arc radiation filtered through water and Pyrex glass; in these experiments nitrogen dioxide (not ozone as previously supposed) appeared in the gas. Radiation in the near ultraviolet but not in the visible was found to be effective.

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THERMODYNAMIC PROPERTIES OF FUSED SALT SOLUTIONS. VI. RUBIDIUM BROMIDE IN SILVER BROMIDE

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The investigation described in this paper represents a continuation of a series of studies dealing with the thermodynamic properties of fused salt solutions. The present system, rubidium bromide in silver bromide, concludes that particular phase of the investigation dealing with the change in activity of silver bromide upon dilution with an alkali metal bromide.[1]

Experimental Part

The rubidium bromide was prepared by the neutralization of its hydroxide with pure hydrobromic acid. The neutralization was carried out in a platinum cylinder. After obtaining the rubidium bromide by crystallization from its saturated solution the salt was finally dried by fusing it in a quartz dish. The remaining materials, apparatus and procedure were similar to those previously described in the lithium bromide–silver bromide investigation.[1a]

Briefly the method consisted of applying a reversible bromine gas electrode to the study of fused salt solution cells of the type, Ag(s), AgBr(l), RbBr(l), Br$_2$(g). Hydrolysis and oxidation products occasioned by the filling and sealing of the cell container were removed by bubbling dry hydrogen bromide gas through the melt for at least two hours. Bromine gas generated by electrolysis of fused lead bromide was then bubbled over a treated[2] graphite rod dipping into the melt. After equilibrium was reached, readings were taken at regular temperature intervals in both ascending and descending series. Both series were in complete agreement. The exact composition of each solution was finally determined by electrolytic analysis of the cell contents.

Table I gives the observed results plus a correction to take care of the thermoelectric effect[3] involved in each cell. Figure 1 presents the results

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[1] (a) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4650 (1930); (b) Salstrom, *ibid.*, **53**, 1794 (1931); *ibid.*, **53**, 3385 (1931).

[2] Salstrom and Hildebrand, *ibid.*, **52**, 4641 (1930).

[3] Ref. 2, p. 4644.

graphically. The e. m. f. values for the cell containing pure silver bromide are those obtained in the previous silver bromide–lithium bromide investigation.[1a] The extreme deviation of the results from a straight line drawn through them in Fig. 1 is 0.4 millivolt, while the mean deviation is less than 0.2 millivolt.

TABLE I

Ag(s), AgBr(l), RbBr(l), Br_2(g)

Mole fraction of AgBr	Temp., °C.	E. m. f. obs., volt	Mole fraction of AgBr	Temp., °C.	E. m. f. obs., volt
1.000A	456.0	0.7989	0.596C	537.7	0.8304
1.000A	467.0	.7956	.596C	557.9	.8254
1.000A	490.9	.7887	.596C	579.0	.8203
1.000A	499.9	.7866	.596C	598.0	.8154
1.000A	521.4	.7803	.596C	598.1	.8153
1.000A	524.4	.7795	.596C	617.0	.8112
1.000A	531.7	.7769	.467D	488.8	.8723
1.000A	538.3	.7751	.467D	519.5	.8653
1.000A	556.2	.7702	.467D	537.4	.8609
1.000A	565.0	.7680	.467D	557.2	.8564
0.747B	462.8	.8215	.467D	557.9	.8562
.747B	495.3	.8128	.467D	584.0	.8504
.747B	504.9	.8101	.467D	595.0	.8478
.747B	519.4	.8065	.467D	617.6	.8429
.747B	519.8	.8062	.352E	518.5	.9001
.747B	544.2	.7997	.352E	528.7	.8981
.747B	560.9	.7956	.352E	539.1	.8958
.747B	580.7	.7905	.352E	549.3	.8937
.747B	601.0	.7852	.352E	561.1	.8913
.747B	617.9	.7811	.352E	573.6	.8891
.596C	468.8	.8478	.352E	592.5	.8853
.596C	494.7	.8411	.352E	592.7	.8852
.596C	505.9	.8383	.352E	609.3	.8812
.596C	506.1	.8486	.352E	621.7	.8788

In order to determine the volume changes involved in the mixing of rubidium bromide and silver bromide, density determinations were made upon a fused solution containing a half mole fraction of each salt. The method employed consisted of weighing a quartz bulb weighted with tungsten, first in air, then in water and finally at various temperatures in the fused salt solution. At each temperature corrections[4] were made for the expansion of quartz. To avoid the accumulation of any gas bubbles on the bulb it was sharply tapped before each reading. The observed density values are given in Table II.

[4] A calculation of the effect 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 did not exceed 0.09 mm. it is believed that such corrections would also prove negligible.

Densities of 0.5 Mole Fraction of Rubidium Bromide in Silver Bromide

Temp., °C.	514.0	527.2	537.5	551.5	563.2	576.6	591.0	609.0	623.6
Density	3.838	3.822	3.808	3.791	3.778	3.762	3.743	3.720	3.702

The above density values may be expressed by the equation $d^t = 4.470 - 0.00123t$. With the aid of the density values for silver bromide obtained
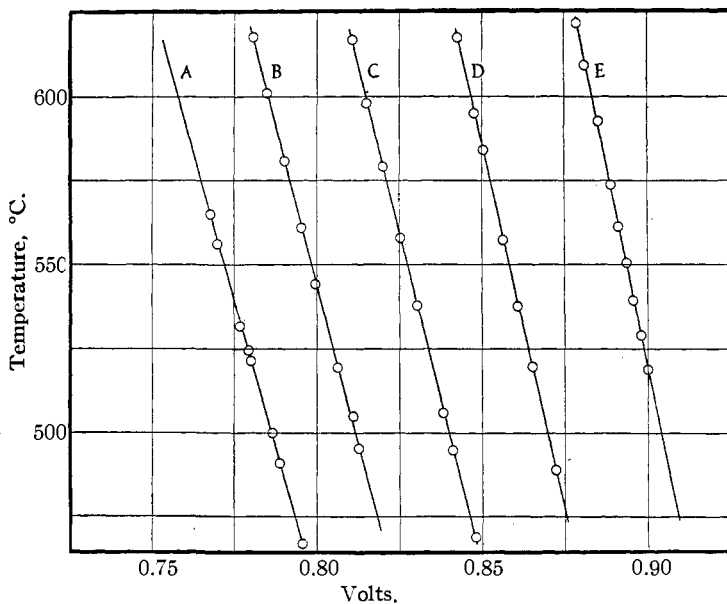

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag–AgBr–RbBr–Br$_2$. Mole fraction of silver bromide in A is 1.000, B is 0.747, C is 0.596, D is 0.467, and E is 0.352.

by Lorenz and Hochberg[5] and for rubidium bromide obtained by Brunner,[6] the molal volumes of silver bromide and rubidium bromide at 600° have been calculated to be 34.74 cc. and 59.07 cc.,[7] respectively. A solution containing a half mole fraction of each salt has an observed molal volume of 47.32 cc., which is 0.42 cc. more than additive.

Discussion of Results

To show the effect of both temperature and composition upon the thermodynamic properties of the fused salt solution the plot shown in Fig. 1 was made upon a large scale and the values of the e. m. f., **E,** determined for each

[5] Lorenz and Hochberg, Z. anorg. allgem. Chem., **94,** 288 (1916).

[6] Brunner, ibid., **38,** 350 (1904).

[7] Since rubidium bromide is solid below 683°, this molal volume would be for the hypothetical supercooled liquid.

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, Δs_1, the entropy change upon dilution or the partial molal entropy, $\bar{s}_1$, the free energy of formation, ΔF_1, the free energy of dilution or the partial molal free energy, $\bar{F}_1$, the heat of formation, ΔH_1, and the heat of dilution, $\bar{H}_1$, the activity of silver bromide, a_1, and the activity coefficient, a_1/N_1, where N_1 represents the mole fraction of silver bromide.

The values so calculated are given in Table III and in Fig. 2 are shown in Curve A, values of $-\bar{F}_1$ at 600° plotted against log $(1/N_1)$. If it is assumed that the activity is proportional to the mole fraction, it is found that both the assumption of complete ionization of both salts or of no ionization yield the same results, namely, $a_1 = N_1$. A calculation of $\bar{F}_1$ on this basis, represented by curve B, Fig. 2, is much lower than the observed. There is, therefore, a strong negative deviation from Raoult's law, *i. e.*, the activity is less than the simple mole fraction. Attention may be called to the fact that the calculated values of $\bar{F}_1$ would not differ from those calculated above if both salts were assumed to be equally ionized regardless of the degree. However, it is believed desirable not to consider partial ionization.

TABLE III

ENERGY RELATIONS OF SILVER BROMIDE WHEN DILUTED WITH RUBIDIUM BROMIDE

N_1	1.000	0.747	0.596	0.467	0.352
$dE/dT \times 10^6$ (volts/deg.)	−290	−260	−247	−229	−207
Δs_1 (cal./deg.)	−6.69	−6.00	−5.70	−5.28	−4.78
$\bar{s}_1$ (cal./deg.)	0.00	0.69	0.99	1.41	1.91
500°, E (volt)	0.7865	0.8116	0.8398	0.8697	0.9040
500°, ΔF_1 (cal.)	−18150	−18730	−19380	−20070	−20860
500°, $\bar{F}_1$ (cal.)	0	−580	−1230	−1920	−2710
500°, ΔH_1 (cal.)	−23320	−23370	−23790	−24150	−24550
500°, $\bar{H}_1$ (cal.)	0	−50	−470	−830	−1230
500°, a_1	1.000	0.686	0.449	0.287	0.172
500°, a_1/N_1	1.000	0.918	0.754	0.614	0.487
550°, E (volt)	0.7720	0.7986	0.8275	0.8582	0.8937
550°, ΔF_1 (cal.)	−17810	−18430	−19090	−19800	−20620
550°, $\bar{F}_1$ (cal.)	0	−620	−1280	−1990	−2810
550°, a_1	1.000	0.687	0.457	0.297	0.180
550°, a_1/N_1	1.000	0.920	0.767	0.635	0.511
600°, E (volt)	0.7577	0.7856	0.8151	0.8468	0.8833
600°, ΔF_1 (cal.)	−17480	−18130	−18810	−19540	−20380
600°, $\bar{F}_1$ (cal.)	0	−650	−1330	−2060	−2900
600°, a_1	1.000	0.688	0.466	0.306	0.188
600°, a_1/N_1	1.000	0.921	0.782	0.655	0.535

The theoretical significance of the deviation of this system from Raoult's law together with a comprehensive treatment of the three previous studies

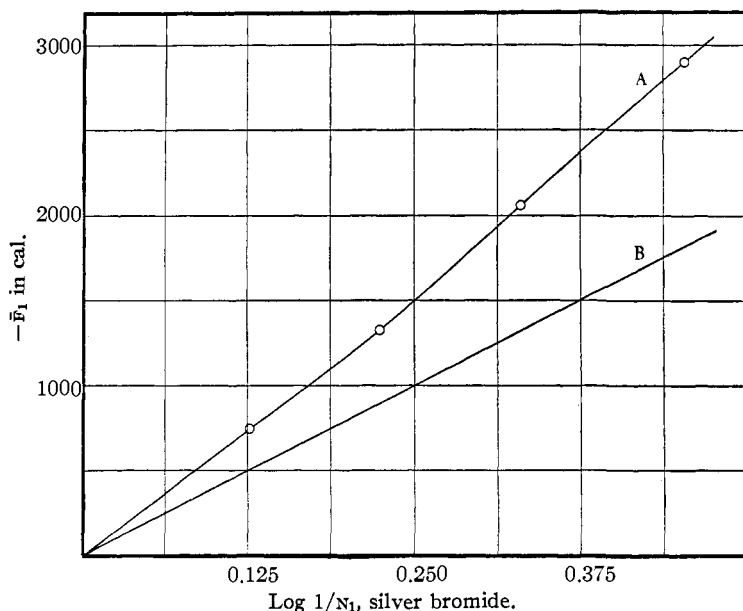on silver bromide–alkali metal bromide solutions is being presented in the following paper.

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

Summary

1. A reversible bromine gas electrode has been applied to the study of the thermodynamic properties of fused solutions of rubidium bromide in silver bromide.

2. E. m. f. values are given for the cell, $Ag(s), AgBr(l), RbBr(l), Br_2(g)$, at 1.000, 0.747, 0.596, 0.467 and 0.352 mole fractions of silver bromide.

3. The density of a half mole fraction solution of rubidium bromide in silver bromide has been measured between the temperatures 514 and 624°.

4. Calculations of the free energy of formation, free energy of dilution, heat of formation, entropy changes, activity and activity coefficients are given at the temperatures 500, 550 and 600°.

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