[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ROLLINS COLLEGE]

Thermodynamic Properties of Fused Salt Solution. IX. Lithium Chloride in Silver Chloride

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The following is a continuation of the general program of investigating fused salts and their solutions.

The apparatus and details of procedure have been described previously.[1]

The silver chloride and lithium chloride used in the cells were of the highest purity obtainable commercially. A pure silver wire inserted through a glass tube in the bottom of the cell container served as the negative electrode. The positive electrode was created by bubbling chlorine gas over a treated graphite rod. This treatment consisted of heating the graphite rod at 600° for twenty-four hours in chlorine gas at several atmospheres pressure. Just before using the rod as an electrode it was heated to a bright yellow heat to free it from all volatile products. The chlorine gas for the electrode was obtained by electrolysis of fused lead chloride of highest purity. The fused chlorides of silver and lithium in the cells and of lead in the chlorine generator were freed from all traces of moisture and oxides by bubbling dry hydrogen chloride gas through the filled containers for not less than an hour.

Other investigators, notably Lorenz and coworkers,[2] Hildebrand and Ruhle,[3] and Wachter and Hildebrand,[4] have worked with the chlorine electrode in fused salts. With the exception of the latter work, all previous attempts involved polarization methods and hence uncertainties.

As in previous studies these cells involved thermoelectric effects of from four to seven millivolts due to the temperature gradient existing at each electrode. The results of the e. m. f. measurements upon the cells plus these thermal corrections are given in Table I, and are shown graphically in Fig. 1. The mean deviation of the points from the straight lines drawn through them is less than 0.2 millivolt, while the maximum deviation is about three times this value.

To obtain the relations of free energy to composition at 500 and 600°, the data in Table I were plotted on a large scale and the e. m. f. values at these temperatures determined. These values of the e. m. f. are given under **E** in Table II, together

TABLE I

E. M. F. VALUES OF THE CELL, Ag(s), LiCl IN AgCl(l), Cl_2(g)

Temp., °C.	E. m. f. obsd., volt
Cell A	
$N_1 = 1.000$	
498.1	0.9009
509.8	.8968
512.1	.8964
536.3	.8890
538.3	.8883
551.8	.8844
562.0	.8822
566.5	.8804
567.8	.8802
568.0	.8801
573.2	.8786
597.8	.8718
600.3	.8715
Cell B	
$N_1 = 0.804$	
551.8	0.8949
580.0	.8864
583.5	.8859
591.3	.8839
594.7	.8832
605.7	.8801
623.5	.8757
Cell C	
$N_1 = 0.690$	
503.3	0.9149
510.8	.9129
518.5	.9108
547.3	.9033
563.7	.8993
577.3	.8957
580.7	.8947
582.9	.8946
588.0	.8931
590.7	.8923
599.8	.8901
600.3	.8898
626.5	.8834

Temp., °C.	E. m. f. obsd., volt
Cell D	
$N_1 = 0.573$	
529.0	0.9130
531.8	.9120
537.4	.9109
567.6	.9041
580.8	.9012
590.0	.8989
598.0	.8973
609.4	.8946
617.0	.8927
635.6	.8882
Cell E	
$N_1 = 0.469$	
545.5	0.9152
565.5	.9108
574.3	.9092
587.0	.9070
591.4	.9059
604.3	.9033
611.0	.9015
617.3	.9003
619.2	.9000
629.0	.8980
Cell F	
$N_1 = 0.252$	
552.5	0.9340
554.2	.9338
573.2	.9304
575.0	.9300
584.5	.9288
592.0	.9276
613.0	.9234
624.1	.9218
Cell G	
$N_1 = 0.136$	
592.5	0.9509
595.0	.9506
614.2	.9477
619.2	.9470
629.0	.9463
631.4	.9458

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(1) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930).

(2) Lorenz, "Die Electrolyze geschmolzener Salze," Dritte Teil, Elektromotorische Kräfte, Verlag Wilhelm Knapp, Halle a. S., 1906; *Z. physik. Chem.*, **62**, 119 (1908); **63**, 109 (1908); *Z. angew. Chem.*, **39**, 88 (1926).

(3) Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

(4) Wachter and Hildebrand, *ibid.*, **52**, 4655 (1930).

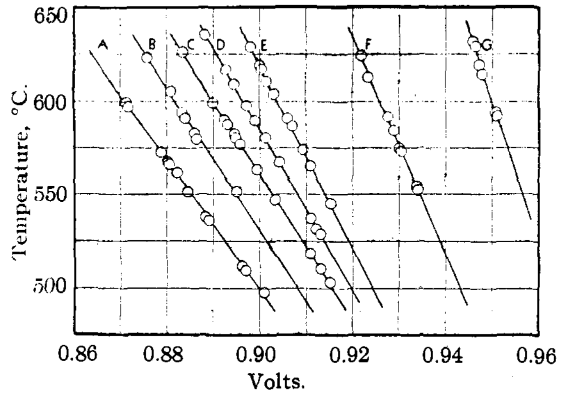

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag, AgCl in LiCl, Cl_2. The mole fractions of cells A to G are 1.000, 0.804, 0.690, 0.573, 0.469, 0.252, 0.136, respectively.

with the values of dE/dT for the different cells. From these have been calculated the free energy of formation of silver chloride from silver and chlorine vapor, ΔF_1, the free energy of dilution of silver chloride by lithium chloride, $\bar{F}_1$, the entropy change, ΔS_1, the partial molal entropy, $\bar{S}_1$, the heat of formation, ΔH_1, the partial molal heat $\bar{H}_1$, the activity of silver chloride in the solutions, a, taking pure silver chloride as the standard state, and the activity coefficient of silver chloride, λ.

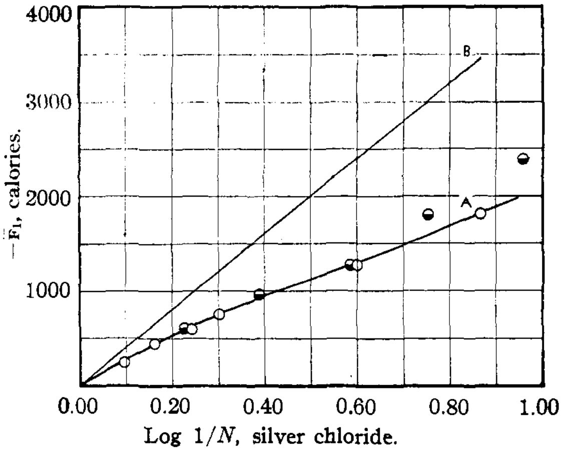

Fig. 2.—Change in free energy of silver chloride at 600° upon dilution with lithium chloride. Curve A shows the observed values, while B is that for a perfect solution. The shaded circles show the values previously obtained for the silver bromide–lithium bromide system.

TABLE II

THERMODYNAMIC PROPERTIES OF SILVER CHLORIDE DILUTED WITH LITHIUM CHLORIDE AT 500°

Cell	A	B	C	D	E	F	G
N_1	1.000	0.804	0.690	0.573	0.469	0.252	0.136
log $1/N_1$	0	.095	.161	.242	.329	.599	.867
E, volt	0.9001	.9085	.9156	.9199	.9249	.9424	.9626
ΔF_1, cal.	−20770	−20960	−21130	−21230	−21340	−21750	−22210
$\bar{F}_1$, cal.	0	−190	−360	−460	−570	−980	−1440
ΔS_1, cal./deg.	−6.74	−6.21	−5.88	−5.40	−4.87	−3.78	−2.98
$\bar{S}_1$, cal./deg.	0	0.53	0.86	1.34	1.87	2.96	3.76
d**E**/dT, mv./deg.	− .292	− .269	−0.255	−0.234	−0.211	−0.164	−0.129
a_1	1.000	.884	.791	.741	.690	.529	.392
γ_1	1.000	1.099	1.147	1.294	1.471	2.097	2.881
			At 600°				
E, volt	0.8709	0.8816	0.8901	0.8965	0.9038	0.9260	0.9497
ΔF_1, cal.	−20100	−20340	−20540	−20690	−20850	−21370	−21910
$\bar{F}_1$, cal.	0	−240	−440	−590	−750	−1270	−1810
a_1	1.000	0.824	0.775	0.712	0.649	0.487	0.352
γ_1	1.000	1.083	1.124	1.242	1.384	1.931	2.592
ΔH_1, cal.	−25980	−25760	−25680	−25400	−25100	−24670	−24510
$\bar{H}_1$, cal.	0	220	300	580	880	1310	1470

Table II contains these calculated values while Fig. 2, curve A shows the partial molal free energy $-\bar{F}_1$, at 600° plotted against log $1/N_1$, where N_1 is the mole fraction of silver chloride. Curve B is that of a perfect solution where $a_1 = N_1$. Assumptions of no ionization or of complete ionization of both salts make no difference in the curve predicted by Raoult's law since in either case $a_1 = N_1$ and curve B results. There is then a marked positive deviation of the results from ideal behavior *i. e.*, in the direction of unmixing. This is in close agreement with the values previously obtained for the dilution of silver bromide by lithium bromide, shown in Fig. 2 by shaded circles except in the case of the highest concentration of added lithium chloride[1] (p. 4650).

A previous treatment of the deviations from ideality of solutions of silver bromide with alkali bromides[5] based upon Hildebrand's definition of regular solutions[6] thus holds equally well for this system. The excess of the partial molal free energy, $\bar{F}_1$, over the ideal, $\bar{F}_1^i$, given by $\bar{F}_1 - \bar{F}_1^i = RT \ln \gamma_1$, fits fairly well the relation, $\bar{F}_1 - \bar{F}_1^i = bN_2^2$, where N_2 is the mole fraction of lithium chloride, and the value of b in calories is 2100 compared to 1880 for the silver bromide-lithium bromide system. That b is practically independent of temperature is shown readily in Table III.

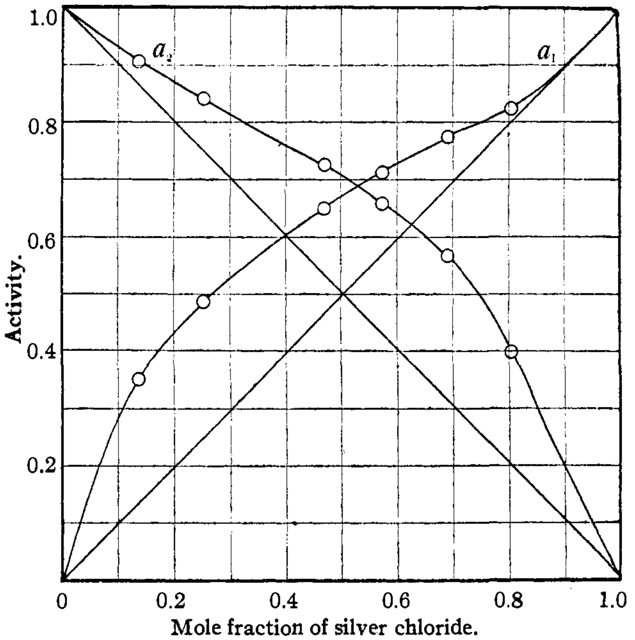

Fig. 3.—Relations of the activities of silver chloride, a_1, and lithium chloride, a_2, to their compositions at 600°.

TABLE III

N_1	1.000	0.804	0.690	0.573	0.469	0.252	0.136
$RT \ln \gamma_1$ at 500°	0	140	210	360	590	1140	1630
$RT \ln \gamma_1$ at 600°	0	140	200	380	560	1140	1650
bN_2^2	0	80	200	380	670	1170	1560

From this it may be concluded that the partial molal entropy is the same as it would be in an ideal solution, *i. e.*, $\bar{S}_1 = R \ln N_1$, indicating that the randomness of arrangement is the same in both cases. The bond between lithium and chloride ions may thus as before be regarded as being completely polar, while that between silver and chloride ions as tending to tighten into a nonpolar bond, this tendency being hindered most by the presence of a small ion such as lithium, without in any case altering the simple cubic lattice arrangement which may probably be assumed to persist into the liquid state.

The activities and activity coefficients of the solute, lithium chloride, have been obtained by integrating graphically the equation given by the Duhem relationship

$$\log a_2/N_2 = -\int_0^{N_2} N_1/N_2 \, d \log a_1/N_1$$

In performing this integration the difficulty is encountered that N_1/N_2 rapidly approaches infinity as $\log a_1/N_1$ approaches zero. However, no change in the ratio between any two values of a_2/N_2 will be produced regardless of what method of extrapolation may be used. It thus becomes more convenient to calculate the activity of the solute by choosing the standard state of lithium chloride as the pure salt rather than the customary standard of infinite dilution. The partial molal free energy of lithium chloride was also obtained from its activity by use of the equation, $\bar{F}_2 = RT \ln a_2$. These values are given in Table IV while Fig. 3 shows the activities of silver chloride and lithium chloride plotted against the mole fraction of silver chloride at 600°.

TABLE IV

THERMODYNAMIC PROPERTIES OF LITHIUM CHLORIDE IN THE SOLUTIONS

Cell	A	B	C	D	E	F	G
N_2	0.00	0.196	0.310	0.427	0.531	0.748	0.864
a_2 at 500°	.00	.436	.614	.687	.740	.851	.912
γ_2 at 500°		2.22	1.98	1.61	1.39	1.14	1.06
$-\bar{F}_2$ at 500°	0	1280	770	580	460	250	140
a_2 at 600°	0.00	0.399	0.567	0.658	0.725	0.841	0.906
γ_2 at 600°		2.04	1.83	1.54	1.37	1.12	1.05
$-\bar{F}_2$ at 600°	0	1590	980	730	700	300	170

Summary

E. m. f. measurements of the cells, Ag (s), AgCl in LiCl (l), Cl_2 (g), have been made at mole fractions of silver chloride varying between 1.000 and 0.136 from temperatures of 500 to 635°.

Calculations of the activity, activity coefficient, free energy of formation and of dilution, entropy, and heat of formation of silver chloride have been made at 500 and 600°.

The activity, activity coefficient, and partial molal free energy of lithium chloride have been evaluated from the Duhem relationships.

A marked positive deviation of the activities of the salts in the solutions from ideality was found and has been discussed briefly.

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(5) Hildebrand and Salstrom, THIS JOURNAL, **54**, 4257 (1932).

(6) J. H. Hildebrand, *ibid.*, **51**, 66 (1929).