

Summary

1. It has been shown by conductimetric titration of several nominally trivalent ammine bases prepared from aquo ammine bromides that the complexly held water molecules have in these instances been completely displaced by an equivalent number of the hydroxyl ions. The adjustment of these displacement equilibria is rapid and the hydroxo groups formed are firmly held.

2. The apparent ionizations of the hydroxyl groups remaining outside of the complex are high and are nearly identical in each of these cases, irrespective of the nature of the central atom, the coordinated groups and the valence of the cation.

3. The replacement of the complexly held water molecules is not, however, universally complete. Stated otherwise, the hydroxo group may in certain cases be largely replaced by a water molecule and thereafter ionized.

4. This interaction between these aquo ions and hydroxyl ions is comparable to that between aquo ions and anions in general, although the replacement of water molecules by the hydroxyl group is relatively extensive and the attainment of equilibrium is unusually rapid.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 12]

THERMODYNAMIC PROPERTIES OF FUSED SALT SOLUTIONS. V. LEAD BROMIDE IN SILVER BROMIDE

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The investigation described in this paper represents a continuation of a series of studies on the thermodynamics of fused salt solutions begun by Hildebrand and Ruhle.¹ The system lead bromide in silver bromide was chosen because the melting points of their solutions permitted a study extending over the entire range of their composition. Thus it was believed that the activities of both the solvent and solute could be determined.

Experimental Part

The lead bromide was prepared by precipitation from a solution of lead acetate with excess hydrobromic acid. The precipitate was repeatedly washed by decantation with a 3% solution of hydrobromic acid and finally dried at 150° for several days. Silver bromide was similarly prepared by precipitation from a silver nitrate solution. The bromine and hydrogen bromide were prepared as previously described in the lithium bromide-silver bromide study.²

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

² Salstrom and Hildebrand, *ibid.*, **52**, 4650 (1930).

The cells, apparatus and procedure remained essentially unchanged.² In short, the method was as follows. Silver bromide and lead bromide were weighed out in the desired proportions. The salts were carefully melted together in a Pyrex tube, mixed by stirring and poured in the molten state into the Pyrex cell containers. The final traces of moisture, oxidation and hydrolysis products occasioned by filling and sealing the cell containers were swept out by bubbling through the melt a dry stream of hydrogen bromide gas for at least an hour and a half. Bromine gas generated by the electrolysis of fused lead bromide which had been similarly purified was then bubbled through the electrolyte over a treated graphite rod³ which served as the positive electrode. The negative electrode was a pure silver wire inserted into a tube leading into the bottom of the cell. Molten tin served as a thermostat bath. Equilibrium was attained in a couple of hours but in practice the cell was allowed to run overnight. Readings were then taken at regular temperature intervals in both ascending and descending series, all of which were in complete agreement.

The results are given in Table I and plotted in Fig. 1. The e. m. f. values given are the observed results corrected to take into account a thermoelec-

TABLE I
E. M. F.'S OF THE CELLS: Ag(s), AgBr(l), PbBr₂(l), Br₂(g)

Temp., °C.	E. m. f. obs., volt	Temp., °C.	E. m. f. obs., volt	Temp., °C.	E. m. f. obs., volt
Cell A ($N_1 = 1.00$)		Cell D ($N_1 = 0.60$)		Cell G ($N_1 = 0.30$)	
442.3	0.8031	429.0	0.8391	438.0	0.8756
453.6	.8000	451.4	.8331	474.6	.8683
456.0	.7989	452.2	.8329	511.5	.8615
467.0	.7956	474.3	.8271	529.5	.8584
490.9	.7887	502.5	.8198	547.2	.8549
499.9	.7866	520.7	.8152	560.6	.8525
521.4	.7803	554.5	.8071		
524.4	.7795	567.1	.8038	Cell H ($N_1 = 0.20$)	
531.7	.7769			427.0	0.9012
538.3	.7751	Cell E ($N_1 = 0.50$)		432.9	.9000
556.2	.7702	428.5	0.8496	436.0	.8993
565.0	.7680	441.4	.8466	457.3	.8966
		468.8	.8399	488.3	.8916
Cell B ($N_1 = 0.80$)		496.0	.8334	494.7	.8904
437.6	0.8183	521.9	.8275	508.9	.8881
468.5	.8099	545.2	.8221	513.9	.8877
499.5	.8014	547.4	.8216	518.9	.8866
520.5	.7958	567.7	.8173	541.1	.8831
551.0	.7878			562.7	.8798
551.4	.7877	Cell F ($N_1 = 0.40$)			
571.3	.7826	423.6	0.8639	Cell I ($N_1 = 0.10$)	
		429.6	.8627	430.7	0.9426
Cell C ($N_1 = 0.70$)		461.9	.8549	459.2	.9399
429.1	0.8295	485.5	.8501	483.6	.9369
439.8	.8264	507.7	.8453	508.0	.9342
475.7	.8169	545.5	.8364	530.0	.9316
510.0	.8077	568.5	.8316		
541.7	.7993				
569.7	.7921				

³ Salstrom and Hildebrand, THIS JOURNAL, 52, 4641 (1930).

tric effect³ caused by the fact that a definite temperature gradient exists in each electrode. Values for the cell containing pure silver bromide were those obtained in a previous lithium bromide-silver bromide investigation.²

The extreme deviation of the observed values from a straight line drawn through them in Fig. 1 is 0.5 millivolt and the mean deviation is less than 0.1 millivolt.

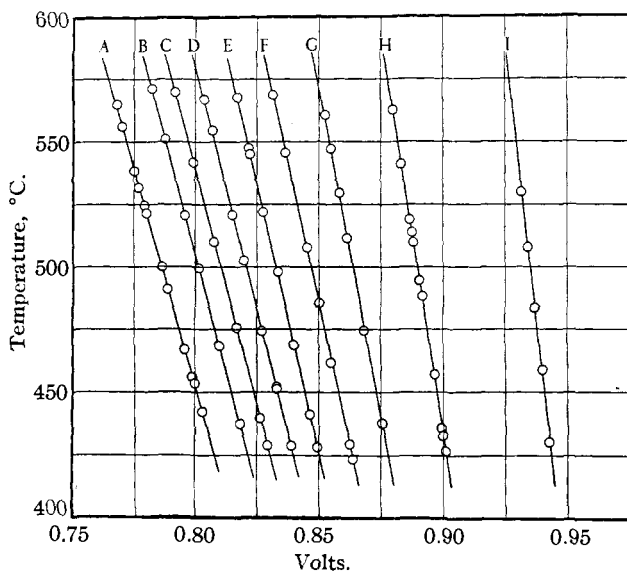


Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag, AgBr, PbBr₂, Br₂. See Table I for mole fractions of silver bromide.

To determine how the volume of a mole of solution varies with composition, 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, correcting⁴ 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 for two hours.

The observed density values may be expressed by the equation, $d^t = 6.243 - 0.00146t$ and are given in Table II.

⁴ A calculation of the effect of the buoyancy of air upon the bulb was made and it was found to be negligible. Data are not available for calculating the influence of surface tension of the fused solution upon the suspending wire but since its diameter was less than 0.1 mm. it is believed that such corrections would also prove to be negligible.

TABLE II
DENSITIES OF A 0.5 MOLE FRACTION OF LEAD BROMIDE IN SILVER BROMIDE

Temp., °C.	Density	Temp., °C.	Density
493.7	5.523	545.9	5.446
507.9	5.502	558.2	5.428
522.0	5.481	572.2	5.409
533.9	5.463	581.6	5.395

With the aid of density values for silver bromide obtained by Lorenz and Höchberg⁵ and for lead bromide obtained by Lorenz, Frei and Jabs,⁶ the molal volumes of silver bromide and lead bromide have been calculated at 500° to be 34.10 cc. and 66.53 cc., respectively. A half mole fraction solution of lead bromide in silver bromide at this temperature has an observed molal volume of 50.32, which is identical with that calculated on the basis of additivity.

Discussion of Results

To show the effect of both temperature and composition upon the properties of the solutions, Fig. 1 was plotted on a large scale and the values of the e. m. f. determined for each composition at the temperatures 450, 500 and 550° by noting the intersections of the curves with these temperature ordinates. By applying the usual thermodynamic equations³ to these e. m. f.'s, values have been calculated for the free energy of formation of silver bromide from solid silver and bromine vapor, ΔF_1 , the free energy of dilution or the partial molal free energy, \bar{F}_1 , the entropy change, ΔS_1 , and the partial molal entropy, \bar{S}_1 , the heat of formation, ΔH_1 , the activity of silver bromide in the solutions taking pure silver bromide as the standard state, a_1 , and the activity coefficient, a_1/N_1 , where N_1 is the mole fraction of silver bromide.

These values are given in Table III, and Fig. 2, curve C, shows the partial molal free energy, $-\bar{F}_1$ at 500°, plotted against $\log(1/N_1)$.

In order to compare this observed curve with that calculated on the assumption that Raoult's law is obeyed it may be assumed, first, that both salts are un-ionized. Then the partial molal free energy is given by the equation, $\bar{F}_1 = RT \ln N_1$, where $N_1 = a_1$. This gives curve B, Fig. 2, which agrees perfectly with the observed results up to a half mole fraction of added lead bromide. With increasing concentration of lead bromide there is a slight but increasing positive deviation of the activity of silver bromide from Raoult's law, since a_1/N_1 becomes greater than unity. However, even at the maximum concentration of lead bromide (0.9 mole fraction) the calculated partial molal free energy of silver bromide is only 110 calories more than the observed. To make sure that these small deviations were not fortuitous, the cells were carefully checked. Their respective

⁵ Lorenz and Höchberg, *Z. anorg. allgem. Chem.*, **94**, 288 (1916).

⁶ Lorenz, Frei and Jabs, *Phil. Trans. Royal Soc.*, **7**, 468 (1908).

TABLE III

ENERGY RELATIONS OF FUSED LEAD BROMIDE-SILVER BROMIDE SOLUTIONS

N_1	1.00	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10	0.00 ^a
$dE/dt \times 10^6$ (volt/deg.)	-290	-268	-266	-258	-234	-222	-191	-158	-112	-607
Δs_1 (cal./deg.)	-6.69	-6.18	-6.14	-5.95	-5.40	-5.12	-4.41	-3.65	-2.58	-28.01
\bar{s}_1 (cal./deg.)	0	0.51	0.55	0.74	1.29	1.57	2.28	3.04	4.11	0
450°, E (volt)	0.8010	0.8149	0.8238	0.8336	0.8446	0.8580	0.8733	0.8976	0.9407	1.0624
450°, ΔF_1 (cal.)	-18480	-18800	-19010	-19230	-19490	-19800	-20150	-20710	-21710	-49030
450°, \bar{F} (cal.)	0	-320	-530	-750	-1010	-1320	-1670	-2230	-3230	0
450°, a_1	1.000	0.800	0.692	0.594	0.495	0.399	0.313	0.212	0.106	
450°, a_1/N_1	1.00	1.00	0.99	0.99	0.99	1.00	1.04	1.06	1.06	
500°, E (volt)	0.7865	0.8015	0.8106	0.8207	0.8328	0.8470	0.8637	0.8897	0.9352	1.0321
500°, ΔF_1 (cal.)	-18150	-18490	-18700	-18940	-19220	-19540	-19930	-20530	-21580	-47630
500°, \bar{F}_1 (cal.)	0	-340	-550	-790	-1070	-1390	-1780	-2380	-3430	0
500°, ΔH_1 (cal.)	-23320	-23270	-23440	-23540	-23390	-23500	-23340	-23350	-23580	-69280
500°, a_1	1.000	0.801	0.699	0.600	0.500	0.404	0.314	0.213	0.107	
500°, a_1/N_1	1.00	1.00	1.00	1.00	1.00	1.01	1.05	1.06	1.07	1.08
550°, E (volt)	0.7720	0.7882	0.7972	0.8078	0.8212	0.8358	0.8542	0.8818	0.9295	1.0017
550°, ΔF_1 (cal.)	-17810	-18190	-18390	-18640	-18950	-19290	-19710	-20350	-21450	-46230
550°, \bar{F}_1 (cal.)	0	-380	-580	-830	-1140	-1480	-1900	-2540	-3640	0
550°, a_1	1.000	0.794	0.700	0.603	0.500	0.406	0.313	0.212	0.108	
550°, a_1/N_1	1.00	0.99	1.00	1.01	1.00	1.02	1.06	1.06	1.08	

^a These values are for the cell: Pb(l), PbBr₂(l), Br₂(g).

temperature—e. m. f. curves agreed within 0.2 millivolt which would correspond to a deviation of ± 5 calories in the partial molal free energy.

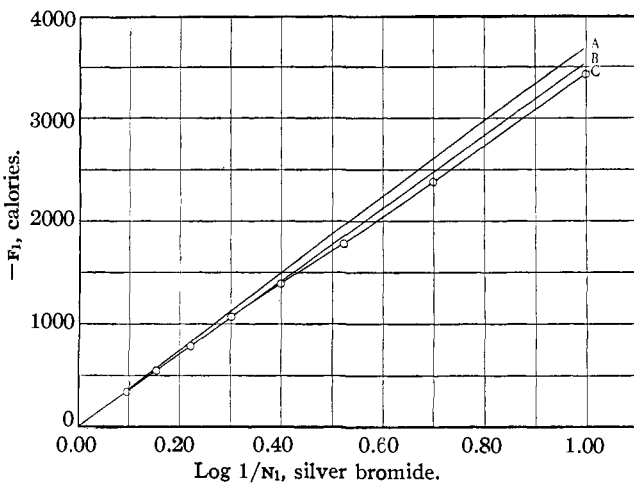


Fig. 2.—Change in free energy of silver bromide at 500° upon dilution with lead bromide: C, observed; A, calculated on the basis of complete ionization of both salts; B, calculated on the basis of no ionization.

If it is assumed, second, that Raoult's law is obeyed and that both salts are completely ionized, but that the partial substitution of silver by lead ion can be made without changing any of the interionic forces, then if n_1 moles of silver bromide and n_2 moles of lead bromide are taken, there will then be n_1 moles of Ag^+ , n_2 moles of Pb^{++} and $n_1 + 2n_2$ moles of Br^- . The activity of Ag^+ would then be $2n_1/(2n_1 + 3n_2)$, the activity of Br^- , $2(n_1 + 2n_2)/(2n_1 + 3n_2)$, and the activity of silver bromide, the product of the two, or

$$a_1 = 4n_1(n_1 + 2n_2)/(2n_1 + 3n_2)^2$$

The $-\bar{F}_1$ calculated on this basis, curve A in Fig. 2, is found to be too high.

Since the deviation of the activity of silver bromide from Raoult's law though small is undoubtedly real, it is believed worth while to calculate the activity of the solute, namely, lead bromide, in the solutions. This may be done by employing the general partial molal equation⁷ showing for any infinitesimal alteration in composition at constant temperature and pressure, the relation between the change in any one partial molal quantity and the change in all others, namely

$$N_1 \left(\frac{\partial \bar{G}_1}{\partial N_1} \right)_{P,T} + N_2 \left(\frac{\partial \bar{G}_2}{\partial N_2} \right)_{P,T} + \dots = 0$$

⁷ Cf. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 43.

where \bar{G}_1 and \bar{G}_2 are any partial molal quantities. Introducing the free energy into this equation and choosing the standard state of lead bromide in the solution at infinite dilution, *i. e.*, $a_2/N_2 = 1$ when $N_2 = 0$, this general equation may be brought into the form

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

In general when the above equation is integrated graphically by plotting N_1/N_2 against $\log a_1/N_1$ the difficulty is encountered that N_1/N_2 rapidly approaches infinity as N_2 approaches zero. However, in this case it is not necessary to go beyond the value of 1.0 for N_1/N_2 , for from this point on Raoult's law is obeyed, *i. e.*, $a_1/N_1 = 1$, and its logarithm is therefore zero.

By such graphical integration the activity, a_2 , and activity coefficient, a_2/N_2 , of lead bromide were obtained. By using the equation $\bar{F}_2 = RT \ln a_2$ the partial molal free energy, \bar{F}_2 , of lead bromide was also calculated, which when added to the free energy of formation of fused lead bromide³ from molten lead and bromine vapor yields ΔF_2 . The values so obtained are given in Table IV and Fig. 3, curve A, shows $-\bar{F}_2$ plotted against $\log (1/N_2)$. To see how this agrees with Raoult's law it may be assumed first, that both salts are un-ionized. Calculation of $-\bar{F}_2$ on this basis gives curve C, Fig. 3, which agrees very well with the observed results, the maximum positive deviation being less than 80 calories.

TABLE IV
THERMODYNAMIC RELATIONS OF FUSED LEAD BROMIDE-SILVER BROMIDE SOLUTIONS

N_2	a_2	a_2/N_2	\bar{F}_2	ΔF_2
At 500°				
1.000	0.962	0.962	0	-47630
0.900	.873	.970	- 150	-47780
.800	.782	.978	- 320	-47950
.700	.692	.988	- 510	-48140
.600	.598	.996	- 730	-48360
.500	.500	1.000	-1010	-48640
.400	.400	1.000	-1350	-48980
.300	.300	1.000	-1790	-49420
.200	.200	1.000	-2410	-50040
At 550°				
1.000	0.959	0.959	0	-46230
0.900	.871	.967	- 160	-46390
.800	.781	.977	- 340	-46570
.700	.690	.986	- 540	-46770
.600	.597	.995	- 780	-47010
.500	.500	1.000	-1070	-47300
.400	.400	1.000	-1430	-47660
.300	.300	1.000	-1900	-48130
.200	.200	1.000	-2600	-48830

If it is assumed, second, that both salts are completely ionized and that the partial substitution of lead by silver ion can be made without changing any of the interionic forces, then if n_1 moles of AgBr and n_2 moles of PbBr_2 are taken there would be n_2 moles of Pb^{++} , n_1 moles of Ag^+ and $2n_2 + n_1$ moles of Br^- . The activity of Pb^{++} would then be $3n_2/(3n_2 + 2n_1)$, the activity of Br^- would be $3(2n_2 + 1)/2(3n_2 + 2n_1)$ and the activity of lead bromide the former times the square of the latter, or

$$a_2 = 27n_2(2n_2 + n_1)^2/4(3n_2 + 2n_1)^3$$

Such calculations are represented by curve B, Fig. 3, which is slightly higher than that calculated on the basis of no ionization.

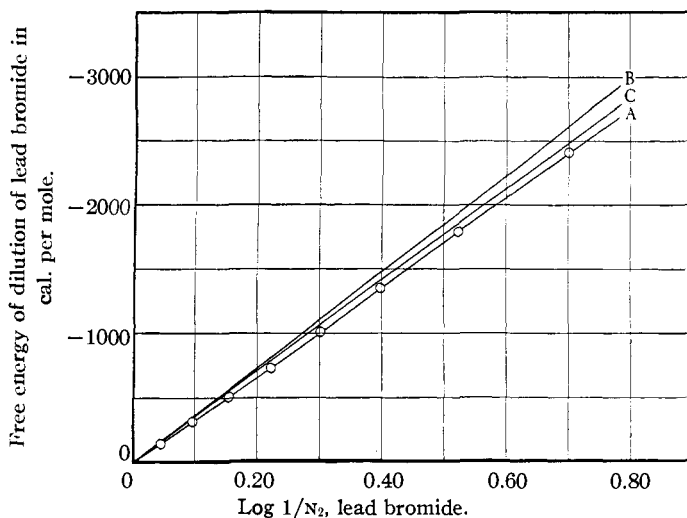


Fig. 3.—Change in free energy of lead bromide at 500° upon dilution with silver bromide: A, observed; B, calculated on the basis of complete ionization of both salts; C, calculated on the basis of no ionization.

It is thus evident that the observed free energies of dilution of both silver bromide (Fig. 2) and lead bromide (Fig. 3) agree very well with that calculated on the basis that Raoult's law is obeyed if it is assumed that both salts are un-ionized, while they agree less well with that calculated on the assumption that both salts are completely ionized. However, the calculations of \bar{F} based on these two assumptions hardly differ sufficiently to warrant a choice between them. The activity coefficients of the two salts in Tables III and IV also show that this close agreement with Raoult's law is not a fortuitous one at a single temperature but persists practically unchanged throughout the whole range of temperature studied. These considerations coupled with the fact that the molal volume of the solution is additive make it clear that we are dealing here with a system that conforms very closely with the perfect solution laws.

Summary

1. Measurements of the e. m. f. of the cell, Ag(s), AgBr(l), PbBr₂(l), Br₂(g) have been made at mole fractions of silver bromide varying from 1.00 to 0.10 between the temperatures 425 and 575°.

2. Densities of a 0.5 mole fraction solution of lead bromide in silver bromide are given by the relation $d^t = 6.243 - 0.00146t$ between the temperatures 490 and 580°.

3. The relations between composition and free energy, heat of formation, entropy change and activity coefficient of the solvent, fused silver bromide, have been calculated for 450, 500 and 550°.

4. The relations between composition and free energy and activity coefficient of the solute, fused lead bromide, have been calculated at 500 and 550°.

5. The activities of both solvent and solute agree very well with that predicted by Raoult's law throughout the entire range of temperature studied.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

QUANTUM MECHANICS OF ACTIVATED ADSORPTION

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The experiments of Taylor and Sherman¹ showed that activated adsorption is involved in the ortho-para hydrogen conversion at a variety of surfaces. On charcoal the activation energy must be small—approximately 2 kg. cal.—since the conversion occurs at liquid hydrogen temperatures.² The conversion on a given charcoal surface was shown by Taylor and Sherman to be bimolecular at room temperatures, and the surface action exhibited a temperature coefficient less than unity between liquid air temperatures and 0°. It becomes a matter of considerable interest to apply the methods used by Eyring and Polanyi³ for calculation of activation energies to determine the necessary conditions for so low an activation energy. The calculations presented in the following pages seem sufficiently accurate to indicate clearly the process by which the reaction proceeds, although, of course, the exact numerical results are subject to revision.

The mechanism for the conversion of ortho to para hydrogen on charcoal probably involves three steps: (1) activated adsorption; (2) collision

¹ Taylor and Sherman, *Trans. Faraday Soc.*, Symposium on Adsorption (1932).

² Bonhoeffer and Harteck, *Z. physik. Chem.*, B4, 113 (1929).

³ Eyring and Polanyi, *ibid.*, B12, 279 (1931).