THERMODYNAMIC PROPERTIES OF LIQUID SOLUTIONS OF SILVER BROMIDE WITH ALKALI BROMIDES

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The series of investigations begun by us,[1] and since continued by the junior author, on the free energy of dilution of molten silver bromide by the alkali bromides, now includes all of the latter except cesium bromide and has reached a stage where their theoretical interpretation may be attempted, for the regularities are such that the inclusion of cesium bromide could hardly yield any additional information of importance.

A graphic summary of the results[2] is given in Fig. 1, where $\bar{F}_1 - \bar{F}_1^i$ is plotted against N_2^2. $\bar{F}_1$ is the partial molal free energy of the silver bromide in the solution, connected with the activity by the relation $\bar{F}_1 = RT \ln a_1$. If the solution were ideal, a_1 would equal N_1 and $\bar{F}_1^i = RT \ln N_1$. From this it is seen that $\bar{F}_1 - \bar{F}_1^i = RT \ln a_1/N_1 = RT \ln \gamma_1$, where γ_1 is the activity coefficient. N_2 is the mole fraction of the alkali bromide.

It is evident, from Fig. 1, that the data plotted in this way show a remarkably linear relation. The pairs of points are for 550 and 600°; they fall so close together as to indicate that temperature is practically without effect. We may conclude from this that the partial molal entropy is the same as it would be in an ideal solution, i. e., $\bar{s}_1 - \bar{s}_1^i = 0$, or $\bar{s}_1^i = R \ln N_1$, indicating that the randomness of the arrangement is the same in both cases. These systems agree with the senior author's definition of regular solutions.[3]

The deviation from ideal behavior of the solutions with lithium bromide and sodium bromide is in the direction of unmixing, while those with potassium bromide and rubidium bromide deviate in the direction of compound formation. This is in harmony with the fact reported by Sandonnini and Scarpa[4] of the non-congruent freezing-out of a solid, probably AgBr·RbBr,

[1] E. J. Salstrom and J. H. Hildebrand, THIS JOURNAL, **52**, 4650 (1930); E. J. Salstrom, *ibid.*, **53**, 1794, 3385 (1931); **54**, 4252 (1932).

[2] Since publication of the paper on the system AgBr–LiBr, an additional cell has been studied containing a solution with 17.63 mole per cent. of AgBr, yielding the following results

t, °C.	$E - E_0$ millivolts	$-\bar{F}_1$. cal.	$\bar{F}_1 - \bar{F}_1^i$, cal.	γ
500	61.7	1425	1240	2.20
550	69.9	1610	1230	2.11
600	78.0	1800	1210	2.01

These data have been included in Fig. 1.

[3] J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

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

in the case of the last-named system.   This suggests that the solutions deviating in this direction may be explained by assuming an equilibrium of the type $Br^- + AgBr = AgBr_2^-$.   We shall not adopt this point of view, however, because, first, it seems not to harmonize with the above-mentioned fact regarding the entropy and, second, a different type of explanation would then have to be applied to the solutions with lithium bromide and sodium bromide, whereas it is evident from Fig. 1 that we are dealing with a family of curves showing a quite regular trend from one extreme to the other, and that a single type of explanation should, if possible, be found for all four systems.
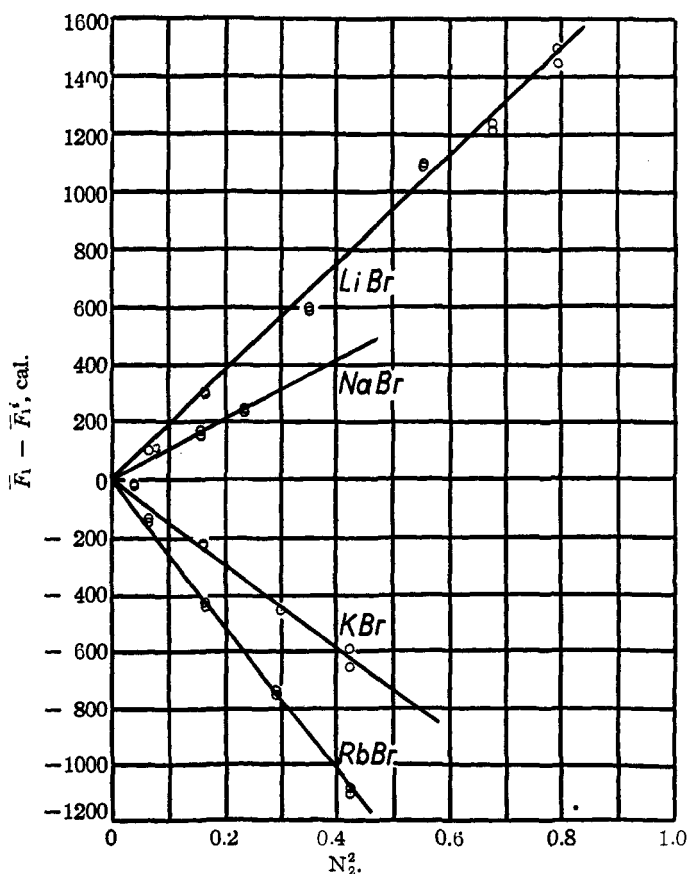

Fig. 1.

We will consider, first, the magnitude and nature of the interionic forces involved.   All of the salts comprised in these systems crystallize in simple cubic lattices.   The lattice constants are given in order in Table I.

TABLE I

	LiBr	AgBr	NaBr	KBr	RbBr
Lattice constant, Å.	2.745	2.885	2.97	3.29	3.43
Molal volume, cc. at 700°	35.4	35.6	43.4[a]	55.4[a]	61.5

[a] Extrapolated below the freezing point.

It is seen that silver bromide falls almost midway between lithium bromide and sodium bromide. The molal volumes of the molten salts, also given in Table I, show that lithium bromide and silver bromide are in this respect nearly identical. If, as is probable, something like the simple cubic arrangement persists in the liquid state, we might expect the electrostatic "lattice energies" of these two salts to be nearly identical (except for the uncertainty of the repulsive term for Ag^+) and their solutions to show a close approximation to Raoult's law, which is far from being the case. However, the energy involved in forming solid silver bromide from its gaseous ions is greater than the corresponding figure for lithium bromide, and, on account of the greater expansion of the latter on melting, the difference for the molten salts would be still greater in favor of silver bromide. Evidently, then, the "lattice energies" for the liquids are in the order silver bromide, lithium bromide, sodium bromide, potassium bromide, rubidium bromide, while the order indicated by Fig. 1 would have to be lithium bromide, sodium bromide, silver bromide, potassium bromide, rubidium bromide. Moreover, while likeness in "lattice energies" might be expected to lead to ideal solutions, unlikeness in the *magnitudes* of internal forces usually leads to positive deviations for both components, regardless of which is greater, and not to the negative deviations shown with potassium bromide and rubidium bromide.

Positive deviations from Raoult's law are frequently accompanied by an expansion on mixing and *vice versa;* this might be expected to cause a weakening or strengthening, respectively, of the internal forces accounting for the direction of the departure from ideality. However, such an explanation is not applicable to these systems. The changes of volume, in cc., on mixing 0.5 mole of silver bromide with 0.5 mole each of lithium bromide, sodium bromide, potassium bromide and rubidium bromide are, respectively, −0.13, +0.17, +0.27, +0.42. These volume changes are in the opposite order to that required by the above explanation.

We are led, consequently, to the conclusion that the behavior of these systems depends upon a difference in the kind of bond existing in silver bromide on the one hand and the alkali bromides on the other, the latter being completely, the former incompletely, ionic. We may note that the electric conductivity of liquid silver bromide has a temperature coefficient very different from those of the alkali bromides. The melting point of silver bromide is much lower than that of lithium bromide, in spite of the similar lattice constant. We recall the existence of $AgBr_2^-$ in aqueous solution

and the solid, probably $RbAgBr_2$, mentioned earlier.   These and other differences indicate that a simple electrostatic treatment of silver bromide is inappropriate.   We will accordingly regard the bond between silver and bromine as tending to tighten into a non-polar bond, this tendency being hindered most by the presence of the small lithium ion and assisted most by the large rubidium ion, but without, in any case, altering the lattice arrangement.

It is possible to justify the form of the equation, $\bar{F}_1 - \bar{F}_1^i = b N_2^2$, by the following statistical treatment, based upon that of Heitler[5] for non-ionic solutions.

Let us consider a solution of n_1 moles of silver bromide with n_2 moles of MBr, M being any alkali metal.   We will assume that Ag^+ and M^+ can replace each other without altering the arrangement, which is probably simple cubic, although the following analysis will apply to any arrangement. The potential of a silver ion will be altered by the substitution of an alkali ion by an amount depending upon the distance of the latter from the former. We will designate the nearest as first order, the next as second order, etc. In a simple cubic lattice there are twelve first order positive ions, six second order, twelve third order, etc.; but we will make the treatment general for other types of lattice by denoting these by $2q$, $2q'$, $2q''$, etc.   The probability that a given pair of ions in any order are both Ag^+ is N_1^2; the probability for two M^+ is N_2^2 and that one is Ag^+ and the other M^+ is $2N_1N_2$, where N_1 and N_2 are the respective mole fractions.   The total number of first order pairs is $(n_1 + n_2)qA$, where A is the Avogadro number.   The number of first order pairs in which both are Ag^+ is $(n_1 + n_2)qAN_1^2$; for both M^+, it is $(n_1 + n_2)qAN_2^2$ and for one Ag^+ and one M^+ it is $2(n_1 + n_2)qAN_1N_2$. By substituting q' and q'', respectively, we obtain expressions for the number of second and third order combinations.

We will designate by φ_{11}, φ_{11}', φ_{11}'', etc., the contribution of each pair of Ag^+ toward the potential of the lattice and, similarly, use φ_{22} for $M^+ - M^+$ and φ_{12} for $Ag^+ - M^+$.   The necessary Br^- will be considered as included in these potentials rather than accounted for by extra terms.

The energy of the lattice of $n_1 + n_2$ moles of solution can then be expressed by

$$E_{12} = (n_1 + n_2) A(N_1^2 \Sigma q\varphi_{11} + N_2^2 \Sigma q\varphi_{22} + 2N_1N_2\, q\Sigma \varphi_{12})$$

where $\Sigma q\varphi = q\varphi + q'\varphi' + q''\varphi'' + \ldots\ldots\ldots$

This expression we will abbreviate by substituting ϵ_{11} for $A\Sigma q\varphi_{11}$ and similarly, ϵ_{22} and ϵ_{12}, yielding

$$E_{12} = (n_1 + n_2)(N_1^2 \epsilon_{11} + N_2^2 \epsilon_{22} + 2N_1N_2\epsilon_{12})$$

The corresponding energies of the pure constituents would be $E_{11} = n_1\epsilon_{11}$ and $E_{22} = n_2\epsilon_{22}$, hence the energy of mixing, ΔE_{12}, remembering that

[5] Heitler, *Ann. Physik*, [4] **80**, 630 (1926).

$N_1 = n_1/(n_1 + n_2)$, etc., would be $\Delta E_{12} = \dfrac{n_1 n_2}{n_1 + n_2}(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$. It can be readily shown that this corresponds to $\bar{E}_1 - E_1 = N_2^2(2\epsilon_{12} - \epsilon_{22})$ and $\bar{E}_2 - E_2 = N_1^2(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$, where $\bar{E}$ is the partial molal energy and E the molal energy.

From the equation $F = E - TS + PV$, we can write $\bar{F}_1 - \bar{F}_1^i = \bar{E}_1 - \bar{E}_1^i = T(\bar{S}_1 - \bar{S}_1^i) + P(\bar{V}_1 - \bar{V}_1^i)$, but $\bar{E}_1^i = E_1$ and $P(\bar{V}_1 - \bar{V}_1^i)$ is here negligible; furthermore, the measurements show (*vide supra*) that $\bar{S}_1 - \bar{S}_1^i = 0$, hence we can write $\bar{F}_1 - \bar{F}_1^i = N_2^2(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$, which is the type of function shown in Fig. 1 to fit the data very satisfactorily. The slope of the line depends upon whether $2\epsilon_{12}$ is greater or less than $\epsilon_{11} + \epsilon_{22}$. We see no way, at present, of calculating this, except from the measurements themselves, which yield, for $\bar{F}_1 - \bar{F}_1^i$, when $N_1 = 0$, for silver bromide in lithium bromide, $+1880$ cal., in sodium bromide $+1050$ cal., in potassium bromide, -1480 cal., in rubidium bromide, -2580 cal.

Summary

The experimental data for the excess of the actual partial molal free energy over the ideal, for molten solutions of silver bromide in lithium bromide, sodium bromide, potassium bromide and rubidium bromide, are shown to fit the relation $\bar{F}_1 - \bar{F}_1^i = bN_2^2$; the values of b, in cal., are, respectively, 1880, 1050, -1480, -2580. The constant, b, is practically independent of temperature, hence the actual partial molal entropy is the same as the ideal for solutions of the same composition.

A statistical treatment of the solutions is shown to yield an equation of the above form. This is based upon the concept that the presence of a large alkali ion, such as rubidium ion, in a lattice of silver bromide allows a tightening of the bond between silver and bromine, while a small alkali ion has the reverse effect.

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