}.$$

Assuming that $\xi''_{\text{Li}^+} = \xi''_{\text{Cl}^-}$ and that $\xi'_{\text{Li}^+} = \xi'_{\text{Cl}^-}$, therefore the chloride ion

$$-\Delta F_1 = E_1.F = RT \log_e \frac{\xi''(\text{LiCl})}{\xi'(\text{LiCl})} = 2RT \log_e \frac{\xi''_{\text{Cl}^-}}{\xi'_{\text{Cl}^-}}. \quad (4)$$

If this assumption is not true, and most probably it is not, then the calculated ratio of the activities of the chlorine ions may be taken as the ratio of the square roots of the products of the activities of the two ions.

The free energy of dilution in joules per gram-equivalent weight is equal

to E_1 , the electromotive force without transference, multiplied by the value of the faraday, or 96494 coulombs.

Materials and Apparatus.

The conductivity water used throughout the work was prepared according to the method of Jones and Mackay.¹

Ethyl Alcohol.—Ordinary 95% 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 sulfate 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 pure dry silver nitrate and it was then 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 a drying train containing fused calcium chloride. In each distillation a fractionating column was used and only that middle portion passing over between 77.9° and 78° (uncorr.) was retained.

The remaining alcohols, *viz.*, methyl, *n*-propyl, *n*-butyl and isoamyl, were of Kahlbaum's best grade. These were further purified in the same manner as was the ethyl alcohol, except that the treatment with quicklime was omitted. The uncorrected distillation temperatures were: methyl, 64.9–65.1°; *n*-propyl, 95.7–95.9°; *n*-butyl, 115.8–116.2°; isoamyl, 129.9–130.2°.

Lithium Chloride.—Kahlbaum's best grade of lithium chloride was recrystallized four times by passing pure hydrogen chloride into a hot 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°. The dry salt was then finely powdered in a hot 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. All traces of the latter were removed by a stream of dry hydrogen, after which the boats were allowed to slide quickly into large glass-stoppered weighing tubes.

Solutions.—All of the solutions were prepared by first dissolving an amount of the salt in excess of that required for the highest concentration. The chloride content was then determined in at least four separate samples by the Drechsel² modification of the Volhard method. All of the various concentrations in any given solvent were made by the proper dilution of this mother solution, the greatest care being taken to secure the least possible contact with the air. All of the measuring apparatus was certified and the solutions were made up to volume at 25°.

¹ *Am. Chem. J.*, 19, 83 (1897).

² *Z. anal. Chem.*, 16, 351 (1877).

Mercury.—The mercury used was repeatedly washed by spraying through dilute nitric acid, and then further purified by distilling in a current of air under reduced pressure.

Lithium Amalgam.—This was prepared by the electrolysis of a saturated solution of the salt in pyridine, using pure redistilled mercury as the cathode. It was then washed with absolute alcohol, quickly dried by gentle heating under reduced pressure (Gaede pump), then filtered through a fine 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. On passing a current from a single 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 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 difference between each electrode and another taken as standard. Only those varying by less than 0.05 mv. were chosen. Three of these electrodes were placed in each half cell. After they had been in contact with each other for four or five hours the potential readings were taken. In taking these readings the electrodes in each half-cell were first checked against each other. Unless at least two electrodes differed by less than 0.02 mv., the cell was disconnected and the electrodes replated. When the potential deviations proved to be within these limits the potentials were read between each single electrode of one cell and the separate electrodes of the other cell and the mean value taken. For a further check the electrodes in each half cell were connected and the electromotive force between the combined electrodes was then determined.

The form of cell adopted was such that concentration cells, both with and without transference, could be obtained from a single set-up of the apparatus. Two half-cells of the form used by Ferguson,¹ each having two side tubes and containing solutions of the desired concentrations in contact with the chloride electrodes, were so arranged that from one set of side tubes a liquid junction could be made and the electromotive force with transference thus obtained. The other set of tubes were thus left

¹ *Loc. cit.*

free for liquid connection with small cells into which dipped the amalgam electrodes, thus forming the cell without transference.

Liquid connection between the half cells was effected by means of an inverted T-tube fitted with a three-way stopcock. To minimize diffusion loose plugs of cotton were inserted into the bore of these stopcocks. For cells with transference it is very essential that a sharp boundary be produced between the solutions immediately before measurements are taken. Fresh contacts were readily made by drawing more of each solution into the free limb of the T-tube. It was found that the electromotive forces of cells directly connected remained constant for several days when this precaution was observed.

The amalgam electrodes were similar to those used by MacInnes and Parker;¹ the method of procedure was also the same. As a result of numerous experiments, a concentration of 0.002 % was found to give the best results. It was found that by dropping from 20 to 30 drops per minute no appreciable bubbling occurred and the voltage remained very constant for several minutes. Occasionally, the galvanometer would waver slightly but it would immediately return to zero upon the formation of another drop of the amalgam.

All measurements of the electromotive force were made with a Wolff potentiometer in connection with a sensitive Leeds and Northrup, "Type H," wall galvanometer. A Cadmium-Weston cell which had been recently standardized and frequently rechecked against a similar element, also recently standardized 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 $25^{\circ} \pm 0.01^{\circ}$.

Precision and Duplication of Results.

The resistance of the solutions increases with increasing molecular weight of the solvent; obviously, the precision to be obtained decreases somewhat accordingly. However, it was not found difficult to duplicate potentiometer readings for any pair of concentrations in any of the solvents used.

Quadruplicate determinations of the electromotive force were made for all pairs of concentrations in water, methyl alcohol and ethyl alcohol. This involved four distinctly different set-ups of the apparatus, including new solutions and three freshly plated concordant electrodes for each half cell. The results recorded represent, therefore, the mean of four "mean" potential differences which, over all, do not differ by more than 0.05 mv.

The electromotive forces recorded for solutions in *n*-propyl and isoamyl alcohols are the mean of duplicate measurements, made as previously described. This was deemed sufficient, since the potentiometer readings checked exactly to the last significant figure. The supply of *n*-butyl

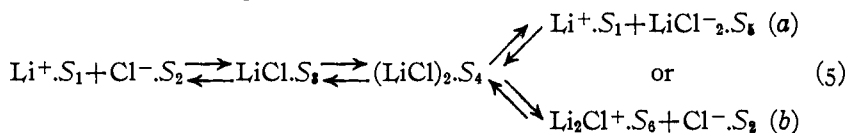
¹ *Loc. cit.*

alcohol at our disposal permitted but a single determination of the electromotive force for a single pair of concentrations in this solvent. Since, however, each half cell contained three electrodes which checked over all to 0.02 mv., and since each electrode was measured directly against each of the three electrodes in the opposite cell, the results obtained for this solvent may be considered as the mean of six different determinations for the same pair of solutions.

Discussion.

Lithium chloride was chosen as the electrolyte because of its relatively high solubility in all of the solvents under consideration. Its use is hampered, however, by certain disadvantages. Various lines of evidence point to its inherent tendency to polymerize when dissolved in the alcohols and other organic solvents,¹ and also to the tendency of both the molecules and the ions to form complex solvates with the solvents.² Washburn and MacInnes³ have calculated for a 0.5 *N* aqueous solution of lithium chloride a probable hydration of 18 moles of water to one mole of the salt.

For a given temperature, the complexity of these solvates must increase with increase in the proportion of the solvent. When the phenomenon of association is present, it is very probable also that both the polymerized molecules and their ions are solvated to some extent. For any given concentration of the salt in any one of the solvents, except perhaps water, we must take into consideration the possible existence of an equilibrium not only between the solvated simple and complex molecules, but also between the two molecular species and their solvated ions, *e. g.*,



where S_1, S_2, S_3 , etc., represent the number of moles of combined solvent.

Slight association, if any, should be expected in water, methyl alcohol and ethyl alcohol. For the alcohols, the relative degree of association of the salt should increase with the decrease in the dissociating power of the solvent, or, as in the present work, with an increase in the molecular weight of the alcohols.

An increase in the concentration of the salt will tend to displace the above equilibrium toward the right. With an increase in the concentration of the polymerized salt molecules there is very probably associated also an increase in the formation of complex ions of greater electro-affinity.⁴

¹ Andrews and Ende, *Z. phys. Chem.*, **17**, 136 (1905).

² Jones and Getman, *Ibid.*, **46**, 261 (1903); *Am. Chem. J.*, **32**, 338 (1904); Jones and McMaster, *Ibid.*, **35**, 445 (1906).

³ THIS JOURNAL, **33**, 1705 (1911).

⁴ Sachanov, *J. Russ. Phys. Chem. Soc.*, **44**, 324 (1912); Pearce, *J. Phys. Chem.*, **19**, 14 (1915).

On the other hand, a sufficient decrease in the concentration will naturally result in the formation of the solvated simple molecules and their ions. While the magnitude of the solvation per mole of the solute decreases with increase in concentration, the total amount of solvent removed from action as combined solvent will be greater, the greater the concentration of the salt. With a decrease in the amount of effective solvent, due to solvation, there is an abnormal increase in the actual concentration of the solute particles, and very probably, therefore, a corresponding abnormal increase in the activity of both the molecules and the ions, whether simple or complex. It is obvious therefore that for such equilibria as that represented above we should expect anomalous relations to appear as we pass from very dilute to very concentrated solutions.

Changes in the extent of polymerization, in ion complexity and in solvation with change in concentration must abnormally effect the electromotive forces of cells without transference. These changes together with the accompanying changes in viscosity must also affect the mobilities of the ions and, therefore, the electromotive forces of cells with transference.

Solvation and polymerization of the salt are not the only factors involved in the study of solutions of electrolytes in organic solvents. The activity of the dissolved molecules and ions is a function of their concentration. According to the Nernst-Thomson rule, the dissociating power of the solvent will be greater, the greater is its dielectric constant. Consequently, considering a given concentration of the electrolyte in various solvents, that solution will contain the greatest concentration of ions, and hence the greatest ion activity, whose solvent possesses the highest dielectric constant.

Euler¹ has found that the dielectric constants of solutions increase with their ion concentration. In some work carried out in this laboratory several years ago² it was found that the dielectric constant of solutions of silver nitrate in methyl and ethyl alcohol increases linearly with the concentration up to 0.05 *N*.

Walden³ has found that the dielectric constants of solvents of feeble ionizing power are increased by dissolving in them certain binary salt. The increase in the value of the constant is dependent upon the constitution of the salt. Strong salts, *e. g.*, lithium chloride, when dissolved possess high dielectric constants and exhibit a great tendency to ionize. The degree of ionization of the salt depends both on the dissociating power of the solvent and the ionizing tendency of the salt. As both of these factors increase with the dielectric constant the highest degree of ionization—hence of ion concentration and ion activity for a given concentration of

¹ *Z. phys. Chem.*, 28, 619 (1899).

² Unpublished.

³ *THIS JOURNAL*, 35, 649 (1913).

the salt,—will be found in a system where both the solvent and the solute possess large dielectric constants.

TABLE I.—ELECTROMOTIVE FORCES WITH TRANSFERENCE (VOLTS).
Concentration ratios (10 : 1).

| Solvent. | Concentration ratios (10 : 1). | | | |
|---------------------------|--------------------------------|-----------|-----------|-------------|
| | 1.0-0.1. | 0.5-0.05. | 0.1-0.01. | 0.05-0.005. |
| Water..... | 0.03194 | 0.03503 | 0.03583 | 0.03640 |
| Methyl alc..... | ... | 0.03857 | 0.04004 | 0.04104 |
| Ethyl alc..... | ... | 0.03323 | 0.03560 | 0.03820 |
| <i>n</i> -Propyl alc..... | ... | 0.02817 | 0.02845 | 0.0311 |
| <i>n</i> -Butyl alc..... | 0.02740 | 0.0271 | 0.0242 | 0.0250 |
| Isoamyl alc..... | 0.02630 | 0.0255 | 0.0243 | 0.0240 |

For solutions in water, methyl, ethyl, and propyl alcohols the electromotive forces with transference increase regularly with increase in dilution. Normally this is just what we should expect. In the *n*-butyl alcohol the electromotive force first decreases, passes through a minimum and then increases slightly upon further dilution. For the isoamyl alcohol there is a corresponding decrease in the values of the electromotive force, tending toward a minimum in the most dilute pair.

TABLE II.—ELECTROMOTIVE FORCES WITHOUT TRANSFERENCE (VOLTS).
Concentration ratios (10 : 1).

| Solvent. | Concentration ratios (10 : 1). | | | |
|---------------------------|--------------------------------|-----------|-----------|-------------|
| | 1.0-0.1. | 0.5-0.05. | 0.1-0.01. | 0.05-0.005. |
| Water..... | 0.11433 | 0.10868 | 0.10433 | 0.09957 |
| Methyl alc..... | ... | 0.09387 | 0.07978 | 0.07162 |
| Ethyl alc..... | ... | 0.08875 | 0.07170 | 0.06143 |
| <i>n</i> -Propyl alc..... | ... | 0.07885 | 0.05890 | 0.0575 |
| <i>n</i> -Butyl alc..... | 0.0825 | 0.0772 | 0.0579 | 0.0501 |
| Isoamyl alc..... | 0.0701 | 0.0625 | 0.0535 | 0.0430 |

For cells without transference the electromotive force of all pairs in the same solvent decreases with increase in dilution. This is exactly the opposite of what we should expect; for, with a normality ratio of 10 : 1, it would be expected that the concentration ratios, as well as the activity ratios, of the ions should gradually increase to the value of 10 at infinite dilution. It is evident that lithium chloride behaves abnormally in all of these solvents. A discussion of this abnormality will be taken up later.

Using the conductivity data of Greene¹ for solutions of lithium chloride in water and those of Jones and Turner² for solutions in ethyl alcohol, we calculated the electromotive forces for cells both with and without transference. In both solvents the calculated values increase with increasing dilution, but in neither type of cell does the Nernst equation apply even approximately.

The transference number of the lithium ion increases with increase in dilution in each of the solvents studied. For a given change in the dilution

¹ *Trans. Chem. Soc.*, **93**, 2042 (1908).

² *Am. Chem. J.*, **40**, 558 (1908).

this increase is least in the aqueous and greatest in the ethyl alcohol. Except for the most dilute cell in the ethyl alcohol, the highest values for the transference number are obtained for solutions in methyl alcohol. For similar concentrations in the alcohols the transference number decreases with increase in the molecular weight of the solvent until isoamyl alcohol is reached, where the corresponding values are found to increase.

TABLE III.—TRANSFERENCE NUMBERS OF THE LITHIUM ION.

| Solvent. | Concentration ratios (10 : 1). | | | |
|---------------------------|--------------------------------|-----------|-----------|-------------|
| | 1.0-0.1. | 0.5-0.05. | 0.1-0.01. | 0.05-0.005. |
| Water..... | 0.279 | 0.322 | 0.343 | 0.365 |
| Methyl alc..... | ... | 0.411 | 0.502 | 0.573 |
| Ethyl alc..... | ... | 0.374 | 0.497 | 0.622 |
| <i>n</i> -Propyl alc..... | ... | 0.357 | 0.483 | 0.541 |
| <i>n</i> -Butyl alc..... | 0.332 | 0.351 | 0.418 | 0.499 |
| Isoamyl alc..... | 0.375 | 0.408 | 0.454 | 0.555 |

When the concentration is such that the possibility of the presence of complex ions exists, the transference number obtained for an ion, *e. g.*, the anion, will be the sum of the transference numbers of the simple and complex anions present. Only at sufficiently high dilutions will we obtain the transference number of the simple ion.

The values for the transference numbers obtained by the electromotive-force method are the mean values between the two concentrations constituting the cell. It is therefore difficult to make a comparison with data directly determined. Table IV gives the values determined by Kohlrausch and Holborn¹ for the transference number of the lithium ion in aqueous solutions at 25°. The mean values have been calculated and are inserted for comparison.

TABLE IV.—COMPARISON OF THE TRANSFERENCE NUMBERS OF THE LITHIUM ION.

| | 1.0-0.1 | | 0.5-0.05. | | 0.1-0.01. | | 0.05-0.005. | |
|------------------------------------|-----------------|-------|-----------|-------|-----------|-------|-------------|-------|
| | Kohlrausch..... | 0.261 | 0.310 | 0.270 | 0.330 | 0.310 | 0.370 | 0.330 |
| Mean N_c (K)..... | 0.285 | | 0.300 | | 0.340 | | 0.360 | |
| Mean N_c (<i>e. m. f.</i>).... | 0.279 | | 0.322 | | 0.343 | | 0.365 | |

The agreement is as satisfactory as could be expected and it confirms the applicability of this method of determining transference numbers.

TABLE V.—FREE ENERGY OF DILUTION (JOULES).

| Solvent. | Concentration ratios (10 : 1). | | | |
|---------------------------|--------------------------------|-----------|-----------|-------------|
| | 1.0-0.1. | 0.5-0.05. | 0.1-0.01. | 0.05-0.005. |
| Water..... | 11032 | 10487 | 10067 | 9608 |
| Methyl alc..... | ... | 9205 | 7698 | 6911 |
| Ethyl alc..... | ... | 8564 | 6919 | 5928 |
| <i>n</i> -Propyl alc..... | ... | 7608 | 5684 | 5548 |
| <i>n</i> -Butyl alc..... | 7961 | 7450 | 5587 | 4834 |
| Isoamyl alc..... | 6764 | 6031 | 5162 | 4149 |

¹ "Leitvermögen der Elektrolyte," p. 201.

² Extrapolated.

It will be observed that for a given normality ratio (10 : 1) the free energy of dilution of lithium chloride decreases regularly as we pass from the lower to the higher members of the same homologous series. Furthermore, for any one of the solvents studied the free energy decreases as the pair of concentrations involved become more dilute. Since the free energy of dilution is proportional to the logarithm of the ratio of the activities of the chlorine ions, we should expect, for the normality ratio used, that the free energy would increase to a maximum at infinite dilution.

Table VI gives a summary of the activity ratios of the ions as calculated by a simple rearrangement of Equation 4. This ratio in the various solvents decreases with increase in dilution of the pairs constituting the cells, and this in spite of an increase in the normal ionization of the electrolyte. A similar decrease was observed by Noyes and Ellis¹ for concentrated solutions of hydrochloric acid. For concentrations ranging from 4.484 *N* to 0.5 *N* they found a decrease in the activity ratios with dilution, followed by an increase in the value of the ratio with further dilution between 0.5 *N* and 0.00338 *N*.

TABLE VI.—ACTIVITY RATIOS OF THE IONS.

| Solvent. | Concentration ratios (10 : 1). | | | |
|---------------------------|--------------------------------|-----------------|-----------------|-------------------|
| | A. 1.0-0.1. | B. 0.5-0.05. | C. 0.1-0.01. | D. 0.05-0.005. |
| Water..... | 9.254 | 8.285 | 7.617 | 6.942 |
| Methyl alc..... | ... | 6.215 | 4.725 | 4.031 |
| Ethyl alc..... | ... | 5.626 | 4.037 | 3.305 |
| <i>n</i> -Propyl alc..... | ... | 4.640 | 3.147 | 3.062 |
| <i>n</i> -Butyl alc..... | 4.981 | 4.493 | 3.086 | 2.651 |
| Isoamyl alc..... | 3.913 | 3.375 | 2.833 | 2.309 |

The relative effect due to an increase in the concentration of the lithium chloride by two-, five-, ten-, and twentyfold upon the activity ratios is shown in Table VII, where *A/B*, *C/D*, etc., represent the ratio of the activity of the ions for one pair of concentrations (*A*) to that of another pair (*B*), etc. These values point distinctly to an increase in ionic activity with increase in concentration of the dissolved salt. As might be expected, this increase is least in the aqueous solutions and it increases as we pass upward in the series of the alcohols.

TABLE VII.—COMPARATIVE EFFECT OF CONCENTRATION UPON THE ACTIVITY RATIOS.

| Solvent. | <i>A/B</i> 2-fold. | <i>C/D</i> 2-fold. | <i>B/C</i> 5-fold. | <i>A/C</i> 10-fold. | <i>B/D</i> 10-fold. | <i>A/D</i> 20-fold. |
|------------------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|------------------------|
| Water..... | 1.17 | 1.09 | 1.09 | 1.21 | 1.19 | 1.33 |
| Methyl alc..... | .. | 1.17 | 1.31 | .. | 1.54 | .. |
| Ethyl alc..... | .. | 1.22 | 1.39 | .. | 1.70 | .. |
| Propyl alc..... | .. | 1.03 | 1.47 | .. | 1.51 | .. |
| Butyl alc..... | 1.11 | 1.16 | 1.45 | 1.61 | 1.69 | 1.88 |
| Isoamyl alc..... | 1.16 | 1.22 | 1.19 | 1.38 | 1.46 | 1.69 |

¹ THIS JOURNAL, 39, 2543 (1917).

In the earlier part of the discussion three factors were discussed, one or more of which may affect the activity ratios of the ions. These were the effect of hydration, the effect of polymerization of the solute molecules followed by complex ionization and the effect of change in the dielectric constant of the solution with change in concentration.

Lithium chloride and more especially the lithium ion exhibit a marked tendency to form complex hydrates in aqueous solution. Similar solvates are to be expected in the various alcoholic solutions.

For a salt which does not form solvates the degree of ionization, and, hence, both the concentration and the activity of the ions, normally decrease with increase in concentration. For salts which tend to form solvates, the total amount of solvent removed from the solution by solvation increases with increase in the concentration of the salt, thus increasing somewhat abnormally both the concentration and the activity of the ions for any given concentration.

Considering any pair of concentrations constituting the cell and using a normality ratio (10 : 1), this abnormal effect will be greater in the more concentrated solution and the abnormality will become relatively greater as the concentration of each of the solutions is proportionally increased. For this reason the ratio of the activities of the ions should *tend* to increase with increase in concentration. At sufficiently high dilutions, on the other hand, the effect due to solvation becomes a minimum and the amount of combined solvent is negligibly small compared with that actually present as solvent. Hence, increase in dilution should be accompanied by a normal increase in the concentration and activity ratios.

The force tending to bring about the recombination of two oppositely charged ions is given by the well-known relation of Coulomb $f = e.e^1/K.d^2$. Or, if we assume the Nernst-Thomson rule, for a given concentration of the electrolyte in the various solvents, the degree of ionization, likewise the concentration and the activity of the ions, increases with the dielectric constant of the solvent.

Table VIII shows the relation between the activity ratios of the ions and the dielectric constant of the solvent.

TABLE VIII.—RELATION BETWEEN ION ACTIVITY RATIOS AND DIELECTRIC CONSTANTS.¹

| | H ₂ O. | CH ₃ OH. | C ₂ H ₅ OH. | C ₄ H ₇ OH. | C ₆ H ₅ OH. | C ₆ H ₁₁ OH. |
|----------------------|-------------------|---------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
| K_d | 80.0 | 32.2 | 26.1 | 22.0 | 19.0 | 16.0 |
| $\sqrt{K_d}$ | 8.94 | 5.67 | 5.108 | 4.69 | 4.356 | 4.0 |
| $A/\sqrt{K_d}$ | 1.03 | ... | ... | ... | 1.14 | 0.98 |
| $B/\sqrt{K_d}$ | 0.92 | 0.91 | 0.91 | 0.98 | 0.97 | 0.84 |
| $C/\sqrt{K_d}$ | 0.85 | 0.83 | 0.79 | 0.67 | 0.71 | 0.71 |
| $D/\sqrt{K_d}$ | 0.72 | 0.71 | 0.65 | 0.65 | 0.61 | 0.58 |

where K_d represents the dielectric constant of the solvent and A , B , C , D represent the activity ratios of the ions taken from Table VI.

¹ Nernst, "Theoretical Chemistry," Trans., 7th Ger. ed., p. 345.

These data point unmistakably to the existence of a definite relation between the activity ratios and the dielectric constants. Considering first the dilute solutions, it will be observed that the ratio $(\xi''/\xi')/\sqrt{K_d}$, does increase with increase in the dielectric constant. For all solvents this ratio increases with increase in the concentration of the solutions constituting the cells and at sufficiently high concentrations approaches equal values for all solvents. The striking equality of this ratio for different concentration ratios in water and methyl alcohol is significant.

Hence, for sufficiently high equivalent concentrations of lithium chloride in water and the paraffin alcohols, we may state that the activity ratios of the ions in equivalent concentration ratios (10 : 1) are approximately proportional to the square roots of the dielectric constants of the solvents, or perhaps better still of the solutions. Unfortunately, we do not know the dielectric constants of any of these solutions.

Since the activity ratios of the ions increase both with the concentration and with the dielectric constant, the activity of the ions in a given solution will be greater, the greater both the concentration and the dielectric constant. There is, therefore, an apparently direct relation between the activity of the ions and their electro-affinities.¹

Smale² has studied the effect of various electrolytes upon the dielectric constant of water. Two of these have an important bearing upon this work. The results are expressed in terms of the dielectric constant of water taken as unity.

| Salt... | Conc. | 0.001 | 0.002 | 0.005 | 0.008 | 0.010 | 0.030 |
|---------|-------|-------|-------|-------|-------|-------|-------|
| KCl... | $K =$ | 1.013 | 1.018 | 1.034 | 1.070 | 1.113 | 1.160 |
| HCl... | $K =$ | 0.990 | 1.033 | 1.064 | 1.090 | 1.126 | ... |

Neither potassium chloride nor its ions exhibit any appreciable hydrating power. Hydrogen chloride, on the other hand, shows a marked affinity for water. Both increase the dielectric constant of water. The decrease in the activity ratios of the ions of potassium chloride (MacInnes and Parker) and the increase in the activity ratios of the ions of hydrochloric acid (Noyes and Ellis), both with increase in concentration, may in all probability be due entirely to differences in hydrating power. The activity ratios of the ions should increase with the concentration most rapidly for salts which have high dielectric constants and great hydrating power.

It is obvious, therefore, that changes in the free energy of dilution, of electromotive force and other factors depending upon the activity ratios must be intimately related to changes in the dielectric constants of the solutions.

While the effects due to solvation and changes in dielectric constant may

¹ By electro-affinity is meant the power of a cation to repel, or the power of an anion to attract an electron.

² *Ann. Phys. Chem.*, [ii] 61, 625 (1897).

explain in part the increase in the activity ratios for solutions in water and the lower alcohols, they alone will not suffice for the interpretation of the effects observed in the higher alcohols. In the latter we undoubtedly have present not only the simple molecules and simple ions, but also polymerized molecules and complex ions, all in equilibrium as represented in (5a) or (5b). A continuous increase in the concentration of the salt results in a constantly increasing concentration of one of the complex ions, e. g., $\text{LiCl}_2^-\cdot\text{S}_6$, or $\text{Li}_2\text{Cl}^+\cdot\text{S}_6$. There is also a corresponding increase in the number of the oppositely charged simple ion. The activity ratio of the negative or positive ions now involves the activities of both the simple and complex ions of each.

For any concentration ratio (10 : 1) the effect produced by polymerization will always be greater in the more concentrated solution and it will increase relatively the more rapidly the greater the proportional increase in the concentration of the two solutions constituting the cell. The abnormal increase in the concentration of the complex ions, coupled with an increase in the dielectric constant and with an increase in the total amount of combined solvent, with increase in concentration of the salt, should and do increase the activity ratios of the ions.

TABLE IX.—ACTIVITY RATIOS OF THE MOLECULES.

| Solvent. | Concentration ratios (10 : 1). | | | |
|---------------------------|--------------------------------|-----------|-----------|-------------|
| | 1.0-0.1. | 0.5-0.05. | 0.1-0.01. | 0.05-0.005. |
| Water..... | 85.63 | 68.64 | 58.02 | 48.19 |
| Methyl alc..... | ... | 38.63 | 22.33 | 16.25 |
| Ethyl alc..... | ... | 31.65 | 16.30 | 13.75 |
| <i>n</i> -Propyl alc..... | ... | 21.53 | 9.90 | 9.37 |
| <i>n</i> -Butyl alc..... | 24.81 | 20.19 | 9.52 | 7.03 |
| Isoamyl alc..... | 15.31 | 11.39 | 8.03 | 5.30 |

The effect of solvent and concentration upon the ratio of the molecules is shown in Table IX. From the relation presented in Equation 4 these ratios are equal to the square of the corresponding activity ratios of the ions. Factors influencing the latter will also influence these accordingly. These data require no further discussion.

This work is being continued with other salts.

Summary.

The electromotive forces of concentration cells have been determined for solutions of lithium chloride in water, methyl, ethyl, *n*-propyl, *n*-butyl and isoamyl alcohols. All of the cells measured contained solutions having a normality ratio of 10 : 1.

The electromotive force with transference increases with increasing dilution for all of the solvents used, except butyl and isoamyl alcohols in which it decreases. The electromotive force without transference decreases with increases in dilution in all of the solvents.

The transport number of the lithium ion has been calculated and it has been found to increase in each solvent as the concentration of the salt is diminished.

The free energy of dilution and the activity ratios of both the ions and the molecules, on the other hand, decrease with the dilution.

An attempt has been made to explain the decrease in the activity ratios, and hence the free energy, on the assumption of effects due to hydration and the change in dielectric constant. For the higher alcohols, it has been found necessary to assume a polymerization and subsequent complex ionization of the salt molecules.

For a given pair of concentrations the activity ratios of the ions increase with increase in the dielectric constant of the solvent. The ratio $(\xi''/\xi')/\sqrt{K_d}$ increases with increase in concentration and at the same sufficiently high equivalent concentrations attains an approximately equal value for all solvents. For these concentrations the ratio (ξ''/ξ') is very nearly directly proportional to the square root of the dielectric constant of the solvent. For similar cells in water and methyl alcohol these ratios are practically identical.

The activity of the ions has been found to increase both with the concentration and with the dielectric constant of the solvent, or of the solution.

IOWA CITY, IOWA.

THE NATURE OF THE INOSITE PHOSPHORIC ACIDS OF SOME IMPORTANT FEEDING MATERIALS.¹

BY J. B. RATHER.

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The theory that phytic acid; an inosite phosphoric acid found in seeds of plants as a complex salt known as phytin, corresponds in composition to the formula $C_2H_3P_2O_9$, was first proposed by Posternak.² Much of the work of European investigators does not agree with this view. Investigations made in America by Patten and Hart³ and Hart and Tottingham⁴ and the earlier work of Anderson⁵ gave results in accord with the theory of Posternak. It was found by the present writer however, that cottonseed meal and wheat bran yielded an inosite phosphoric acid richer in carbon and poorer in phosphorus than is required for the formula proposed by

¹ That portion of this work relating to corn and kafir corn and a part of that relating to wheat bran was read before the American Chemical Society in Kansas City, April, 1917.

² *Rev. Gen. Bot.*, 12, 5 and 65; *Compt. rend.*, 137, 35-8.

³ N. Y. (Geneva) Expt. Sta., *Bull.* 250.

⁴ Wisconsin Expt. Sta., *Tech. Bull.* 9.

⁵ N. Y. (Geneva) Expt. Sta., *Tech. Bulls.* 19 and 21.