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Thermodynamic and X-Ray Studies of Solid Solutions of Silver Bromide and Lithium Bromide

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A miscibility gap in AgBr-LiBr solid solutions has been found by the high temperature X-ray diffraction method, and a new phase diagram is presented. Activity, partial molar free energy, enthalpy and entropy of AgBr in AgBr-LiBr solid solutions have been obtained at 350 and 400°C from the e.m.f. data of galvanic cells of the type Ag/AgBr-LiBr/Br_2. It has been found that the solid solution forms a regular solution difined by Hildebrand.

It was shown by Kiukkola and Wagner$^{1)}$ that e.m.f. measurements on galvanic cells involving solid electrolytes can be used for the determination of standard free energies of formation of halides, oxides, sulfides and other compounds at elevated temperatures, and many e.m.f. studies have been carried out ever since.

The authors have determined the miscibility gap in AgBr-NaBr solid solutions by means of a high temperature X-ray diffraction method.$^{2)}$ The authors have also measured the e.m.f. of solid electrolyte cells of the type Ag/AgBr-NaBr/Br_2 and calculated activities and partial molar quantities of AgBr in the AgBr-NaBr solid solution. It was found that the AgBr-NaBr system forms a regular solution above the critical temperature. This paper reports the results of similar studies on the AgBr-LiBr system.

Experimental

High purity lithium bromide and silver bromide, prepared by Yoneyama Chemical Industries Ltd. and Kojima Chemical Co., Ltd., respectively, were used.

Lithium bromide was dried *in vacuo* at about 300°C until the weight of the salt became constant. Lithium bromide and silver bromide were then mixed in a desired proportion, melted in a quartz tube in bromine atmosphere, and heated until the solution became clear. Subsequently, the solution was frozen, kept at about 400°C for several hours and quenched. After cooling, the sample was taken out from the quartz tube and ground in an agate mortar in a dry box.

The apparatus and the experimental procedures for the present work were the same as described in detail previously.$^{2)}$

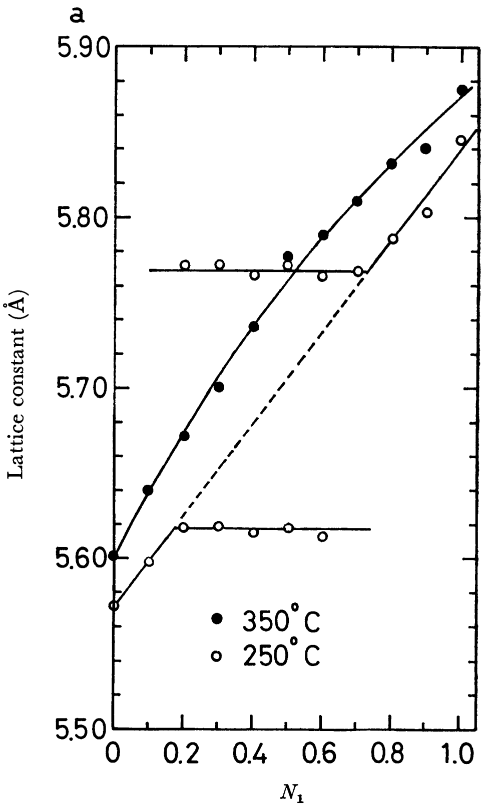

Fig. 1. Plot of lattice constant against the mole fraction of AgBr.

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1) K. Kiukkola and C. Wagner, *J. Electrochem. Soc.*, **104**, 308, 379 (1957).

2) T. Tsuji, K. Fueki and T. Mukaibo, This Bulletin, **42**, 2193 (1969).

Results and Discussion

High Temperature X-Ray Diffraction Study. As reported previously, a miscibility gap exists in the AgBr-NaBr system.[2] Although Sandonnini and Scarpa[3] have reported that the AgBr-LiBr system forms a complete solid solution, a miscibility gap may exist in the system in view of the similarity between AgBr-NaBr and AgBr-LiBr systems.

In order to determine whether or not the solubility limit exists, a study by the high temperature X-ray diffraction method was carried out at temperatures between 50 to 350°C at an interval of 50°C. Lattice constants obtained from the reflections of (200), (220), (222), (422) and (600) planes are shown in Fig. 1 as plots against the mole fraction of silver bromide, N_1. We see that the lattice constant at 350°C increases continuously with the increase in mole fraction of silver bromide, but at lower temperatures such as 250°C, the discontinuities in lattice parameter exist.

Figure 2 shows the phase diagram of the AgBr-LiBr system. The dotted line indicates the result of the present work and the liquidus and solidus lines the data by Sandonnini and Scarpa.[3]

E.m.f. Study. Figure 3 gives the plot of e.m.f. (E) *vs.* $\log P_{Br_2}$ for AgBr-LiBr solid solutions of various compositions. A good linearity holds between the logarithm of bromine vapor pressure and the e.m.f. in a pressure range, 0.0864 to 0.650 Torr. A similar linearity was obtained at temperatures from 250 to 400°C.

TABLE 1. VALUES OF E_0 (mV)

N_1	°C 400	350
0.100	852.5	866.2
0.200	837.6	852.8
0.300	827.5	847.0
0.400	825.0	846.2
0.600	818.0	840.9
0.785	815.8	839.1
0.900	812.8	836.1
1.000	811.9	835.3

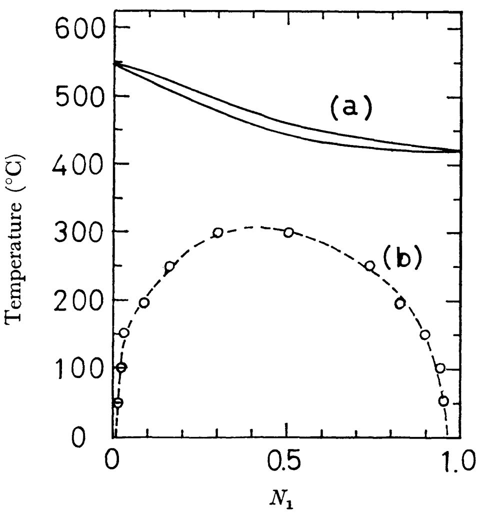

Fig. 2. Phase diagram of the AgBr-LiBr system.
(a): Sandonnini and Scarpa, (b): this work

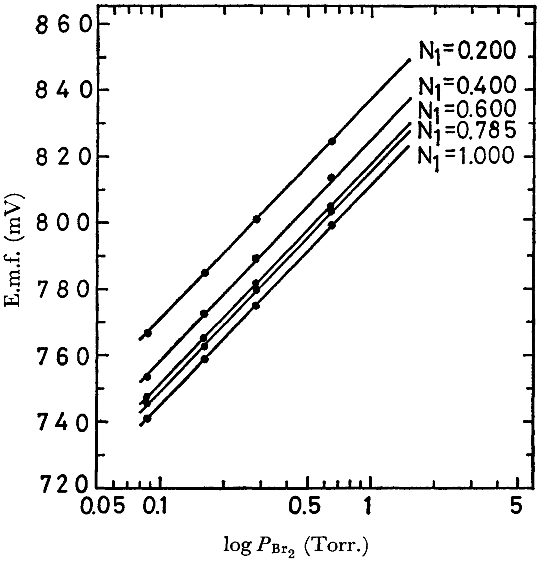

Fig. 3. Plot of E *vs.* log P_{Br_2} at 400°C.

TABLE 2. THERMODYNAMIC DATA OF THE AgBr-LiBr SYSTEM AT 350 AND 400°C

400°C

N_1	ΔG_1 kcal	$\bar{G}_1$ kcal	$\bar{S}_1$ cal/°C	$\bar{H}_1$ kcal	a_1	a_2
0.100	−19.66	−0.94	4.47	2.07	0.497	0.913
0.200	−19.32	−0.60	3.78	1.95	0.642	0.877
0.300	−19.08	−0.36	1.80	0.85	0.764	0.834
0.400	−19.03	−0.31	1.02	0.38	0.798	0.800
0.600	−18.86	−0.14	0.23	0.01	0.900	0.689
0.785	−18.81	−0.09	0.09	0.00	0.935	0.513
0.900	−18.74	−0.02	0.05	0.01	0.985	0.251
1.000	−18.72	0	0	0	1.000	0

350°C

N_1	ΔG_1 kcal	$\bar{G}_1$ kcal	$\bar{S}_1$ cal/°C	$\bar{H}_1$ kcal	a_1	a_2
0.100	−19.98	−0.72	4.47	2.08	0.563	0.914
0.200	−19.67	−0.41	3.78	1.95	0.722	0.879
0.300	−19.53	−0.27	1.80	0.85	0.804	0.855
0.400	−19.51	−0.25	1.02	0.38	0.816	0.855
0.600	−19.39	−0.13	0.23	0.02	0.901	0.755
0.785	−19.35	−0.09	0.09	0.00	0.932	0.586
0.900	−19.28	−0.02	0.05	0.01	0.985	0.287
1.000	−19.26	0	0	0	1.000	0

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[3] C. Sandonnini and G. Scarpa, *At. reale accad. Lincei, Sez. II*, **22**, 517 (1913).

The slope of the plot of E *vs.* $\log P_{Br_2}$ of AgBr-LiBr solid solutions with various compositions is the same as that of pure silver bromide. A similar relationship is found at 350°C. Since it was shown previously2) that pure silver bromide is entirely ionic above 300°C, AgBr-LiBr solid solutions also seem to be an ionic conductor at 350 and 400°C.

Table 1 lists the value of E_0, the e.m.f. at a bromine pressure of 1 Torr., which was obtained by extrapolating the plot of E *vs.* $\log P_{Br_2}$.

If ΔG_1 and ΔG^0 denote the free energy changes of the reaction $Ag+\frac{1}{2}Br_2=(AgBr)$ in solid solution and in pure state, respectively, the partial molar free energy of silver bromide in solid solutions, $\bar{G}_1$, is obtained by the equation

$$\bar{G}_1 = \Delta G_1 - \Delta G^\circ. \qquad (1)$$

From the temperature dependenc of $\bar{G}_1$, the partial molar entropy and enthalpy of silver bromide in solid solutions are calculated. If pure silver bromide is chosen as the standard state, the activity of silver bromide in its solution is calculated by the relation

$$\bar{G}_1 = 2.303\,\boldsymbol{R}T\log a_1. \qquad (2)$$

The activity of lithium bromide, a_2, is obtained by the Gibbs-Duhem equation in the integrated form

$$\log(a_2/N_2) = -\int_0^{N_1}(N_1/N_2)\,\mathrm{dlog}\,(a_1/N_1). \qquad (3)$$

Thermodynamic data of the AgBr-LiBr system at 350 and 400°C are summarized in Table 2.

As seen in Fig. 4, the AgBr-LiBr system shows positive deviations from Raoult's law.

Figure 5 gives the plot of $(\bar{G}_1-\bar{G}_1{}^i)$ *vs.* $N_2{}^2$, where $\bar{G}_1{}^i$ is the partial molar free energy of component 1 in the ideal solution. Linearity holds between $(\bar{G}_1-\bar{G}_1{}^i)$ and $N_2{}^2$, and the two sets of points for 350 and 400°C lie on a single straight line. The result clearly shows that the AgBr-LiBr system above the critical temperature forms a regular solution defined by Hildebrand.4) It is concluded from this result that the partial molar entropy is the same as it would be in the ideal solution, *i.e.*, $S_1=S_1{}^i=\boldsymbol{R}\ln N_1$, and that two kinds of positive ions are distributed at random in the solid solution.

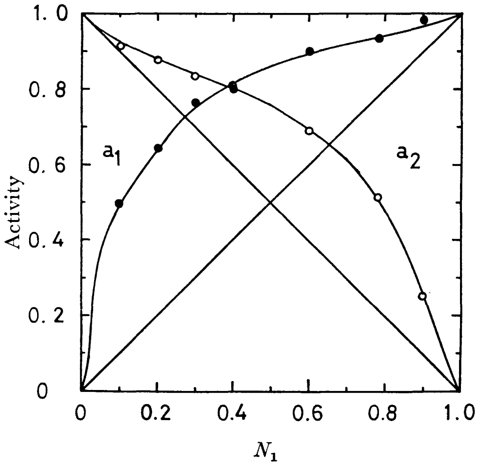

Fig. 4. Activity curves for AgBr-LiBr solid solutions at 400°C.

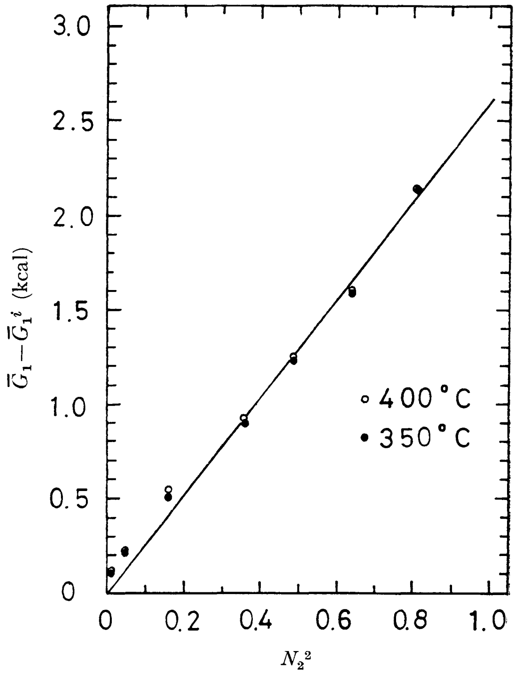

Fig. 5. Plot of $(\bar{G}_1-\bar{G}_1{}^i)$ against $N_2{}^2$.

Summary

1) The solubility limit in the AgBr-LiBr system was determined by means of the high temperature X-ray diffraction method and a new phase diagram of the system was presented.

2) The partial molar free energy of AgBr in the system was determined by the e.m.f. measurement for the galvanic cell, Ag/AgBr-LiBr/Br_2 at 350 and 400°C.

3) The partial molar entropy and the partial molar enthalpy of AgBr in the system were calculated.

4) The system was found to form a regular solution defined by Hildebrand.

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4) J. H. Hildebrand, *J. Amer. Chem. Soc.*, **51**, 66 (1929).