mercury exposed to the helium. Provided this drift was caused by adsorption of helium on the gel bulb only, it should be nearly the same in all cases as the gel bulb was heated and evacuated each time before admitting the helium. The differences in this drift may be caused partly by mercury surfaces in the manometer containing more or less absorbed helium when exposed to the helium in the gel bulb. In the three determinations of volume of dry gel made before the admissions of 1.6867 g., 0.6357 g. and 0.4017 g. of water, the variations from the mean were only +3 and −4 parts in 17,676, although the drifts in the pressure readings were 1.05 mm., 0.25 mm. and 0.85 mm., respectively. The computations were made, therefore, on the basis of the volumes determined directly with helium, using the lowest pressure readings, and considering that a stable pressure equilibrium was reached in each case.

Summary

Values were obtained for the density of water adsorbed on silica gel by volume measurements using a gas dilatometer with helium as the inactive gas. For small quantities of water up to 4.36% these measurements showed that the density of water adsorbed on silica gel at 25.02° is greater than the density of liquid water at the same temperature.

East Lansing, Michigan

[Contribution from the Chemical Laboratory of the University of California]

THE THERMODYNAMIC PROPERTIES OF MOLTEN SOLUTIONS OF LEAD CHLORIDE IN LEAD BROMIDE

By E. J. Salstrom and J. H. Hildebrand

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The investigation described in this paper represents a continuation of the plan begun several years ago in this Laboratory by Hildebrand and Ruhle[1] of studying the thermodynamic properties of fused salt solutions. There were two disturbing factors involved in that investigation, first, the system studied, solutions of lead chloride with potassium chloride, was somewhat complex, as indicated by the existence of several solid compounds; second, the chlorine electrode was produced by polarization, a procedure that did not guarantee its reversibility. In the present investigation a system has been selected, lead bromide with lead chloride, which, according to Monkmeyer,[2] shows no evidence of compound formation in the solid state. The freezing point varies linearly with the composition, indicating a continuous series of solid solutions. The second complication mentioned above has been avoided by our success in constructing a reversible bromine electrode suitable for use under these conditions.

[1] Hildebrand and Ruhle, This Journal, **49**, 722 (1927).

[2] K. Monkmeyer, *Neues Jahrbuch*, **22**, 1 (1906).

Further interest attaches to this system because Professor W. C. Bray[3] made a suggestion in 1908 that the freezing points of this system should offer an opportunity to determine the extent of ionization. Unfortunately the existence of solid solutions invalidates any simple conclusion from the freezing points and makes desirable the use of some other measure of partial molal free energy. Since the completion of our investigation there have appeared measurements of the partial vapor pressures of this system carried out by Jellinek and Bolubowski.[4] These will be referred to later.

Experimental Part

A. **Materials and Apparatus.**—The lead chloride was from commercial sources of high purity. The lead bromide was prepared by precipitation from ammonium bromide and lead acetate solutions in 0.001 *N* hydrobromic acid. The precipitate was washed repeatedly by decantation with a dilute solution of the acid, and dried by suction on a filter. It was then boiled in the acid solution, cooled, washed again by decantation, dried by suction and twice again subjected to this procedure. Tests then showed it to be free from ammonium salts. It was finally dried in a furnace at 130° for over twelve hours. Hydrogen bromide gas was prepared directly from its elements by passing hydrogen and bromine over a heated catalyst of platinized asbestos. The hydrogen used was especially prepared in this Laboratory by the electrolysis of water. It was freed from oxygen by passing it over a hot nickel catalyst, and from water by passing, first, through a sulfuric acid drying tower, and finally over phosphorus pentoxide. The bromine used in the preparation of hydrogen bromide was freed from chlorine and water by standing over powdered anhydrous calcium bromide and then twice distilled from calcium bromide. The bromine used for the electrode in the cell was generated by electrolysis of molten lead bromide. The hydrogen chloride gas was produced by dropping concentrated sulfuric acid on pure concentrated hydrochloric acid, and was dried by bubbling through a tower containing concentrated sulfuric acid. The molten lead used as an electrode was prepared by electrolysis of pure molten lead bromide.

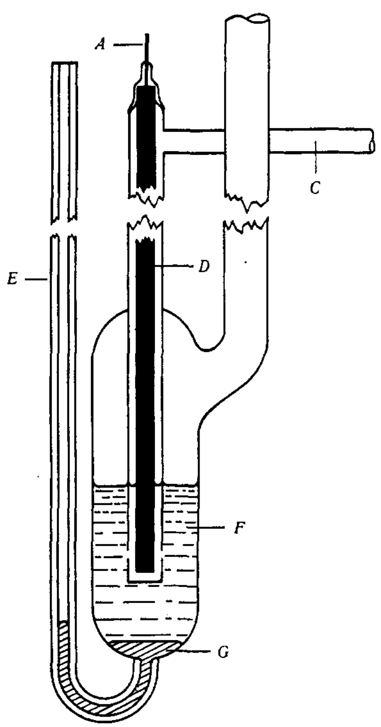

Fig. 1.—Cell container.

The cell containers were made of pyrex glass of cylindrical form, 2–3 cm. in diameter and about 30 cm. long, as shown in Fig. 1. Tungsten wires with copper leads were

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[3] *Cf.* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 219; see also Goodwin and Kalmus, *Phys. Rev.*, **28**, 1 (1909); W. C. Bray, *Z. physik. Chem.*, **80**, 251 (1919).

[4] Jellinek and Bolubowski, *Z. physik. Chem.*, Abt. A, **147**, 461 (1930).

sealed into the tube, E, so as to make contact with the molten lead, G. The positive electrode, D, was a graphite rod 6–10 mm. in diameter, its size depending on the number of heat treatments it had undergone. These rods were sealed into the cells by means of platinum wire leads, A. Tube C served as an inlet for bromine vapor. The large open tube was first used as an opening for charging the cell with salt and metal, after which it was sealed onto a bromine trap, to serve as an exit for bromine. The bromine generator, made of pyrex glass and having positive and negative poles, respectively, of graphite and tungsten wire, was larger than this cell, but similar in construction.

The thermostat consisted of a large electrical resistance pot furnace of high heat capacity and well insulated. The thermostat bath was a mixture of molten lead and tin. An efficient mechanical stirrer kept the bath at a uniform temperature. The pot and stirring fan were of cast iron, and were protected from the solvent action of the bath by several coats of "Insa-lute" cement.

The temperature was measured by two platinum–platinum-rhodium thermocouples, standardized by the U. S. Bureau of Standards. During the course of the investigation the thermocouples were repeatedly checked against each other and were found accurate to within 0.5°. All electromotive force measurements were made on a Leeds–Northrup type K potentiometer.

B. Method of Procedure.—The graphite rods used as electrodes in the cell and generator were first treated for about twenty-four hours with bromine gas under several atmospheres' pressure at 600°. They were then heated in the oxygen flame to a bright yellow heat until no more fumes were evolved, and allowed to cool in an atmosphere of bromine. These rods were used over and over again, but with each new cell or generator the glowing and cooling process was repeated. The only observed difference between graphite rods thus treated and those untreated was that in the former case equilibrium was reached in from one to two hours, while otherwise eighteen to twenty hours were required.

The generator was charged with pure lead bromide and placed in a small cylindrical electrical resistance furnace kept at about 450°. The cells were first charged with pure lead in sufficient amounts to cover completely the sealed-in tungsten wires. Weighed amounts of lead chloride and lead bromide were then added, and the cell was lowered into the thermostat bath and sealed in series with the bromine generator. All connections were of glass only. Stopcocks, where they could not be dispensed with, were lubricated with concentrated sulfuric acid, since bromine attacked the various greases tried, causing them to harden. No openings to the air were permitted except in the bromine exit tube, where a trap of liquid bromine was inserted.

The lead bromide in the generator, and also in the cell, when it contained lead bromide only, was freed from moisture, oxides and hydrolysis products occasioned by the filling and sealing up process by bubbling dry hydrogen bromide gas through the melt for an hour and forty minutes. Without such treatment, the fluctuations in e. m. f. were quite marked. Equilibrium was reached in from one to two hours. Prior to taking each reading, the thermostat was kept constant within one or two degrees for sufficient time to insure constant e. m. f. Each cell was in this way measured at twenty- or thirty-degree intervals over the whole temperature range several times. Ascending and descending series were in complete agreement.

The cells containing solutions of lead bromide and lead chloride were cleaned out with hydrogen chloride gas instead of with hydrogen bromide, since the reaction

$$PbCl_2 + 2HBr = PbBr_2 + 2HCl$$

was found experimentally to proceed almost quantitatively as written.

Using the free energy of formation of lead bromide given in this paper, the free energy value of lead chloride, given by Wachter and Hildebrand in a paper shortly to appear as −58,720 cal., and the free energy equations for the formation of hydrogen chloride and hydrogen bromide gas

$$\text{for HCl, } \Delta F = -21{,}870 + 0.45\, T \ln T - 0.000025\, T^2 - 5.31\, T$$
$$\text{for HBr, } \Delta F = -11{,}970 + 0.45\, T \ln T - 0.000025\, T^2 - 5.74\, T$$

as given by Lewis and Randall,[5] we have calculated the free energy change of this reaction to be −8050 cal. at 500°. That the reverse reaction is negligible in effect was proved by passing hydrogen chloride gas through the cell for thirty minutes, then measuring the e. m. f. over a range of temperatures, again passing in hydrogen chloride for thirty minutes and again determining the e. m. f.–temperature curve. No difference was observed in the two sets of readings.

To test the effect of polarization on the e. m. f. of the pure lead bromide, the cell was electrolyzed by a current of 0.1 to 0.15 ampere for one hour without shutting off the bromine stream from the generator. After such polarization, no change in the readings of the cell was observed. However, when an electrolyzing current of 2 to 3 amperes was used, the e. m. f. immediately after electrolysis was from two to three centivolts higher, thus being more in accord with the results of Lorenz and Czepinski,[6] obtained by a polarization method.

The cells used involved a thermoelectric effect. To correct for this, cells were made up, identical with those used with molten salts with the exception that the contact between tungsten and graphite was in this case made by a platinum wire instead of molten salts. The e. m. f. of these cells, placed in the thermostat in the same position as the other cells, was measured over a temperature range, using two types of graphite rods, some treated as previously described, and others untreated. These gave identical and very reproducible e. m. f.'s.

Since it was hoped that lattice energy considerations would prove useful in interpreting the experimental results, density determinations were made by a pycnometer method, using pyrex bulbs of about 15-cc. capacity and having a capillary stem of 3 mm. The problem of filling these bulbs with the molten salts made a smaller capillary impracticable. The data of Peters and Cragoe[7] indicate that the coefficient of expansion for pyrex glass can be satisfactorily applied up to a temperature of 500°.

Experimental Results

Measurements for this system are given in Table I and plotted in Fig. 2.

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[5] Lewis and Randall, Ref. 3.

[6] Lorenz, "Die Elektrolyse geschmolzener Salze," Dritte Teil, p. 207, "Elektromotorische Kräfte," Knappe, Halle a.S., 1906.

[7] Peters and Cragoe, *Bur. of Stand. Sci. Papers*, **16**, 449–487 (1920).

TABLE I

$Pb/PbBr_2, PbCl_2/Br_2$

Mole fraction of $PbBr_2$	Temp., °C.	E. m. f. observed, volts	Mole fraction of $PbBr_2$	Temp., °C.	E. m. f. observed, volts
1.000 C	438.3	1.0692	0.600 E	445.3	1.0888
1.000 B	443.5	1.0665	.600 E	468.5	1.0765
1.000 A	451.0	1.0615	.600 E	493.9	1.0626
1.000 A	453.0	1.0601	.600 E	514.2	1.0514
1.000 C	465.6	1.0525	.600 E	531.4	1.0422
1.000 B	468.0	1.0516	.600 E	535.5	1.0400
1.000 A	484.3	1.0416	.600 E	552.6	1.0304
1.000 A	496.2	1.0330	.600 E	578.9	1.0160
1.000 C	501.1	1.0306	.600 E	583.6	1.0136
1.000 C	517.1	1.0215	.500 F	450.1	1.0957
1.000 A	520.0	1.0200	.500 F	464.3	1.0879
1.000 B	527.6	1.0156	.500 F	488.2	1.0750
1.000 A	536.0	1.0100	.500 F	516.2	1.0599
1.000 A	556.0	0.9979	.500 F	536.3	1.0490
1.000 B	561.2	1.9945	.500 F	580.2	1.0249
1.000 A	576.0	1.9856	.450 G	448.0	1.1053
0.800 D	450.7	1.0731	.450 G	475.7	1.0897
.800 D	486.3	1.0523	.450 G	501.3	1.0756
.800 D	515.6	1.0350	.450 G	507.5	1.0730
.800 D	551.6	1.0148	.450 G	528.4	1.0616
.800 D	576.5	1.0002	.450 G	553.9	1.0468
			.450 G	584.0	1.0308

Three cells were run for pure lead bromide, cell A containing a graphite electrode treated as above described and cells B and C with untreated graphite rods. Each was run over the whole temperature range of 450 to 580°. In no case was a deviation from a straight line observed in excess of 0.5 millivolt, and the average deviation was less than 0.2 millivolt. The cells containing solutions of lead bromide with lead chloride were found to give equally accurate and reproducible results. The cells containing pure lead bromide yield the relation that $\Delta F = -69270 + 28t$ over the range studied.

The values of Lorenz and Czepinski for the e. m. f. of pure lead bromide obtained by polarization deviate from their smoothed out curve by as much as 5 to 6 millivolts. The curve chosen by them to smooth out their results is about 0.024 volt higher than ours at 450° and 0.030 volt higher at 550°. However, since they carried out their experiments in open vessels and, as far as we can determine, made no effort to eliminate impurities due to oxidation and hydrolysis, we can readily understand why their figures should differ considerably from those herein given.

To determine whether we were actually dealing with a reversible electromotive force, and one which is in accord with the assumed cell reaction, we studied the effect of pressure changes on the e. m. f. of the cell. The bromine passing through the cell was allowed to escape against a reduced external pressure. Table II gives the results. It will be seen that the observed e. m. f.s agree to 0.2 millivolt or better with those calculated by the aid of the usual formula. We may therefore claim a high degree of accuracy for this electrode.

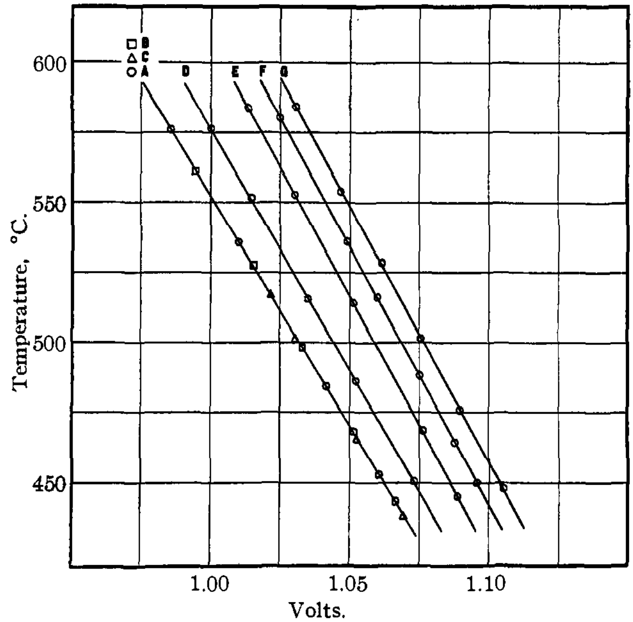

Fig. 2.—Temperature, e. m. f. and composition relations of the cells Pb/PbBr$_2$, PbCl$_2$/Br$_2$. Mole fraction of lead bromide in A, B and C is 1.000, D is 0.800, E is 0.600, F is 0.500 and G is 0.450.

Table II

The Effect of Pressure Upon the Bromine Electrode in the Lead Bromide Cell

Pressure, cm. of mercury	74.96	60.04	43.80	55.21	60.8
Temperature, °C.	443.3	438.6	442.3	443.3	441.7
E (obs.)	1.0671	1.0634	1.0511	1.0576	1.0609
E (calcd.)	1.0671	1.0632	1.0510	1.0576	1.0611

It was found that when the concentration of lead chloride in the molten solution reached a mole fraction of 0.6, the reaction

$$PbCl_2 + Br_2 = PbBr_2 + Cl_2$$

first became noticeable by a gradual falling off in the e. m. f. of the cell if observed over a period of twenty-four hours. Subtracting the free energy of formation of lead chloride from its elements, −58,720 cal. at 500°, from that for the formation of lead bromide from its elements herein given, we arrive at +11,090 cal. as the free energy change of this reaction when each substance is at unit activity. Using this value and assuming that the activities of the salts are proportional to their mole fractions, we have calculated the partial pressure of chlorine at 0.6 mole fraction lead chloride to be less than 0.002 atmosphere at equilibrium. This small pressure might be considered negligible were it not for the fact that chlorine is constantly being swept out as fast as formed by the bromine stream passing through the cell. That the above reaction does not occur appreciably at lower concentrations of lead chloride is shown by the fact that no falling off in the e. m. f. with time is discernible, even though allowed to run for several days. In view of the above considerations, we do not give any measurements upon cells containing lead chloride above 0.55 mole fraction.

In order to determine how the molal volumes of the solutions vary in going from pure lead bromide to pure lead chloride, density determinations were made of the pure salts and solutions of them. The results are given in Table III. The density value given for lead chloride in Table III at 500° was obtained by extrapolation of the molal volumes–composition curve, since the salt freezes at 501°. Extrapolating the density values obtained by Lorenz, Frei and Jabs,[8] we obtain 4.897 for lead chloride at 507° and 5.45 for lead bromide at 500° compared to our measured values of 4.879 and 5.4735, respectively. Since we have extrapolated the values of these investigators below the region for which they were given as valid, the agreement is quite satisfactory.

TABLE III

RELATIONS BETWEEN COMPOSITION, DENSITY AND MOLAL VOLUMES OF LEAD BROMIDE–LEAD CHLORIDE SOLUTIONS AT 500°

Mole fraction lead bromide	1.000	0.800	0.600	0.500	0.450	0.200	0.000
Density of soln.	5.4735	5.381	5.2537	5.2013	5.1219	5.027	4.887 (extrapolated)
Obs. volume of 1 mole of soln. in cc.	67.05	64.86	63.01	61.92	61.335	58.70	56.75 (extrapolated)
Calcd. on basis of additivity	67.05	64.97	62.91	61.88	61.34	58.79	56.75

Discussion of Results

To show the effects of both temperature and composition upon the thermodynamic properties of the salt solution we have proceeded as follows. The plot shown in Fig. 2 was made upon a large scale and the values of the e. m. f., **E**, determined for each solution at the temperatures 450, 500 and 550°. Using then the relation $\Delta F_1 = -23{,}070\ \mathbf{NE}$, where **N** is the number of equivalents per mole, here 2, we calculate ΔF_1, the free energy of formation of lead bromide in calories, from molten lead and bromine vapor at 1 atmosphere. This varies with the mole fraction of $PbBr_2$, N_1, and we will write ΔF_1° to denote pure lead bromide. The partial

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[8] Lorenz, Frei and Jabs, *Phil. Trans. Royal Society*, **7**, 468 (1908).

molal free energy of lead bromide in a solution, $\bar{F}_1$, is then $\bar{F}_1 = \Delta F_1 - \Delta F_1{}^\circ$. The entropy of formation, ΔS_1, is given in calories per degree by $\Delta S_1 = 23{,}070\ \mathbf{N}\ dE/dT$, and the partial molal entropy $\bar{S}_1 = \Delta S_1 - \Delta S_1{}^\circ$. The heat of formation is $\Delta H_1 = \Delta F_1 + T\Delta S_1$ and the partial molal heat $\bar{H}_1 = \Delta H_1 - \Delta H_1{}^\circ$. The activity of lead bromide in its solutions, a_1, taking pure lead bromide as the standard state, is calculated by the relation $\bar{F}_1 = RT \ln a_1$. By dividing the activity by the mole fraction of lead bromide, the activity coefficient, γ, is obtained.

The values so calculated are given in Table IV, and in Fig. 3 are shown, in Curve A, the values of $-\bar{F}_1$ at 500° plotted against log $(1/N_1)$, where N_1 is the mole fraction of lead bromide. In order to see how these values agree with simple assumptions regarding ionization, we will assume, first, that both salts are un-ionized, and that the activity of lead bromide is proportional to its mole fraction. This gives curve B, Fig. 3, much lower than the observed. This corresponds to a negative deviation from Raoult's law, *i. e.*, the activity is less than the simple mole fraction. This can be seen quite clearly by comparing the values of a_1 in the table with the corresponding values of N_1. This result does not accord with the measurements of Jellinek and Bolubowski,[4] who found Raoult's law obeyed by the vapor pressures at temperatures from 660 to 780°. We are at a loss to explain the discrepancy, as neither the difference in the temperature range nor departure of the vapors from the gas laws would seem to be sufficient to account for it.

TABLE IV

ENERGY RELATIONS OF LEAD BROMIDE, WHEN DILUTED WITH LEAD CHLORIDE

N_1	1.000	0.800	0.600	0.500	0.450
$dE/dT \times 10^6$ (volts/deg.)	−607	−580	−548	−544	−542
ΔS_1 (cal./deg.)	−28.01	−26.77	−25.29	−25.10	−25.01
$\bar{S}_1$ (cal./deg.)	0	1.24	2.72	2.91	3.00
450°, **E** (volts)	1.0624	1.0736	1.0866	1.0959	1.1038
450°, ΔF_1 (cal.)	−49030	−49540	−50140	−50570	−50940
450°, $\bar{F}_1$ (cal.)	0	−510	−1110	−1540	−1910
450°, ΔH_1 (cal.)	−69280	−68890	−68420	−68720	−69020
450°, $\bar{H}_1$ (cal.)	0	+390	+860	+560	+260
450°, a_1	1.000	0.698	0.460	0.341	0.265
450°, γ	1.000	.873	.766	.682	.588
500°, **E** (volts)	1.0321	1.0447	1.0593	1.0687	1.0768
500°, ΔF_1 (cal.)	−47630	−48210	−48880	−49320	−49690
500°, $\bar{F}_1$ (cal.)	0	−580	−1250	−1690	−2060
500°, a_1	1.000	0.685	0.442	0.333	0.261
500°, γ	1.000	.856	.737	.667	.581
550°, **E** (volts)	1.0017	1.0156	1.0318	1.0415	1.0496
550°, ΔF_1 (cal.)	−46230	−46870	−47620	−48060	−48440
550°, $\bar{F}_1$ (cal.)	0	−640	−1390	−1830	−2210
550°, a_1	1.000	0.676	0.428	0.326	0.259
550°, γ	1.000	.845	.713	.652	.576

If we assume, second, that both salts are completely ionized, but that the partial substitution of bromide by chloride ion can be made without changing any of the interionic forces (an assumption which is obviously incorrect) then, if we take n_1 moles of $PbBr_2$ to n_2 moles of $PbCl_2$, we get $n_1 + n_2$ moles of Pb^{++}, 2 n_1 moles of Br^- and 2 n_2 moles of Cl^-. The activity of Pb^{++} would then be constant, unity; the activity of Br^- would be $n_1/(n_1 + n_2)$, the activity of $PbBr_2$ the former times the square of the latter, or N_1^2. This makes $-\bar{F}_1$ calculated upon this assumption, curve C in Fig. 3, just twice what it is on the former assumption. This agrees better with the observed values but is too high. We have, therefore, two alternatives, either to assume partial ionization, or, what is obviously preferable, to attempt to take into account the change in the interionic forces due to the substitution of the smaller chloride ion for the larger bromide ion. This we will postpone to a later communication where we will treat at the same time data obtained for other systems.

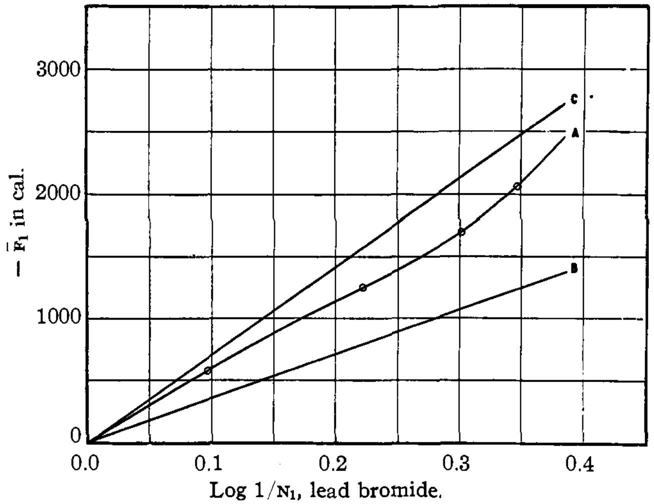

Fig. 3.—Change in free energy of lead bromide at 500° upon dilution with lead chloride: A, observed; B, calculated, no ionization; C, calculated, complete ionization.

Summary

1. A reversible and reproducible bromine electrode has been applied to the study of molten salts and their solutions.

2. Density determinations have been made on lead bromide and lead chloride and solutions of these at 500°. The molal volumes of these solutions have been found to be additive within the limits of experimental error.

3. The energy changes of molten lead bromide upon dilution with lead

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.

BERKELEY, CALIFORNIA

[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).