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## THERMODYNAMIC PROPERTIES OF FUSED SALT SOLUTIONS. IV.<sup>1</sup> POTASSIUM BROMIDE IN SILVER BROMIDE

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The present paper is the continuation of a series of studies dealing with the thermodynamic properties of fused salt solutions. The system selected, potassium bromide in silver bromide, extends particularly that phase of the investigation dealing with the change in activity of fused silver bromide upon dilution with an alkali metal bromide.

### Experimental Part

The potassium bromide was obtained from commercial sources of high purity. The remaining materials and apparatus were similar to those previously described in the lithium bromide-silver bromide investigation.<sup>1</sup> The procedure also remained essentially unchanged. In brief, the method consisted of removing hydrolysis and oxidation products from cells of the type, Ag(s), AgBr(l), KBr(l), Br<sub>2</sub>(g) by bubbling through the melt a stream of dry hydrogen bromide gas for at least two hours. Bromine gas generated by the electrolysis of fused lead bromide, which had been similarly purified, was then bubbled over a graphite rod dipping into the cell solution. A pure silver wire led in through the bottom of the cell container served as the negative pole of the cell. As in previous investigations equilibrium was reached in about two hours. However, in this study it was found more convenient to allow the cell to attain equilibrium by bubbling bromine through the cell overnight at a much reduced rate, about 0.15 ampere electrolyzing current proving sufficient. The bromine flow was then increased by using an electrolyzing current of 0.6 ampere, and e. m. f. readings were taken at certain temperature intervals over the whole permitted temperature range several times. Ascending and descending series were in complete agreement. The exact composition of the cell contents was determined after the run by electrolytic analysis.

The experimental results for this system are given in Table I and are shown graphically in Fig. 1. The e. m. f. values given are the observed results corrected to take into account the thermoelectric effect<sup>2</sup> involved in each cell. The values for the cells containing pure silver bromide are those obtained in the earlier lithium bromide-silver bromide investigation.<sup>1</sup>

<sup>1</sup> Papers I, II and III of this series are, respectively, "Lead Chloride in Lead Bromide," *THIS JOURNAL*, **52**, 4641 (1930); "Lithium Bromide in Silver Bromide," *ibid.*, **52**, 4650 (1930); and "Sodium Bromide in Silver Bromide," *ibid.*, **53**, 1794 (1931).

<sup>2</sup> Salstrom and Hildebrand, *THIS JOURNAL*, **52**, 4644 (1930).

TABLE I

Ag, AgBr, KBr, Br <sub>2</sub>					
Mole fraction of AgBr	Temp., °C.	E. m. f. obsd., volt	Mole fraction of AgBr	Temp., °C.	E. m. f. obsd., volt
1.000A	467.0	0.7956	0.6005C	555.3	0.8163
1.000A	490.9	.7887	.6005C	578.3	.8109
1.000A	499.9	.7866	.6005C	578.4	.8108
1.000A	521.4	.7803	.6005C	597.9	.8063
1.000A	524.4	.7795	.6005C	610.0	.8035
1.000A	531.7	.7769	.4502D	522.0	.8542
1.000A	538.3	.7751	.4502D	542.4	.8495
1.000A	556.2	.7702	.4502D	563.6	.8450
1.000A	565.0	.7680	.4502D	568.7	.8440
0.8000B	467.0	.8104	.4502D	588.5	.8397
.8000B	482.0	.8064	.4502D	609.6	.8354
.8000B	482.7	.8061	.3538E	577.3	.8680
.8000B	509.1	.7992	.3538E	580.4	.8675
.8000B	515.1	.7975	.3538E	584.2	.8668
.8000B	533.1	.7928	.3538E	588.2	.8660
.8000B	553.0	.7874	.3538E	591.5	.8653
.8000B	568.6	.7834	.3538E	592.5	.8650
.8000B	586.6	.7790	.3538E	602.3	.8635
.8000B	587.3	.7788	.3538E	609.1	.8622
.8000B	603.9	.7745	.3538E	612.1	.8618
.6005C	472.2	.8364	.3538E	614.3	.8614
.6005C	487.4	.8327	.3538E	617.6	.8610
.6005C	501.1	.8297	.3538E	618.4	.8608
.6005C	528.6	.8228	.3538E	618.9	.8607
.6005C	554.9	.8164			

The extreme deviation of the observed values from the straight line drawn through them in Fig. 1 is 0.4 millivolt, and the average deviation is less than 0.15 millivolt.

Since a knowledge of the volume changes involved in the mixing of fused silver bromide and potassium bromide may prove important in the final theoretical treatment of the results, density determinations were made upon a solution containing a half mole fraction of each salt. The method used consisted of weighing a tungsten-weighted quartz bulb suspended by a very fine platinum wire first in air, then in water and finally at various temperatures in the fused salt solution, correcting<sup>3</sup> each time for the expansion of quartz. The bulb was sharply tapped before each reading to remove any adhering bubbles of gas. The fused solution used in the density measurements was purified as in the case of the cells by bubbling dry hydrogen bromide gas through the melt. The observed densities are given in Table II.

<sup>3</sup> A calculation of the buoyancy of air upon the bulb was made and found to be negligible. Data are not available for calculating the effect of surface tension of the fused solution upon the suspending platinum wire, but since its diameter was only 0.09 mm. it is believed that such corrections would prove to be less than experimental errors.

TABLE II  
DENSITIES OF 0.5 MOLE FRACTION OF KBr IN AgBr

Temp., °C.	Density	Temp., °C.	Density
546.0	3.515	591.0	3.469
552.6	3.508	596.2	3.463
558.5	3.502	602.3	3.457
562.9	3.498	607.2	3.452
571.1	3.489	616.0	3.442
576.6	3.483	622.8	3.436
583.8	3.476	628.3	3.430
		629.4	3.429

The maximum deviation of the observed values from a straight line drawn through them is 0.5 mg., while the mean deviation is less than

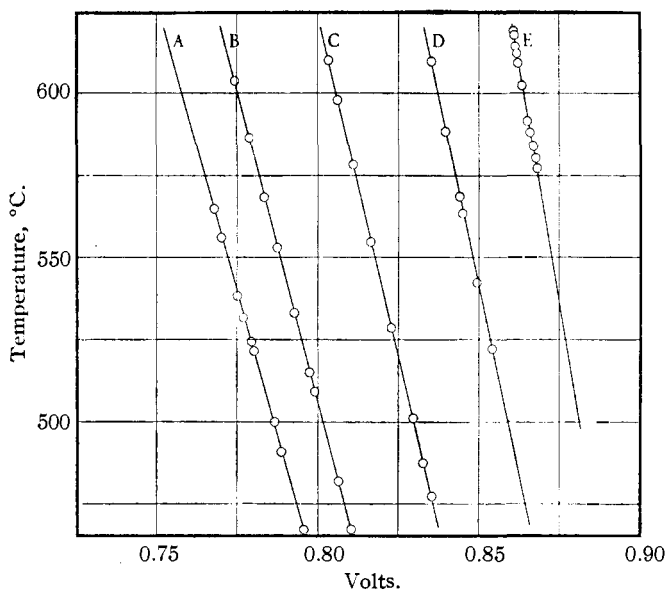


Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag, AgBr, KBr, Br<sub>2</sub>. Mole fraction of silver bromide in A is 1.0000, B is 0.8000, C is 0.6005, D is 0.4502 and E is 0.3538.

0.1 mg. The density of a half mole fraction of potassium bromide in silver bromide may be expressed by the equation,  $d^t = 4.077 - 0.00103t$ . With the aid of the density values for silver bromide obtained by Lorenz and Höchberg<sup>4</sup> and for potassium bromide<sup>5</sup> obtained by Jaeger<sup>6</sup> the molal volumes of silver bromide and potassium bromide have been calculated at

<sup>4</sup> Lorenz and Höchberg, *Z. anorg. allgem. Chem.*, **94**, 288 (1916).

<sup>5</sup> Since potassium bromide melts at 730°, this density would be for the hypothetical supercooled liquid.

<sup>6</sup> Jaeger, *Z. anorg. allgem. Chem.*, **101**, 16 (1917).

600° to be 34.74 cc. and 53.41 cc., respectively. A half mole fraction solution of potassium bromide in silver bromide at this temperature has a molal volume of 44.35 cc. which is 0.28 cc., more than additive.

### Discussion of Results

Since the chief interest lies in the relation of free energy to composition at constant temperature, Fig. 1 was plotted on a large scale and the values of the e. m. f.,  $E$ , determined for each composition by noting the intersections of the lines with the temperature ordinates at 500, 550 and 600°. From these values have been calculated, by the aid of the usual thermodynamic equations, values of the entropy of formation,  $\Delta S_1$ , the partial molal entropy,  $\bar{s}_1$ , the free energy of formation,  $\Delta F_1$ , the free energy of dilution or the partial molal free energy,  $\bar{F}_1$ , the heat of formation,  $\Delta H_1$ , the activity of silver bromide,  $a_1$ , and the activity coefficients,  $a_1/N_1$ .

These values are summarized in Table III, and Fig. 2; curve B shows the free energy of dilution,  $-\bar{F}_1$ , plotted against  $\log(1/N_1)$ , where  $N_1$  is the

TABLE III  
ENERGY RELATIONS OF SILVER BROMIDE WHEN DILUTED WITH POTASSIUM BROMIDE

$N_1$	1.0000	0.8000	0.6005	0.4502	0.3538
$dE/dT \times 10^6$ (volts/deg.)	- 290	- 263	- 240	- 214	- 175
$\Delta S_1$ (cal./deg.)	- 6.69	- 6.07	- 5.54	- 4.94	- 4.04
$\bar{s}_1$ (cal./deg.)	0	0.62	1.15	1.75	2.65
500°, $E$ (volt)	0.7863	0.8016	0.8297	0.8588	0.8815
500°, $\Delta F_1$ (cal.)	- 18150	- 18500	- 19140	- 19820	- 20340
500°, $\bar{F}_1$ (cal.)	0	- 350	- 990	- 1670	- 2190
500°, $\Delta H_1$ (cal.)	- 23320	- 23190	- 23420	- 23640	- 23460
500°, $a_1$	1.000	0.795	0.521	0.335	0.241
500°, $a_1/N_1$	1.000	0.994	0.868	0.745	0.680
550°, $E$ (volt)	0.7720	0.7884	0.8177	0.8483	0.8727
550°, $\Delta F_1$ (cal.)	- 17810	- 18190	- 18870	- 19570	- 20140
550°, $\bar{F}_1$ (cal.)	0	- 380	- 1060	- 1760	- 2330
550°, $a_1$	1.000	0.794	0.525	0.341	0.242
550°, $a_1/N_1$	1.000	0.992	0.875	0.758	0.684
600°, $E$ (volt)	0.7577	0.7753	0.8057	0.8374	0.8640
600°, $\Delta F_1$ (cal.)	- 17480	- 17890	- 18590	- 19320	- 19940
600°, $\bar{F}_1$ (cal.)	0	- 410	- 1110	- 1840	- 2460
600°, $a_1$	1.000	0.791	0.528	0.347	0.243
600°, $a_1/N_1$	1.000	0.989	0.880	0.770	0.688

mole fraction of silver bromide. If a calculation of  $\bar{F}_1$  is attempted by assuming the activity to be given by the mole fraction, it is found that the assumptions of complete ionization of both salts or of no ionization yield the same result, namely,  $a_1 = N_1$ . It may be well to point out that this also remains true if both salts are equally ionized regardless of the degree. Such calculations are represented by curve A, Fig. 2, much lower

than the observed. There is therefore a strong negative deviation of the activity of silver bromide from Raoult's law, since  $a_1/N_1$  is less than unity.

It is of interest to note that at constant mole fraction of silver bromide, successive dilution by lithium bromide, sodium bromide and potassium bromide produces a corresponding increase in the lowering of the activity of silver bromide.

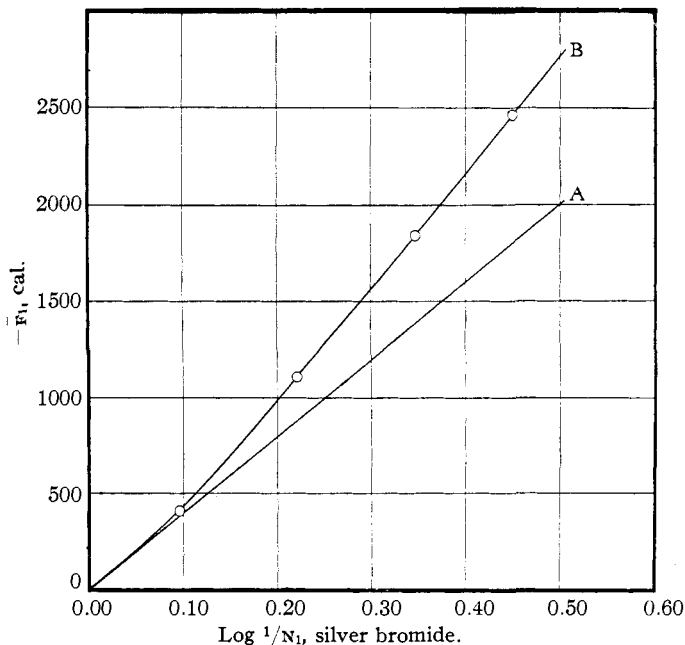


Fig. 2.—Change in free energy of silver bromide at 600° upon dilution with potassium bromide: A, calculated; B, observed.

Data for the rubidium bromide–silver bromide system together with a paper giving a more searching analysis of the results obtained for the alkali metal bromides–silver bromide series will be submitted shortly.

### Summary

1. Measurements of the e. m. f. of the cell,  $\text{Ag}(s)$ ,  $\text{AgBr}(l)$ ,  $\text{KBr}(l)$ ,  $\text{Br}_2(g)$  have been made at mole fractions of silver bromide varying from 1.0000 to 0.3538 between the temperatures 465 and 620°.
2. Densities of a 0.5 mole fraction solution of potassium bromide in silver bromide have been measured between the temperatures 546 and 630°.
3. Calculations for silver bromide have been made of the free energies of formation, free energies of dilution, heats of formation, entropy changes, activities and activity coefficients at the temperatures 500, 550 and 600°.