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

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

Kiukkola and Wagner[1] showed new potentialities and inherent limitations of e.m.f. measurements on galvanic cells with solid electrolytes for the determination of standard molal free energies of formation of halides, oxides, sulfides and other compounds at elevated temperatures. Although many e.m.f. studies were made for simple oxides, halides and sulfides, only a few studies have been carried out for the solid solutions consisting of

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

these simple salts.

Wachter,[2] and Panish and his co-workers[3] have reported the e.m.f. of the cell with solid electrolyte AgCl-NaCl and Pal'guev *et al.*[4] have measured the e.m.f. of electrochemical cells of a different type

$$Ag/AgBr//AgBr\text{-}NaBr/Br_2,$$
$$Ag/AgBr//AgBr\text{-}NaBr/Ag,$$
$$Br_2/AgBr//AgBr\text{-}NaBr/Br_2.$$

In the present paper, the result of studies on the activity, and partial molal quantities of AgBr in AgBr-NaBr solid solutions and miscibility gap by means of the galvanic cell $Ag/AgBr\text{-}NaBr/Br_2$ are given. For the determination of miscibility gap, high temperature X-ray diffraction study was also carried out.

Experimental

Samples. Sodium bromide and silver bromide of high purity were supplied from Junsei Pure Chemicals & Co., Ltd. and Kojima Chemical Co., Ltd., respectively. Silver bromide was prepared from pure silver nitrate and sodium bromide. No difference in e.m.f. due to the source of silver bromide was found in the experiment.

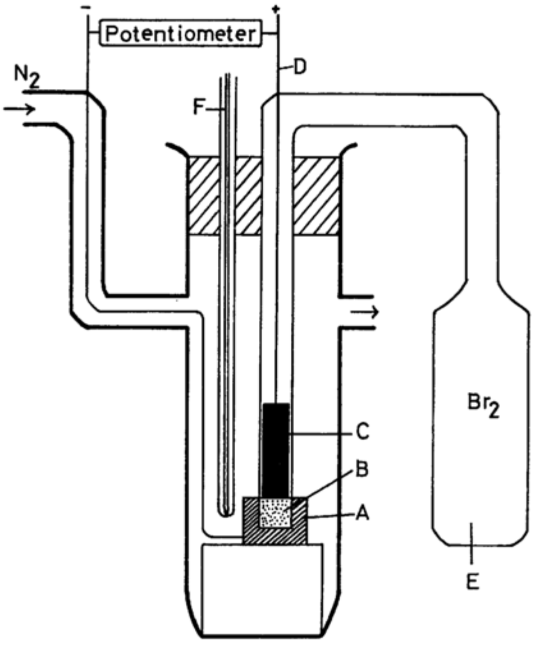

Fig. 1. Cell for the e.m.f. measurement.

A: silver crucible, B: AgBr-NaBr solid solution.
C: graphite, D: platinum wire,
E: bromine reservoir, F: thermocouple

Silver bromide and sodium bromide were mixed in a desired proportion and ground together in an agate mortar. The mixture was melted in a quartz tube in bromine atmosphere, heated until the solution became clear, kept at about 400°C for several hours and then quenched. After cooling the sample was taken out from the quartz tube and ground again.

E. M. F. Measurement. The apparatus used for the e.m.f. measurement of galvanic cells is shown in Fig. 1. Powder of solid solution was put into a silver crucible, A, which serves as the anode of the cell. This crucible also serves to keep the temperature of the electrolyte uniform. A quartz tube of 10 mm in diameter was inserted into the crucible. After the powder was melted, a graphite electrode of high purity, C, connected with platinum wire, D, was put into the fused solution. The salt was slowly solidified and kept at 400°C, and then the quartz tube was evacuated. After checking airtightness, bromine which had been purified by vacuum-distillation and dried with a magnesium perchlorate column, was introduced into the quartz tube and purified nitrogen stream was kept flowing along outside the tube.

The thermoelectric potential was measured on a cell which was constructed by replacing of the solid electrolyte with a silver block. It was found that the thermoelectric potential ranged from 1.4 to 4.1 mV depending on the temperature and was quite reproducible. Correction of the thermoelectric potential was made for all e.m.f. data.

The temperature of the furnace was maintained constant within ±0.5°C by means of an electronic controller. The e.m.f. of the thermocouple was measured with a P-42 type pyrometer of Murayama Denki Ltd. The temperature of the reservoir of bromine was controlled within ±0.05°C so that the fluctuation of the vapor pressure of bromine was less than 0.2% of the total pressure. The vapor pressure of bromine at each temperature was calculated from the temperature of the reservoir and the vapor pressure data in the Nesmeyanov table.[5] At a temperature range of 200 to 400°C the e.m.f. was measured by means of a potentiometer of Yokogawa Electric Works Ltd. in conjunction with a G-52 type galvanometer of Murayama Denki Ltd. When a new graphite electrode was employed, it took about 20 hr to attain a constant potential. When the vapor pressure of bromine was changed, the equilibrium was attained in two hours. The e.m.f. was reversible with regard to temperatures and the vapor pressure of bromine, but at low concentrations of silver bromide the conductivity of solid solutions was too small to measure the e.m.f.

High Temperature X-Ray Diffraction. In order to determine the exact solubility limit the powdered sample prepared in the same method as described above was mounted on a platinum sample holder and the lattice constant was measured by means of a high temperature X-ray diffractometer, type D-8C of Rigaku Denki Co., Ltd.

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[2] A. Wachter, *J. Am. Chem. Soc.*, **54**, 919 (1932).

[3] M. B. Panish, F. F. Blankenship, W. R. Grimes and R. F. Newton, *J. Phys. Chem.*, **62**, 1325 (1958).

[4] S. F. Pal'guev, S. V. Karpachev and L. D. Yushina, *Trudy Inst. Elektrokhim., Akad. Nauk S. S. S. R., Ural. Filial.*, **1**, 105 (1960).

[5] A. N. Nesmeyanov, "Vapour Pressure of the Elements," translated and edited by J. I. Carasso, Academic Press, New York (1963), p. 366.

Results and Discussion

Figure 2 shows the plot of E *vs.* $\log P_{Br_2}$ for AgBr-NaBr solid solutions with various compositions at 400°C. A good linear relationship is seen between the vapor pressure of bromine and the e.m.f. within a pressure range 0.0864 and 0.650 Torr. A similar linear relationship was obtained at temperatures from 200 to 400°C.

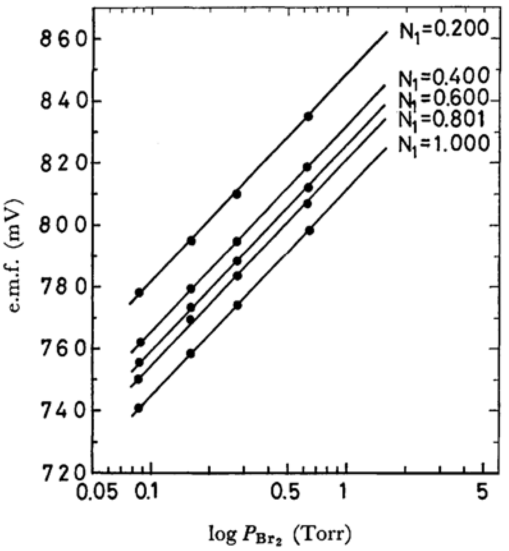

Fig. 2. Plot of E *vs.* $\log P_{Br_2}$ at 400°C.

TABLE 1. VALUES OF E_0 (mV)

N_1	°C				
	400	350	300	250	200
0.100	870.1	(885.2)	(898.2)		
0.200	849.1	865.8	(885.1)	(903.6)	
0.300	836.0	854.1	873.4	892.5	
0.400	832.4	851.4	870.9	886.5	906.9
0.500	826.5	846.9	867.6	889.1	910.8
0.600	826.6	847.4	869.4	885.9	904.0
0.700	823.5	845.3	869.5	890.2	914.0
0.801	821.7	844.8	870.5	888.5	906.5
0.901	818.5	841.4	864.6	885.1	907.6
1.000	811.9	835.3	858.9	878.2	895.3

Table 1 shows E_0, the e.m.f. at a bromine pressure of 1 Torr, which was obtained by extrapolating the plot of E *vs.* $\log P_{Br_2}$. The data with parentheses are those less reproducible.

According to Wagner⁶⁾ the open circuit potential, E, for an electrochemical cell, Ag/AgBr-NaBr/Br$_2$, is given by the equation

$$E = \frac{1}{F}\int_{\mu'_{Br_2}}^{\mu''_{Br_2}} (1-t_e)\mathrm{d}\mu_{Br_2}, \tag{1}$$

where t_e is the transference number of electrons, μ'_{Br_2} and μ''_{Br_2} the chemical potentials of bromine at the metal-solid solution interface and at the gas-solid solution interface, respectively, and F the Faraday constant.

Using the free energy change ΔG_1 of the reaction Ag+1/2Br$_2$=(AgBr) in solid solution, Eq. (1) is rewritten as

$$E = \frac{-\Delta G_1}{F} - \frac{1}{F}\int_{\mu'_{Br_2}}^{\mu''_{Br_2}} t_e \mathrm{d}\mu_{Br_2}. \tag{2}$$

Wagner⁷⁾ has reported that the second term in Eq. (2) resulting from electronic conduction in pure silver bromide is 3.8 mV for $P_{Br_2}=0.23$ Torr at 277°C.

Tubandt and Reinhold⁸⁾ have shown that pure solid silver bromide is an entirely ionic conductor at temperatures from 200 to 300°C and Pal'guev *et al.*⁹⁾ have mentioned that according to the e.m.f. measurements of the electrochemical cell, Ag/AgBr/Br$_2$, the conductivity of the solid electrolyte were entirely ionic over a temperature range of 100 to 434°C.

In our experiment above 300°C the slope of the plots between E and $\log P_{Br_2}$ of pure silver bromide is close to the theoretical value, $2.303\,\boldsymbol{R}T/2F$, where $\boldsymbol{R}$ is the gas constant and T the absolute temperature. Our experimental values of e.m.f. for pure silver bromide at 300°C is 1.1 mV lower than those calculated by Hamer *et al.*¹⁰⁾ From these results, it is concluded that pure silver bromide is a purely ionic conductor above 300°C. At lower temperatures our experimental data tend to deviate and are about 10 mV lower than those of Hamer *et al.*¹⁰⁾ because of the contribution of electronic conduction.

As shown in Fig. 2 the slope of the plot between E and $\log P_{Br_2}$ of AgBr-NaBr solid solutions with various compositions is the same as that of pure silver bromide. A similar relationship is found at 300 and 350°C. Since pure silver bromide is entirely ionic at the temperatures mentioned above, the solid AgBr-NaBr system is supposed to be also an ionic conductor above 300°C. Therefore, the second term in Eq. (2) can be eliminated for AgBr-NaBr solid solutions as well as pure silver bromide, and ΔG_1 is obtained from the e.m.f. data. If ΔG° denotes the free energy of formation of pure silver bromide, the partial molal free energy of silver bromide in solid solutions,

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6) C. Wagner, *Proc. Intern. Comm. Electrochem. Thermodyn. Kinet.*, **7**, 361 (1957).

7) C. Wagner, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 4, ed. by P. Delahay, Interscience, New York (1966), p. 1.

8) C. Tubandt and H. Reinhold, *Z. Elektrochem.*, **29**, 313 (1923); **31**, 84 (1925).

9) L. D. Yushina, S. F. Pal'guev and S. V. Karpachev, *Zh. Fiz. Khim.*, **35**, 342 (1961).

10) W. J. Hamer, M. S. Malmberg and B. Rubin, *J. Electrochem. Soc.*, **112**, 750 (1965).

Table 2. Thermodynamic data of the AgBr-NaBr system at 350 and 400°C

	N_1	ΔG_1, kcal	$\overline{G}_1$, kcal	$\overline{S}_1$, cal/°C	$\overline{H}_1$, kcal	a_1	a_2
400°C	0.100	−20.06	−1.34	3.83	1.24	0.367	0.912
	0.200	−19.58	−0.86	3.09	1.22	0.527	0.861
	0.300	−19.28	−0.56	2.45	1.09	0.660	0.801
	0.400	−19.19	−0.47	2.03	0.89	0.702	0.774
	0.500	−19.06	−0.34	1.38	0.59	0.778	0.707
	0.600	−19.06	−0.34	1.20	0.47	0.776	0.700
	0.700	−18.99	−0.27	0.74	0.23	0.819	0.628
	0.801	−18.95	−0.23	0.14	−0.13	0.845	0.569
	0.901	−18.87	−0.15	0.23	0.00	0.893	0.447
	1.000	−18.72	0	0	0	1.000	0
350°C	0.100	−20.41	−1.15	3.83	1.24	0.395	0.916
	0.200	−19.96	−0.70	3.09	1.22	0.567	0.867
	0.300	−19.69	−0.43	2.45	1.09	0.705	0.809
	0.400	−19.63	−0.37	2.03	0.89	0.741	0.786
	0.500	−19.53	−0.27	1.38	0.60	0.806	0.727
	0.600	−19.54	−0.28	1.20	0.47	0.798	0.724
	0.700	−19.49	−0.23	0.74	0.23	0.830	0.664
	0.801	−19.48	−0.22	0.14	−0.13	0.838	0.650
	0.901	−19.40	−0.14	0.23	0.00	0.893	0.501
	1.000	−19.26	0	0	0	1.000	0

$\overline{G}_1$, is obtained by the equation

$$\overline{G}_1 = \Delta G_1 - \Delta G^\circ. \tag{3}$$

From the temperature dependence of $\overline{G}_1$, the partial molal 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

$$\overline{G}_1 = 2.303\,\boldsymbol{R}T\ \log a_1. \tag{4}$$

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

$$\log\frac{a_2}{N_2} = -\int_0^{N_1}\frac{N_1}{N_2}\,\mathrm{d}\log\frac{a_1}{N_1}\,. \tag{5}$$

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

Kleppa and Meschel[11] have determined the heat of solution of AgBr-NaBr by high temperature solution calorimetry at 350°C using pure liquid silver nitrate as the solvent. Table 3 gives the data by Kleppa and Meschel together with those obtained by the present study. Agreement is fairly good except for the data at $N_1=0.801$.

The deviation from Raoult's law is illustrated in Figs. 3 and 4. As can be seen from the figures, the system shows positive deviations from Raoult's law. Figures 3 and 4 also show that the solid solution is completely miscible at 400°C, but partially miscible at 300°C.

Table 3. Partial molal enthalpies of AgBr in AgBr-NaBr solid solutions at 350°C

N_1	This work $\overline{H}_1$ kcal	Kleppa and Meschel[11] $\overline{H}_1$ kcal
0.100	(1.24)	2.01
0.200	1.22	1.50
0.300	1.09	1.08
0.400	0.89	0.74
0.500	0.60	0.48
0.600	0.47	0.28
0.700	0.23	0.15
0.801	−0.13	0.06
0.901	0.00	0.01

Zemczuzny[12] has reported that the AgBr-NaBr system forms a complete solid solution. A recent work by Stokes and Li[13] have indicated the existence of a miscibility gap with a critical temperature near 175°C for the AgCl-NaCl system. In view of the similarity of the AgCl-NaCl and AgBr-NaBr system, a miscibility gap can be expected.

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[11] O. J. Kleppa and S. V. Meschel, *J. Phys. Chem.*, **69**, 3531 (1965).

[12] S. F. Zemczuzny, *Z. Anorg. Allgem. Chem.*, **153**, 47 (1926).

[13] R. J. Stokes and C. H. Li, *Acta Met.*, **10**, 535 (1962).

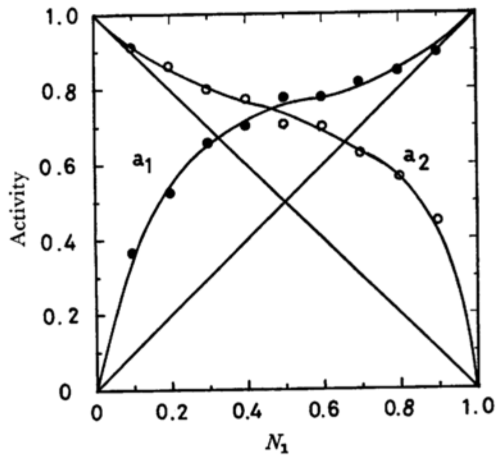

Fig. 3. Activity curves for AgBr-NaBr solid solutions at 400°C.

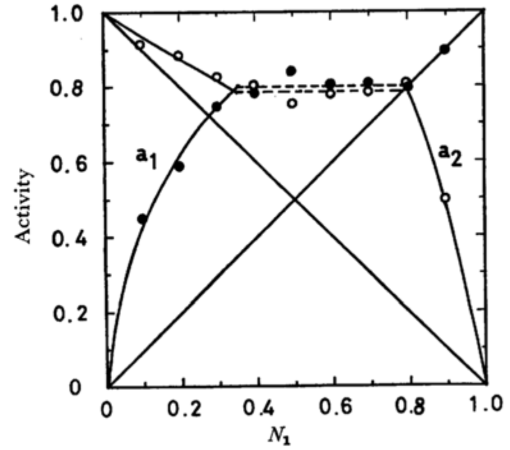

Fig. 4. Activity curves for AgBr-NaBr solid solutions at 300°C.

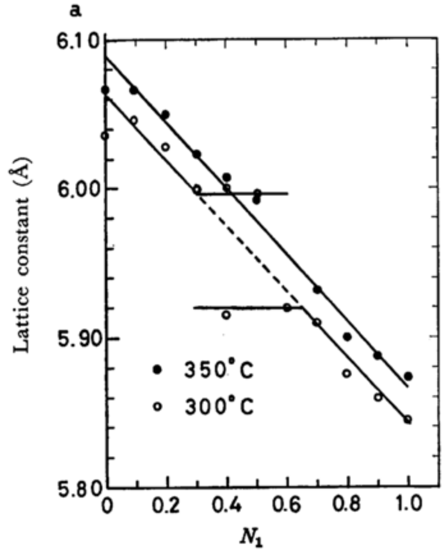

Fig. 5. Plot of lattice constant against mole fraction of AgBr.

In order to determine the exact solubility limit, a high temperature X-ray diffraction was carried out. Figure 5 shows lattice constants, *a*, plotted against mole fraction of silver bromide, N_1. As can be seen in Fig. 5, the lattice constant at 350°C decreases linearly with the increase in mole fraction of silver bromide (Vegard's law), but at lower temperatures such as 300°C the discontinuity in lattice parameter was found. The solubility limit

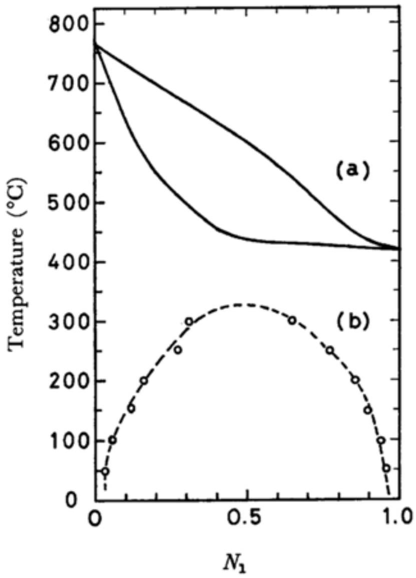

Fig. 6. Phase diagram of the AgBr-NaBr system. (a): Zemczuzny, (b): this work

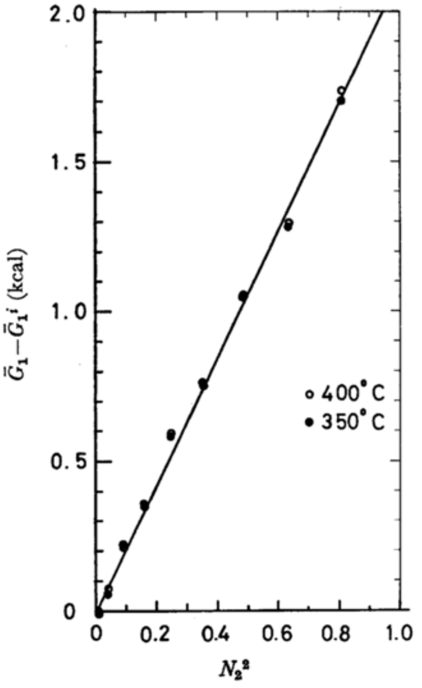

Fig. 7. Plot of $(\bar{G}_1-\bar{G}_1{}^i)$ against $N_2{}^2$.

was measured at an interval of 50°C from 50 to 350°C.

Figure 6 shows the phase diagram of the AgBr-NaBr system. The dotted line is the result of the present work and the liquidus and solidus lines are obtained from the data of Zemczuzny.[12]

Figure 7 gives the plot of $(\overline{G}_1-\overline{G}_1{}^i)$ *vs.* $N_2{}^2$, where $\overline{G}_1{}^i$ is the partial molal free energy of component 1 in the ideal solution. A good linear relationship exists between $(\overline{G}_1-\overline{G}_1{}^i)$ and $N_2{}^2$ and two sets of points for 350 and 400°C fall on a single straight line. This result clearly shows that the AgBr-NaBr system forms a regular solution which was defined by Hildebrand[14] above the critical temperature. It is concluded from this result that the partial molal entropy is the same as it would be in the ideal solution, *i. e.*, $\overline{S}_1=\overline{S}_1{}^i=R \ln N_1$, and that two kinds of positive ions are distributed at random in the solid solution.

Summary

(1) The partial molal free energy of AgBr in the solid AgBr-NaBr system was determined by the e.m.f. measurement for the cell, Ag/AgBr-NaBr/Br_2, at 350 and 400°C.

(2) The partial molal entropy and the partial molal enthalpy of AgBr in the solid AgBr-NaBr system were calculated.

(3) From the e.m.f. measurement, a miscibility gap was found in the AgBr-NaBr system. The exact solubility limit was determined by high temperature X-ray diffraction.

(4) A new phase diagram of the AgBr-NaBr system was presented.

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

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[14] J. H. Hildebrand, *J. Am. Chem. Soc.*, **51**, 66 (1929).