chloride have been determined at mole fractions of lead chloride varying from 0 to 0.55, between the temperatures of 440 and 585°.

4. The free energy of formation of pure molten lead bromide was found to be $-69270 + 28t$ between $t = 450°$ and $t = 580°$.

5. The results have been discussed on the basis of simple assumptions regarding ionization, without taking into account the changes in interionic forces.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE THERMODYNAMIC PROPERTIES OF MOLTEN SOLUTIONS OF LITHIUM BROMIDE IN SILVER BROMIDE

BY E. J. SALSTROM AND J. H. HILDEBRAND

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The work described in this paper is a continuation of the general program mentioned in the preceding article of collecting data necessary for a general study of molten salt solutions. Solutions of lithium bromide in silver bromide seem well suited to this investigation because their freezing point curves, investigated by Sandoninni and Scarpa,[1] show no evidence of complex salt formation which might add difficulty to any interpretation of the results. This is likewise true of silver bromide diluted with sodium bromide and with potassium bromide. A study of these latter two systems is now in progress in this Laboratory and when completed will furnish information on the influence of the size of the cation of the diluting salt upon the activity of the solvent.

Experimental Part

The silver bromide was prepared by precipitation from a solution of silver nitrate by ammonium bromide. It was washed repeatedly by decantation with a hot 0.001 *N* hydrobromic acid solution until freed from ammonium salts, then dried by suction on a filter, and finally in an oven at 130° for at least twelve hours. The lithium bromide was of high purity from commercial sources. It was freed from moisture by fusing the salt and bubbling dry hydrogen bromide gas through the melt for two hours. It was subsequently kept in a glass-stoppered bottle in a desiccator over anhydrous calcium chloride. The hydrogen bromide gas and the bromine used for the electrode in the cell were prepared as described in the preceding paper.

With the following exceptions, the apparatus and experimental procedure involved in the study of this system were essentially the same as those described for the lead bromide–lead chloride system. A pure silver

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[1] Sandoninni and Scarpa, *Atti. accad. Lincei*, **22**, II, 517 (1913).

wire inserted through the glass tube E, shown in Fig. 1 in the preceding article, served as the negative electrode. The amounts of lithium bromide added to the cells were but roughly weighed. Air and hydrolysis products were removed as before with a stream of dry hydrogen bromide gas continued in this case for at least two hours. After the run, the entire content of each cell was accurately weighed and dissolved in potassium cyanide solution. Measured portions were analyzed electrolytically.

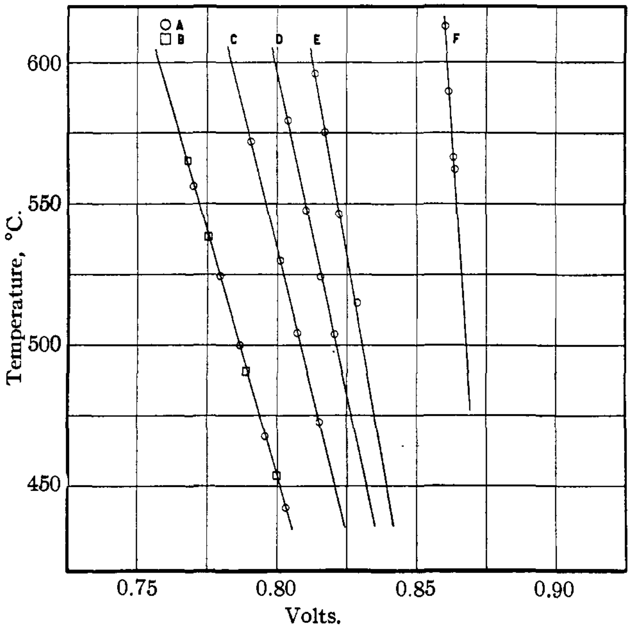

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag/AgBr, LiBr/Br_2. Mole fraction of silver bromide in A and B is 1.0000, C is 0.5937, D is 0.4086, E is 0.2548 and F is 0.1100.

Since the cathode in these cells consisted of solid silver, the effect of any possible strains affecting its activity was investigated by polarizing the cell with 0.1 ampere for half an hour. The subsequent e. m. f. was identical with the previous one, hence at these high temperatures any strains such as are often found at room temperatures are negligible. The thermo-electric effect was measured as before, using in this case silver wire and graphite joined by a short platinum wire.

Measurements for this system are given in Table I and plotted in Fig. 1. The extreme deviation of the observed values from the straight lines drawn through them in Fig. 1 is 0.4 millivolt, and the average deviation is less than 0.15 millivolt.

Values for the e. m. f. of pure silver bromide have been obtained by

TABLE I

$Ag/AgBr, LiBr/Br_2$

Mole fraction of AgBr	Temp., °C.	E. m. f. observed, volt	Mole fraction of AgBr	Temp., °C.	E. m. f. observed, volt
1.000 A	442.3	0.8031	0.5937 C	567.7	0.7918
1.000 B	453.6	.8000	.5937 C	571.9	.7907
1.000 A	456.0	.7989	.4086 D	503.8	.8205
1.000 A	467.0	.7956	.4086 D	524.2	.8154
1.000 B	490.9	.7887	.4086 D	547.5	.8105
1.000 A	499.9	.7866	.4086 D	577.2	.8045
1.000 A	521.4	.7803	.4086 D	579.4	.8040
1.000 A	524.4	.7795	.2548 E	514.9	.8286
1.000 A	531.7	.7769	.2548 E	546.3	.8220
1.000 B	538.3	.7751	.2548 E	549.7	.8213
1.000 A	556.2	.7702	.2548 E	575.3	.8171
1.000 B	565.0	.7680	.2548 E	596.0	.8137
0.5937 C	472.5	.8153	.1100 F	562.0	.8639
.5937 C	501.8	.8081	.1100 F	566.3	.8635
.5937 C	504.2	.8072	.1100 F	589.5	.8616
.5937 C	529.8	.8011	.1100 F	612.8	.8603

Lorenz[2] by a polarization method where the molten salts were not protected from the air, nor, as far as we can determine, were any efforts made to remove oxidation and hydrolysis products. Their results deviate from a straight line by as much as 4 and 5 millivolts. The results chosen by this investigator to smooth out his results are at 450° about 8 millivolts higher than those observed by us, while at 550° they are 6 millivolts lower. Hence, while Lorenz's values are in fair agreement with those herein given, the slope of his curve is very different. Due to the higher melting point of lithium bromide, namely 556°, cells containing high mole fractions of this salt could be run only over a more limited range of temperatures. The experimental results were found to be reproducible within 0.5 millivolt.

The effect of a variable bromine pressure on the e. m. f. of the pure silver bromide cell was again studied. The excellent agreement between the observed and calculated results is shown in Table II.

TABLE II

EFFECT OF PRESSURE ON THE BROMINE ELECTRODE IN THE SILVER BROMIDE CELL

Pressure, cm.	75.66	60.15	44.36	60.36	75.64
Temperature, °C.	456.6	457.2	458.7	458.7	458.7
E (obs.), volt	0.7985	0.7912	0.7814	0.7909	0.7980
E (calcd.), volt	.7985	.7912	.7812	.7909	.7980

In order to determine the volume changes involved in mixing molten silver bromide and lithium bromide, density determinations were made

[2] Lorenz, "Die Elektrolyse geschmolzener Salze," Dritter Teil, p. 30, "Elektromotorische Kräfte," Knappe, Halle a.S., **1906**.

upon a solution containing a half mole fraction of each. The method consisted of weighing a previously standardized quartz cylinder filled with tungsten, first in air and then at various temperatures while suspended in the solution. The measurements are shown in Table III.

TABLE III

DENSITY OF 0.5 MOLE FRACTION LiBr IN AgBr

Temp., °C.	517.4	527.6	533.4	545.6	550.0	555.2
Density	4.051	4.041	4.036	4.026	4.022 (extrapolated)	4.017

Using the density values for silver bromide obtained by Lorenz and Höchberg[3] and for lithium bromide obtained by Brunner,[4] we have shown the densities and molal volumes at 550° in Table IV. The change in volume upon mixing is thus seen to be very slight.

TABLE IV

DENSITIES AND MOLAL VOLUMES OF SILVER BROMIDE AND LITHIUM BROMIDE AND THEIR SOLUTION AT 550°

Composition	Density	Molal volume in cc.
AgBr	5.457	34.40
0.5 mole fraction LiBr in AgBr	4.022	34.15 (34.27 on basis of additivity)
LiBr	2.545	34.15

Discussion of Results

The data for this system have been treated in a manner similar to that described in the preceding paper on the lead bromide–lead chloride system. The results are given in Table V and $-\bar{F}_1$ plotted against log $(1/N_1)$ in curve A, Fig. 2, where N_1 is the mole fraction of silver bromide. If we attempt to calculate $\bar{F}_1$ from N_1 as before, we find that both assumption of no ionization and of complete ionization lead to the same result, $a_1 = N_1$. This gives curve B, Fig. 2, much higher than the observed.

TABLE V

ENERGY RELATIONS OF SILVER BROMIDE WHEN DILUTED WITH LITHIUM BROMIDE

N_1	1.0000	0.5937	0.4086	0.2548	0.1100
$dE/dT \times 10^6$ (volts/deg.)	−290	−248	−204	−170	−76
ΔS_1 (cal./deg.)	−6.69	−5.72	−4.71	−3.92	−1.75
$\bar{S}_1$ (cal./deg.)	0.00	0.97	1.98	2.77	4.94
500°, **E** (volt)	0.7865	0.8085	0.8202	0.8301	0.8686
500°, ΔF_1 (cal.)	−18150	−18660	−18930	−19150	−20040
500°, $\bar{F}_1$ (cal.)	0	−510	−780	−1000	−1890
500°, ΔH_1 (cal.)	−23320	−23080	−22570	−22180	−21400
500°, $\bar{H}_1$ (cal.)	0	+240	+750	+1140	+1920
500°, a_1	1.0000	0.7188	0.6030	0.5197	0.2916
500°, γ	1.000	1.211	1.477	2.040	2.651
550°, **E** (volt)	0.7720	0.7961	0.8100	0.8216	0.8648
550°, ΔF_1 (cal.)	−17810	−18370	−18690	−18960	−19950

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[3] Lorenz and Höchberg, *Z. Krist.*, 288 (1916).

[4] Brunner, *J. Am. Ceram. Soc.*, 350 (1904).

TABLE V (*Concluded*)

550°, $\bar{F}_1$ (cal.)	0	−560	−880	−1150	−2140
550°, a_1	1.0000	0.7119	0.5852	0.4969	0.2703
550°, γ	1.000	1.199	1.432	1.950	2.457
600°, E (volt)	0.7577	0.7836	0.7993	0.8128	0.8610
600°, ΔF_1 (cal.)	−17480	−18080	−18440	−18750	−19870
600°, $\bar{F}_1$ (cal.)	0	−600	−960	−1270	−2390
600°, a_1	1.0000	0.7088	0.5753	0.4808	0.2533
600°, γ	1.000	1.194	1.408	1.887	2.303

In other words, there is a strong positive deviation of the activity from Raoult's law, since a_1 is greater than N_1. It therefore seems that, as with the lead bromide–lead chloride system, the change in interionic forces due to substitution of the smaller lithium ion for the silver ion should be considered. This attempt we will again postpone for a future communication when investigations now in progress will permit a more general treatment.

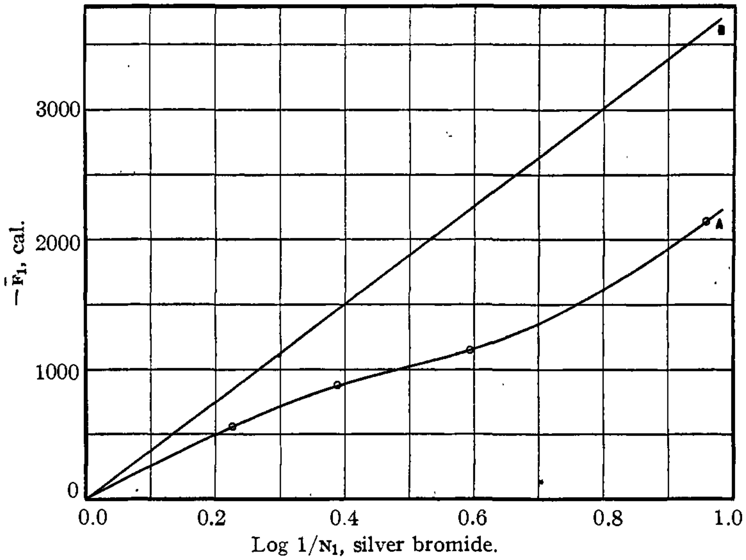

Fig. 2.—Change in free energy of silver bromide at 550° upon dilution with lithium bromide: A, observed; B, calculated.

Summary

1. The energy changes of molten silver bromide upon dilution with lithium bromide have been determined at mole fractions of lithium bromide varying from 0 to 0.89 between the temperatures of 450 to 600°.

2. The free energy of formation of pure molten silver bromide was found to be given by the equation $\Delta F_0 = -21{,}510 + 6.7\,t$ between 440 and 575°.

3. Density determinations of 0.5 mole fraction lithium bromide in silver bromide were made between 517 and 555° and may be expressed by the equation $d^t = 4.504 - 0.000877\ t$.

4. The results have been discussed on the basis of simple assumptions as to ionization, but without taking into account any changes in interionic forces upon dilution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THERMODYNAMIC PROPERTIES OF SOLUTIONS OF MOLTEN LEAD CHLORIDE AND ZINC CHLORIDE

BY A. WACHTER AND J. H. HILDEBRAND

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The following investigation represents a contribution to the program begun by Hildebrand and Ruhle[1] of gathering data upon free energy of dilution of molten salt solutions. The system selected, solutions of lead and zinc chlorides, seemed to be simpler than many others, for the freezing point-composition diagram, obtained by Herrmann,[2] shows no evidence of solid compounds. As in the research of Hildebrand and Ruhle, we started with measurements of the e. m. f. of the cell Pb (liq.) | $PbCl_2$ (liq.) | Cl_2 (gas), but instead of producing the chlorine electrode by polarization, as in the earlier work, and as was done by Lorenz[3] and co-workers for a number of molten chlorides, we succeeded in getting a reversible chlorine electrode, reproducible over a range of pressure and temperature. The lead chloride was then diluted with zinc chloride and the free energy of the dilution determined from the change of e. m. f. of the cell, a procedure which avoids the uncertainty of a liquid junction.

A similar study of certain bromide systems by Salstrom and Hildebrand[4] was carried out approximately at the same time as this one, and the procedure was developed more or less in common. We will therefore avoid needless repetition by referring the reader to the description already given and state here only the features peculiar to this research.

The chlorine, the lead and zinc and their chlorides were from commercial sources of high purity, analyses of which were furnished, and were considered by us to be free from impurities that could affect the e. m. f. Substitution of chlorine generated by electrolysis of pure fused lead chloride made no appreciable difference in the results. The most serious im-

[1] Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

[2] Herrmann, *Z. anorg. Chem.*, 71, 281 (1911).

[3] Lorenz, "Die Elektrolyse geschmolzener Salze," Dritte Teil, Elektromotorische Kräfte, Knappe, Halle a. S., 1906; *Z. physik. Chem.*, **62**, 119 (1908); **63**, 109 (1908); *Z. angew. Chem.*, **39**, 88 (1926).

[4] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4650 (1930).