atom is surrounded by 4 equidistant and equivalent chlorine atoms lying in 1 plane. The close relation of this structure to that of the cubic crystals of the corresponding hexachlorides is pointed out.

PASADENA, CALIFORNIA

THE FREE ENERGY OF DILUTION OF ALCOHOLIC SOLUTIONS OF LITHIUM CHLORIDE AND THE EFFECT OF SOLVENT UPON THE ACTIVITY OF THE IONS

BY J. N. PEARCE AND H. B. HART

While numerous electrometric investigations have been made of the activity and energy relations of electrolytes in aqueous solutions, almost no attempt has been made to apply this method to the study of non-aqueous solutions.

The present paper contains the results of a study of the electromotive forces of concentration cells, using lithium chloride in ethyl and methyl alcohol as solvents. The cells studied were of the types: Ag | AgCl, LiCl (c_1) | Li.Hg$_x$ — Li.Hg$_x$ | Li.Cl (c_2), AgCl | Ag; and Ag | AgCl, LiCl (c_1) | LiCl (c_2), AgCl | Ag.

In addition to determining the electromotive forces of concentration cells using one alcohol as solvent we have also studied some cells of the type Ag | AgCl, LiCl (c_1) | LiHg$_x$ — Li.Hg$_x$ | LiCl (0.1 M), AgCl | Ag.
       (alcoholic)   (aqueous)

In each case the alcoholic cell was opposed to a cell containing an exactly 0.10 M aqueous solution of the salt. This cell differs from that used by Jones[1] and by Kahlenberg[2] in that ion-transference and solvent diffusion are both eliminated. The electromotive forces of these cells give us the data for calculating the free-energy changes involved in the transfer of one mole of the solute from its solution in one pure solvent to its solution in a second solvent, provided, of course, that the simple reaction that we believe to be taking place in the cell is the only one possible.

Materials and Apparatus

Solvents.—Ordinary 95% ethyl alcohol which had been allowed to stand over quicklime for several weeks and then over anhydrous copper sulfate was successively refluxed over and distilled from metallic calcium and pure dry silver nitrate. Only the middle fraction was collected and this was carefully protected from moisture. The methyl alcohol was purified in a similar way except that the treatment with lime was omitted.

Lithium Chloride.—A very pure sample of the salt was recrystallized 4 times from distilled water and 3 times from conductivity water. The hydrated crystals were trans-

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[1] Jones, Z. physik. Chem., **14**, 346 (1894); Am. Chem. J., **23**, 397 (1900).

[2] Kahlenberg, J. Phys. Chem., **3**, 379 (1899).

ferred to a special flask and completely dehydrated in a current of dry hydrogen chloride at 170°, and then gently heated in a stream of dry hydrogen until the last traces of hydrogen chloride were removed.

Solutions.—Stock solutions were prepared by adding to the anhydrous salt in the original vessel the desired volume of the absolute alcohol, and the exact concentration determined. The various concentrations were then made from these mother solutions by the proper dilution by means of a special filling device. The solutions were boiled in a current of hydrogen to remove the oxygen, cooled under hydrogen and then diluted with alcohol similarly treated. At no time during the experiment did the alcoholic solutions come in contact either with oxygen or with moisture.

Lithium Amalgam.—This was prepared by the electrolysis of a saturated solution of pure lithium chloride using pure redistilled mercury as the cathode. The amalgam was quickly washed with absolute alcohol, completely dried by heating at 100° under reduced pressure and finally stored under pure hydrogen.

The silver electrodes were prepared in the usual manner. The amalgam electrodes were identical with those of Lewis and Kraus.[3] All potential measurements were made in an oil-bath electrically controlled to ±0.02°.

Measurement of Alcoholic Concentration Cells without Transference

$$\text{Ag} \mid \text{AgCl, LiCl } (c_1) \mid \text{Li.Hg}_x \; - \; \text{Li.Hg}_x \mid \text{LiCl } (c_2), \text{AgCl} \mid \text{Ag.}$$

The potential readings for cells of this type (Table I) are the mean values for at least 2 different set-ups of the cell. In these and in all other measurements where silver chloride electrodes are employed, 3 of these electrodes have been placed in each half-cell, thus giving a possibility of 9 different combinations for each individual set-up. In a series of readings for any cell the maximum deviation does not in any case exceed 0.06 mv., except for the most dilute cell where, owing to the high resistance, the maximum deviation is 0.14 mv.

TABLE I

ELECTROMOTIVE FORCES OF CONCENTRATION CELLS WITHOUT ION-TRANSFERENCE

(A)   Solutions in methyl alcohol

c_1 1000 g.	c_2 1000 g.	E_{25} Volts	E_{30} Volts	E_{35} Volts
0.63744	0.06296	0.09758	0.09850	0.09943
0.38116	0.03779	0.09108	0.09194	0.09278
0.12621	0.01358	0.09249	0.09365	0.09484
0.06296	0.006302	0.09684	0.09813	0.09956

(B)   Solutions in ethyl alcohol

0.60717	0.06365	0.09642	0.09728	0.09812
0.38717	0.03827	0.09034	0.09123	0.09214
0.13140	0.01334	0.09226	0.09322	0.09419
0.06365	0.00637	0.09438	0.09546	0.09657

The corresponding concentrations in moles of solute to 100 moles of solvent are given in Table V. The electromotive forces for concentration cells in both solvents show a minimum value for the range 0.38–0.038 M. A similar minimum was found by MacInnes and Beattie[4] for aqueous

[3] Lewis and Kraus, THIS JOURNAL, 32, 1459 (1910).
[4] MacInnes and Beattie, ibid., 42, 1123 (1920).

solutions of lithium chloride at approximately 0.1–0.01 M. Further, for corresponding pairs of concentrations in the 2 solvents the electromotive forces are very similar. They are, however, slightly smaller than the electromotive forces for the corresponding concentration cells in aqueous solutions.

TABLE II

THE DECREASE IN FREE ENERGY AND IN THE HEAT CONTENT ACCOMPANYING THE
TRANSFER OF ONE MOLE OF LITHIUM CHLORIDE FROM CONCENTRATION c_1 TO
CONCENTRATION c_2

(A)   Solutions in methyl alcohol

c_1 1000 g.	c_2 1000 g.	$-\Delta F_{25}$ Joules	$\alpha \times 10^6$	$\beta \times 10^6$	$-\Delta H_{25}$ Joules
0.63744	0.06296	9416	+1877	+1.8	4149
0.38116	0.03779	8789	+1910	+4.4	3784
0.12621	0.01358	8924	+2475	+6.6	2340
0.06296	0.006302	9344	+2726	−4.6	1752

(B)   Solutions in ethyl alcohol

0.60717	0.06365	9304	+1816	−6.4	4268
0.38717	0.03827	8717	+1940	+5.2	3676
0.13140	0.01334	8903	+2072	+2.0	3404
0.06365	0.00637	9107	+2256	+5.4	2983

The decreases in free energy attending the transfer of one mole of lithium chloride from concentration c_1 to concentration c_2 were obtained by multiplying the electromotive force of the cell by 96494. The temperature coefficients of free-energy decrease, α and β, have been calculated by means

TABLE III

ELECTROMOTIVE FORCES OF CONCENTRATION CELLS WITH ION-TRANSFERENCE

(A)   Solutions in methyl alcohol

c_1 1000 g.	c_2 1000 g.	E_{25} Volts	E_{30} Volts	E_{35} Volts
0.63744	0.06296	0.02851	0.02923	0.02990
0.38116	0.03779	0.02753	0.02816	0.02883
0.12621	0.01358	0.02907	0.02985	0.03065
0.06296	0.00630	0.03155	0.03212	0.03307

(B)   Solutions in ethyl alcohol

0.60717	0.06365	0.02740	0.02817	0.02882
0.38717	0.03827	0.02653	0.02735	0.02804
0.13140	0.01334	0.02842	0.02926	0.02993
0.06365	0.00637	0.03018	0.03104	0.03165

of an empirical quadratic equation. The decrease in heat content accompanying the cell reaction at 25° has been calculated from the temperature coefficient of free-energy decrease and the free-energy decrease by the aid of the thermodynamic equation: $d/dT(-\Delta F/T) = \Delta H/T^2$. Substituting in this equation the expression for $-\Delta F$ as a temperature function for any concentration, performing the differentiation indicated and rearrang-

ing the terms, we obtain the relation: $-\Delta H_{25} = -\Delta F_{25}(1 - 298\alpha_{25})$. These values are incorporated in Table II.

Measurements of Alcoholic Concentration Cells with Ion-transference

To form the cells with ion-transference, 2 of the half-cells containing the silver chloride electrodes were joined by a flowing-junction device similar to that employed by Lamb and Larson.[5] The potential readings for a series of different set-ups for any single cell do not vary from the mean by more than 0.03 mv. in any case. These values are given in Table III.

The Transference Numbers of the Lithium Ion in Alcoholic Solutions

The transference numbers of the lithium ion in alcoholic solutions can be obtained by dividing the electromotive force of the cell with ion-transference by that of the corresponding cell without ion-transference. The results of these calculations are summarized in Table IV.

TABLE IV

TRANSFERENCE NUMBERS OF THE LITHIUM ION IN ALCOHOLIC SOLUTIONS

(A)   Solutions in methyl alcohol

c_1	c_2	$(N_{Li^+})_{25}$	$(N_{Li^+})_{30}$	$(N_{Li^+})_{35}$
0.63744	0.06296	0.292	0.297	0.301
0.38116	0.03779	0.302	0.306	0.311
0.12621	0.01358	0.314	0.319	0.323
0.06296	0.006302	0.324	0.327	0.332

(B)   Solutions in ethyl alcohol

0.60717	0.06365	0.287	0.290	0.294
0.38717	0.03827	0.294	0.296	0.301
0.13140	0.01334	0.308	0.314	0.318
0.06365	0.00637	0.320	0.325	0.328

It will be observed that both dilution and increase in temperature are accompanied by a gradual increase in the transference number of the lithium ion. On comparing these values with those obtained by Mac-Innes and Beattie[4] for corresponding concentrations and temperatures in aqueous solutions we find a striking similarity in the magnitude of the transference numbers of the lithium ion in all 3 solvents. There is, however, a slight decrease in the values of these numbers as we pass from water to methyl alcohol to ethyl alcohol. Factors influencing these values are variations in the viscosity of the solutions, the extent to which the ions are solvated and the possible existence of complex ions in the alcoholic solutions.

Measurements of Concentration Cells Containing Two Solvents

Let us imagine an alcoholic solution of lithium chloride separated from an aqueous solution of the salt by a membrane permeable to the salt, but inpermeable to either of the solvents. If the activity of the salt is

[5] Lamb and Larson, THIS JOURNAL, 42, 229 (1920).

different in the two solvents, the salt will pass from the solvent in which its activity is high to the solvent in which the activity is low. The salt will continue to pass until an equilibrium is attained at which the activity of the salt is the same in both solvents. At this point the respective mutual affinities of the two solvents for the salt will be satisfied.

The free-energy change involved in the transfer of one mole of the salt from its activity in one solvent to its activity in a second solvent can be measured by means of a cell of the type, Ag | AgCl, LiCl (c) | Li.Hg$_x$ — Li.Hg$_x$ | LiCl (0.1 M), AgCl | Ag.   (alcoholic)
        (aqueous)

A study of a combination cell of this kind shows that for alcoholic solutions of greater concentrations than 0.01 M the activity of the lithium chloride is greater in the alcoholic than in the aqueous solution. In the passage of 1 faraday of electricity through the cell there is removed from the alcoholic solution to the electrodes 1 equivalent each of the lithium and chloride ions. Simultaneously, there are formed from the electrodes 1 equivalent of each of these 2 ions in the aqueous solution. On closed

TABLE V

ELECTROMOTIVE FORCES OF CONCENTRATION CELLS CONTAINING TWO SOLVENTS IN
WHICH AN ALCOHOLIC SOLUTION OF CONCENTRATION (c) IS OPPOSED TO AN
AQUEOUS SOLUTION 0.1 M WITH RESPECT TO LITHIUM CHLORIDE

(A)   Solutions in methyl alcohol

c_g 1000 g.	c_m 100 mols.	E_{25} Volts	E_{30} Volts	E_{35} Volts
0.63744	2.03990	0.14984	0.15133	0.15287
0.38116	1.21977	0.13082	0.13125	0.13314
0.12621	0.40390	0.08928	0.09023	0.09121
0.06296	0.20148	0.05262	0.05323	0.05385
0.03779	0.12095	0.03963	0.04009	0.04054
0.01358	0.043474	−0.00345	−0.00351	−0.00358
0.006302	0.020169	−0.04394	−0.04455	−0.04518

(B)   Solutions in ethyl alcohol

0.60717	2.79600	0.16892	0.17048	0.17206
0.38717	1.78296	0.14987	0.15125	0.15274
0.13140	0.60510	0.10847	0.10956	0.11068
0.06365	0.29312	0.07216	0.07294	0.07373
0.03827	0.17627	0.05928	0.05992	0.06054
0.01334	0.06146	0.01631	0.01651	0.01672
0.006373	0.02935	−0.02238	−0.02266	−0.02295

circuit this process will continue until the activity of the electrolyte becomes the same in both solvents. The free-energy change accompanying this transfer of one equivalent each of the 2 ions from the alcoholic to the aqueous solution is equivalent to the work done in withdrawing isothermally and reversibly one mole of the lithium chloride from its state in the alcoholic solution and adding it in a similar way to the aqueous solution.

Table V contains a summary of the electromotive forces of these cells.

In order to show the influence of solvent upon the free energy changes and the activity of the ions, the concentrations in moles per 1000 g. have been recalculated in terms of moles of lithium chloride per 100 moles of solvent. Each value in this table is the mean of the values obtained for at least 2 different set-ups of the apparatus and each cell as measured contains 3 silver chloride electrodes. The maximum deviation in the electromotive forces of any single cell does not in any case exceed 0.08 mv.

It will be observed that the values for the electromotive forces of these cells are relatively higher with ethyl alcohol as the second solvent. It is interesting to note also that the sign of the potentials changes at a definite concentration in the neighborhood of 0.01 M. At these concentrations the activity of the alcoholic system is identical with that of the 0.1 M aqueous solution.

The decrease in free energy and the heat-content decrease which accompany the transfer of 1 mole of lithium chloride from the alcoholic solution of concentration (c) to 0.1 M aqueous solution have been calculated. These and the corresponding temperature coefficients of electromotive force are incorporated in Table VI.

TABLE VI

THE FREE-ENERGY DECREASE AND THE HEAT-CONTENT DECREASE ATTENDING THE
TRANSFER OF ONE MOLE OF LITHIUM CHLORIDE FROM ALCOHOLIC
CONCENTRATION (c) TO 0.1 M AQUEOUS SOLUTION

(A) Solutions in methyl alcohol

c_g 1000 g.	c_m 100 mols	$-\Delta F_{25}$ Joules	$\alpha \times 10^6$	$\beta \times 10^6$	$-\Delta H_{25}$ Joules
0.63744	2.03990	14459	+1982	+ 4.0	5916
0.38116	1.21977	12623	+2065	− 6.2	4854
0.12621	0.40390	8615	+2090	+ 7.2	3275
0.06296	0.20148	5078	+2299	+ 3.8	1598
0.03779	0.12095	3824	+2348	− 5.2	1148
0.01358	0.04347	− 333	+3194?	+58.0	− 17
0.006302	0.020169	−4240	+2730	+ 9.2	− 794

(B) Solutions in ethyl alcohol

c_g 1000 g.	c_m 100 mols	$-\Delta F_{25}$ Joules	$\alpha \times 10^6$	$\beta \times 10^6$	$-\Delta H_{25}$ Joules
0.60717	2.79600	16300	+1841	+ 1.0	7354
0.38717	1.78296	14461	+1948	+ 2.6	6060
0.13140	0.60510	10467	+1981	+ 5.6	4286
0.06365	0.29312	6963	+2118	+ 2.6	2505
0.03827	0.17627	5720	+2213	−10.6	1947
0.01334	0.06146	1574	+2391	+12.2	452
0.00637	0.02935	−2160	+2457	+ 9.0	−577

The law of independent activity of the ions of uni-univalent salts in aqueous solutions may be considered as definitely established. For equivalent concentrations of salts containing a common ion the activity of the common ion is independent of the ion associated with it. Moreover, if we make the usual assumption that for a given concentration of

potassium chloride the activities of the potassium and chloride ion are equal, it is possible to calculate the activity of any other ion associated with either of these ions in a solution of the same concentration. In the case of alcoholic solutions, however, the relations are by no means so simple. Here we have to deal not only with the simple molecules and the simple ions, but also probably with polymerized molecules and ions. Where these conditions prevail it is impossible to calculate the exact activity of any definite ion.

The relation between the decrease in free energy and the activity of the ions in an aqueous solution is given by the well-known thermodynamic relation

$$-\Delta F = 2RT \ln \frac{a_2}{a_1},$$

where a_2 and a_1 are the geometric mean values of the activities of the 2 ions at the concentrations, c_2 and c_1, respectively.

Although we have no knowledge of the complexity of the solute particles in the alcoholic solutions we have for the sake of comparison calculated the *apparent* mean values of the activity of the ions of lithium chloride in the alcoholic system, using the modified relation

$$-\Delta F = 2RT \frac{a_e}{0.0779}.$$

Here, $-\Delta F$ is the decrease in free energy accompanying the transfer of 1 mole of lithium and chloride ions from the apparent mean activity value a_e of the ions in the alcoholic solution to their mean activity value $(0.0779)[4]$ in the 0.1 M aqueous solution. Whether or not we wish to accept the idea of apparent ionic activities under these conditions, the values of the activities calculated will enable us to calculate the free-energy changes and the relative ionic activities in the alcoholic solutions.

In the physico-chemical study of aqueous solutions most investigators have adopted the molal basis of expressing concentration, that is, moles of solute in 1000 g. of water. Neither this nor the volume normal basis can be used satisfactorily if we are to compare the effect of solvent, upon any particular solution property. For example, on the basis of 1 mole of lithium chloride in 1000 g. of water, methyl alcohol and ethyl alcohol we would have 1 mole of solute in 55.55, 31.25 and 21.74 moles of the respective solvents. In the following tables we have expressed the concentration c_m in moles of lithium chloride in 100 moles of solvent.

Using the values of $-\Delta F_{25}$ from Table VI we have calculated the apparent activities of the ions at the given concentrations. The mean activities of the ions at round concentrations were read from a straight line plot of the logarithms of these activities against the logarithms of the corresponding concentrations. The corresponding values for aqueous solutions of lithium chloride were determined in a similar manner from the data of MacInnes and Beattie.[4] The mean activities of the ions thus

determined together with the calculated values for the free energy of dilution from concentration c_m to 0.01 M in any solvent are collected in Table VII.

TABLE VII

A COMPARISON OF THE MEAN ACTIVITIES OF THE IONS AND OF THE FREE ENERGY OF DILUTION OF LITHIUM CHLORIDE FROM CONCENTRATION (c_m) TO 0.01 M IN 100 MOLES IN WATER, METHYL ALCOHOL AND ETHYL ALCOHOL AT 25°

c_m	Water		Methyl alcohol		Ethyl alcohol	
	a	$-\Delta F_{25}$	a	$-\Delta F_{25}$	a	$-\Delta F_{25}$
3.000	1.1015	26671	2.1040	22381	2.3440	22756
2.000	0.7551	24799	1.5276	19795	1.6945	21147
1.500	0.5728	23421	1.2190	19677	1.3366	19972
1.000	0.3935	21568	0.8872	18102	0.9968	18518
0.500	0.2042	18317	0.5129	15385	0.5611	15669
0.300	0.1259	15920	0.3396	13342	0.3690	13593
0.100	0.04467	10784	0.1432	9061	0.1528	9223
0.050	0.02312	7521	0.08241	6324	0.08710	6436
0.030	0.01435	5156	0.05508	4327	0.05755	4383
0.010	0.00507	...	0.02301	...	0.02377	...

The decrease in the energy accompanying the dilution of lithium chloride from any given concentration c_m to a concentration of 0.01 M in 100 moles of solvent is greatest in water and least in methyl alcohol. The difference in the corresponding values of $-\Delta F_{25}$ for the 2 alcoholic solutions is small at all concentrations and decreases with increase in dilution. The apparent mean activities of the ions for any concentration are least in water and greatest in ethyl alcohol. It will be observed that through the range of concentration (0.01 − 3.0 M) the mean activity in the water solution increases by about 200-fold, whereas the corresponding increase in the 2 alcohols is slightly more than 100-fold. By extrapolation we have found that the mean activities of the 2 ions in the 2 alcohols attain the same value, 0.003724, at 0.001 M. The corresponding activity in the aqueous solution is 0.00507. Owing to the possibility of introducing error by extrapolation, the data for dilutions higher than 0.01 M have been omitted.

Summary

The electromotive forces of concentration cells both with and without ion-transference, and containing alcoholic solutions of lithium chloride have been measured at 25°, 30° and 35°. From these data we have calculated the transference numbers of the lithium ion and we find that they are of approximately the same magnitude as in water. The decrease in free energy and in the heat content accompanying the dilution have also been calculated.

The electromotive forces of cells containing two solvents in which an alcohol solution of concentration (c) is opposed to a 0.1 M aqueous solu-

tion of lithium chloride have been measured at the same temperatures. The decrease in free energy and in heat content accompanying the transfer of one mole of lithium chloride from its solutions in alcohol to an $0.1\ M$ solution in water have been calculated. Using the values of free energy decrease obtained for these cells, we have calculated the free energy of dilution of lithium chloride in methyl and ethyl alcohol from any concentration c_m to a concentration of $0.01\ M$ in 100 moles of solvent. The apparent geometric mean activities of the ions of lithium chloride have been calculated for the round concentrations expressed in moles per 100 moles of solvent.

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[Contribution from the Chemical Department of Victoria University]

THE SPONTANEOUS DECOMPOSITION OF AMMONIUM CHLORATE

By Fred Fairbrother
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It has long been known that ammonium chlorate decomposes explosively when heated alone to about $100°$ or on being struck with a hammer if mixed with combustible matter.[1]

The decomposition of ammonium chlorate on keeping has been briefly studied by Groschuff[2] and by Gelhaar.[3] Groschuff states that ammonium chlorate decomposes easily when kept, evolving oxygen, chlorine, ammonia (nitrogen chloride and chlorine peroxide) and that, heated above $60°$, it explodes, leaving ammonium chloride. He also states that an aqueous solution saturated in the cold undergoes no marked decomposition on boiling.

Vauquelin[4] states that when ammonium chlorate is gently heated, acid-reacting ammonium chloride is left behind.

Gelhaar observed that a small quantity of dry ammonium chlorate when spread out flat lost in about 7 weeks 80% of its weight as gaseous products, and that the nitrogen became partially oxidized to nitric acid.

The present work shows that a cold saturated solution of ammonium chlorate does not appear to undergo any decomposition when kept indefinitely. On the other hand, when any solid phase is present, the decomposition becomes apparent in a few days and may become violent if the quantity of solid be considerable.

A quantity of ammonium chlorate (about 30 g.) was submerged for some time in contact with about 100 cc. of the mother liquor. The salt remained white for longer than 3 weeks, a small quantity of a colorless gas being evolved. It then became tinged greenish-yellow, and a slow

[1] Mitscherlich, *Pogg. Ann.*, **52**, 85 (1841).

[2] Groschuff, *Deut. mechan. Z.*, **145**, 153 (1912).

[3] Gelhaar, *Schiess Sprengstoffw.*, **11**, 166 (1916).

[4] Vauquelin, Gmelin-Kraut, "Handbuch der anorganischen Chemie," *Bd.* 1, *Abt.* 2, p. 187.