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Solubility of Ag_2O in Na_2O-B_2O_3 Melts

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The solubility of silver oxide in Na_2O-B_2O_3 melts was determined as a function of the Na_2O contents, the temperature (825°C—935°C), and the oxygen partial pressures. The results show that the silver oxide dissolves in a borate as a network modifier, just like alkali metal oxides, which destroy the B–O–B bonds to produce four coordinated boron as well as three. In the Ag_2O-B_2O_3 binary system, the solubility of silver oxide increases with an increase in the oxygen partial pressures. In the Ag_2O-Na_2O-B_2O_3 ternary system, the solubility of Ag_2O decreases with an increase in the Na_2O contents. This shows that the silver oxide is a weaker base than sodium oxide. The activity of the oxygen ion, $a_{O^=}$, was determined from the iso-activity lines of silver oxide. In a constant basic oxide content, $a_{O^=}$ increases with an increase in the Na_2O content. By extrapolating the Ag_2O contents to zero, the oxygen-ion activity in the Na_2O-B_2O_3 melt was determined.

Molten oxides are quite interesting because of their special structures and have been studied from various aspects. The borates are especially distinguishable from such other mixed oxides as phosphates and silicates because of their structures. The boron atom can coordinate four oxygen atoms as well as three. Therefore, the borate melts show an exceptional behavior known as the boron anomaly.

Various attempts to explain the structure of molten oxides have been made. Lux and Flood[1,2] explained the thermodynamic properties in terms of acidity and basicity. Krogh-Moe[3,4] and Bray *et al.*[5], studied the structure of borate with techniques of X-ray, NMR, and phase diagrams and measured the ratio of four to three-coordinated boron atoms with various contents of alkali metal oxide. Shartsis *et al.*,[6,7] measured the density, viscosity, and electrical resistivity of molten alkali borates.

The present work was performed in order to clarify whether silver oxide dissolves in a boron oxide as a network modifier and in order to examine the behavior of silver oxide in the presence of sodium oxide. The solubility of silver oxide in B_2O_3 has already been measured by Willis and Hennessy.[8]

Another aim of this investigation was related to the basicity of oxide melts. The oxygen-ion activity in an oxide melt is an important factor, since the basicity of the melts, which varies with the melt composition and kind of basic oxide, is supposed to be determined by this quantity. Pearce[9] measured the solubility of carbon dioxide and obtained the oxygen-ion activity in soda-silica melts. In this work the oxygen-ion activity was determined from the solubility measurements of Ag_2O in the Na_2O-B_2O_3 system.

Experimental

(a) Material and Preparation. Samples were prepared from commercial chemicals of a guaranteed reagent grade. Their impurities were as follows; $SO_4 < 0.003\%$, heavy metals $< 0.001\%$, and $Fe < 0.002\%$ for B_2O_3; $SO_4 < 0.002\%$, $Cu < 0.0005\%$, and $Fe < 0.002\%$ for $AgNO_3$; $Cl < 0.001\%$, $SO_4 < 0.002\%$, and $PO_4 < 0.002\%$ for borax.

To prepare the Na_2O-B_2O_3 mother melt, a suitable quantity of boric oxide and borax were melted in a platinum crucible.

(b) Chemical Analysis. For the determination of silver, a weighed sample of glass was dissolved in dilute HNO_3 and then the solution was titrated with standardized KSCN. The B_2O_3 was determined in the following way. The sample was dissolved in dilute nitric acid and the pH was adjusted with *p*-nitrophenol. Glycerol was then added, and the B_2O_3 was titrated with an NaOH standard solution.

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1) H. Lux, *Z. Elecrochem.*, **45**, 303 (1939).

2) H. Flood and T. Forland, *Acta Chem. Scand.*, **1**, 592 (1947).

3) Krogh Moe, *Acta Cryst.*, **18**, 77 (1965).

4) Krogh Moe, *Phys. Chem. Glasses,* **3**(**1**), 1 (1962).

5) P. Bray and A. Silver, "Modern Aspect of the Vitreous State," Vol. 1, Butterworths, London (1960).

6) L. Shartsis, W. Capps and S. Spinner, *J. Am. Ceram. Soc.*, **36**(**2**), 35 (1953).

7) L. Shartsis, W. Capps and S. Spinner, *ibid.*, **36**(**10**), 319 (1953).

8) G. Willis and F. Hennessy, *Trans. A.I.M.E.*, **197**, 1367 (1953).

9) M. Pearce, *J. Am. Ceram. Soc.*, **47**(**7**), 342 (1964).

(c) Oxygen Pressure. A gas mixture of oxygen and nitrogen, the oxygen partial pressure of which has previously been determined by being introducing it into the gas chromatograph at appropriate time intervals, was bubbled through the melt during each run.

(d) Temperature. The temperature was controlled with an Okura EC-51-type controller. During every run, the temperature was kept constant within ±1°C.

(e) Procedure. The method of Willis and Hennessy was employed. The sample melt was inserted in an Ag crucible and heated in an atmosphere containing oxygen of various partial pressures.

The solution reaction can be expressed by:

$$2\mathrm{Ag} + \tfrac{1}{2}\mathrm{O}_2 = \mathrm{Ag_2O}\ (\text{in borate}) \qquad (1)$$

The equilibrium constant, K, is defined by:

$$K = a_{\mathrm{Ag_2O}}/\sqrt{P_{\mathrm{O_2}}}\,a_{\mathrm{Ag}}^2 \qquad (2)$$

at a given temperature.

Since a_{Ag} is set at unity under the present experimental condition, $a_{\mathrm{Ag_2O}}$ is directly proportional to the square root of the equilibrium oxygen partial pressure. Further, it is convenient to define the standard state of $\mathrm{Ag_2O}$ as the melt which is in equilibrium with 1 atm of oxygen. Therefore, the activity of $\mathrm{Ag_2O}$ is given simply by $\sqrt{P_{\mathrm{O_2}}}$ when $P_{\mathrm{O_2}}$ is expressed in terms of atmosphere. The diameter of the silver crucible is 2 cm, and it is 4 cm deep. The sample in the crucible was maintained at the desired temperature in a tubular resistance furnace. An oxygen-nitrogen gas mixture was bubbled through the silver tube into this sample. The rate of the reaction (1) is very slow to the right direction, since the reaction proceeds one-dimensionally along the circle where the three phases are in contact. On the other hand, the backward reaction proceeds two-dimensionally on the surface of the melt, where the excess silver precipitates from the melt. The preliminary experiments showing this situation are represented in Fig. 1. The backward reaction required only about 20 hr, while it took more than 100 hr for the forward reaction to approach equilibrium. Therefore, the solubility of $\mathrm{Ag_2O}$ was measured mostly from the backward reaction.

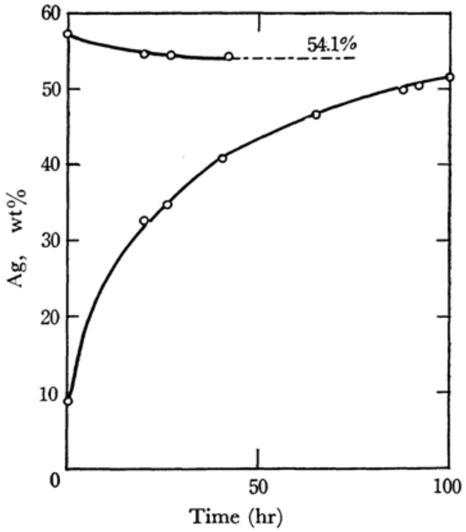


Fig. 1. Preliminary experiment of solution equilibrium of the reaction; $2\mathrm{Ag}+\tfrac{1}{2}\mathrm{O}_2=\mathrm{Ag_2O}$ (in borate) at 900°C under 1 atm of oxygen. The equilibrium value is 54.1%.

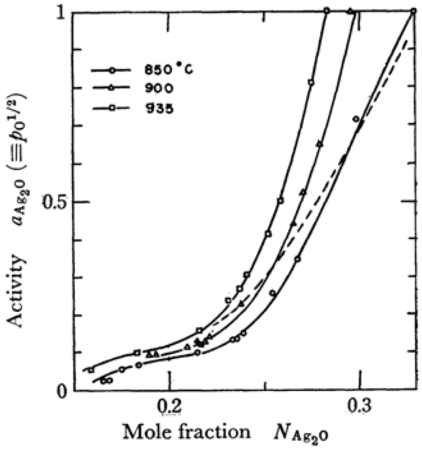


Fig. 2. The activity of $\mathrm{Ag_2O}$, $a_{\mathrm{Ag_2O}}(\equiv P_{\mathrm{O_2}})$, at 850°C, 900°C, and 935°C. The dotted curve represents the Willis and Hennessy's data at 850°C. The standard state for $\mathrm{Ag_2O}$ is the melt in equilibrium with silver and oxygen at 1 atm.

Results and Discussion

(1) $\mathrm{Ag_2O}$-$\mathrm{B_2O_3}$ Binary System. Figure 2 shows the activity of $\mathrm{Ag_2O}$ as a function of the composition of $\mathrm{Ag_2O}$ at a constant temperature. The dotted curve represents the Willis and Hennessy data at 850°C. It should be noted first that the solubility of silver oxide increases with the oxygen pressure in accordance with Eq. (1). The curve of Willis and Hennessy agrees fairly well with that of the present binary system.

The partial-molar Gibbs free energy of the solution of $\mathrm{Ag_2O}$ is obtained from the relation:

$$\overline{G}_{\mathrm{Ag_2O}} = RT \ln a_{\mathrm{Ag_2O}} \qquad (3)$$

$\overline{G}_{\mathrm{Ag_2O}}$ is plotted in Fig. 3 as a function of the $\mathrm{Ag_2O}$ concentration. Here one should note that the standard state is the solution in equilibrium with one atmosphere of oxygen.

From the temperature dependence of the partial-molar free energy of a solution, the partial-molar heat of the solution was derived; it is plotted as a function of the composition in Fig. 4. Because of the narrow temperature ranges, the values of the heat of solution are uncertain within the limits of error of ±1 kcal/mol.

The partial molar entropy is obtained from the equation;

$$\overline{S}_{\mathrm{Ag_2O}} = (\overline{H}_{\mathrm{Ag_2O}} - \overline{G}_{\mathrm{Ag_2O}})/T \qquad (4)$$

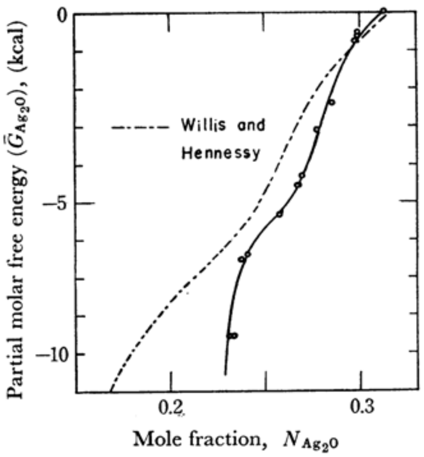


Fig. 3. Partial molar free energies of Ag_2O ($\bar{G}_{Ag_2O}$) in Ag_2O-B_2O_3 melts at 850°C.
The dotted curve represents the Willis and Hennessy's data. The standard state for Ag_2O; Silver and oxygen at 1 atm.

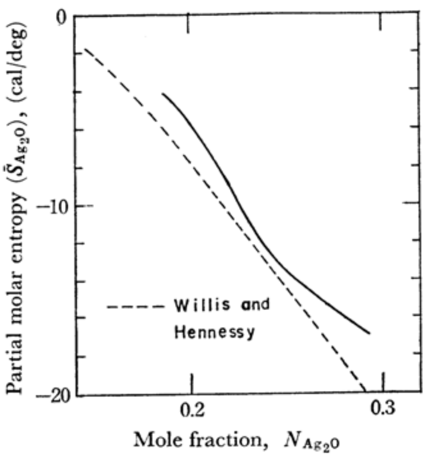


Fig. 5. Partial molar entropies of Ag_2O ($\bar{S}_{Ag_2O}$) in Ag_2O-B_2O_3 melts.
The dotted curve represents Willis and Hennessy's data. Standard state for Ag_2O: Silver and oxygen at 1 atm.

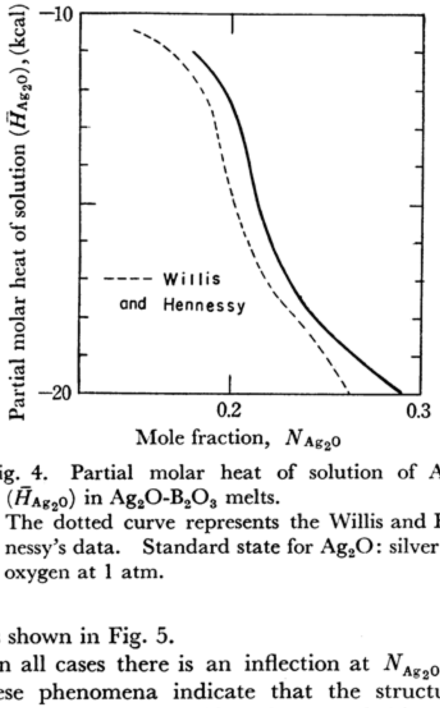
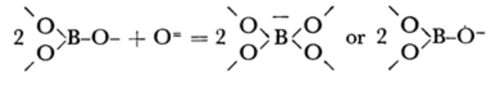


Fig. 4. Partial molar heat of solution of Ag_2O ($\bar{H}_{Ag_2O}$) in Ag_2O-B_2O_3 melts.
The dotted curve represents the Willis and Hennessy's data. Standard state for Ag_2O: silver and oxygen at 1 atm.

it is shown in Fig. 5.

In all cases there is an inflection at $N_{Ag_2O}=0.2$. These phenomena indicate that the structure of Ag-borate changes significantly around this composition. In the alkaline borate melts, the destruction of the network proceeds by means of the following reaction;



$$2\,{}^{O}_{O}{>}B\text{-}O\text{-} + O^{=} = 2\,{}^{O}_{O}{>}\overset{-}{B}{<}^{O}_{O} \text{ or } 2\,{}^{O}_{O}{>}B\text{-}O^{-} \qquad (5)$$

The ratio of four- to three-coordinated boron atoms and the behavior of non-bridging oxygen ions, in the above reaction have been discussed by Beekenkamp[10)] in the case of alkali borate glasses. He proposed the equation;

$$N_4 = X_4(X/1-X) \qquad (6)$$

where X_4 is defined by;

$$X_4 = [1+\exp(-\Delta G/KT)]^{-1} \qquad (7)$$

where ΔG is the thermodynamic potential difference between the BO_3-M unit and the BO_4-M unit, and where X is the mole fraction of alkali oxide. The same mechanism seems to be applicable in the present system. Thus, the inflection around $N_{Ag_2O}=0.2$ can be explained in terms of the equilibrium of the BO_3 unit and BO_4. If one follows the above line of approach, these experimental results seem to show that the formation of four-coordinated boron atoms is predominant to $N_{Ag_2O}=0.2$, while after this composition non-bridging oxygen ions gradually begin to be formed.

The infrared absorption spectra[11)] and the electric conductivity[12)] in the Ag_2O-B_2O_3 system, which have been determined in our laboratory, also support this view.

(2) **Ag_2O-Na_2O-B_2O_3 Ternary System.** Figure 6 shows the square root of the oxygen partial pressure, *i. e.*, a_{Ag_2O}, as a function of the composition, it also shows the Na_2O content at 850°C. The iso-activity lines in the Ag_2O-Na_2O-B_2O_3 ternary composition diagram are shown in Fig. 7. The solubility of silver oxide decreases with an

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[10)] P. Beekenkamp, *Phys. Chem. Glasses*, **9**(**1**), 14 (1968).

[11)] H. Kodama, Y. Kimura, T. Yokokawa and K. Niwa, This Bulletin, **42**, 681 (1969).

[12)] M. Honda, *Hokkaido Kyoiku Daigaku Kiyo* (*J. Hokkaido Univ. of Education*), **2A** **17**(**1**), 33 (1966).

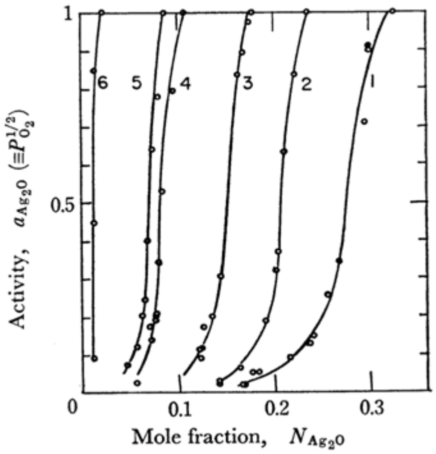

Fig. 6. The activity of Ag_2O, a_{Ag_2O} $(P_{O_2}{}^{1/2})$, at 850°C as a function of Na_2O contents.
Curve 1, 2, 3, 4, 5, and 6 refer respectively to the ratio of $N_{Na_2O}/N_{B_2O_3} = 0$, 1/18, 1/9.0, 1/5.0, 1/4.8, and 1/2.

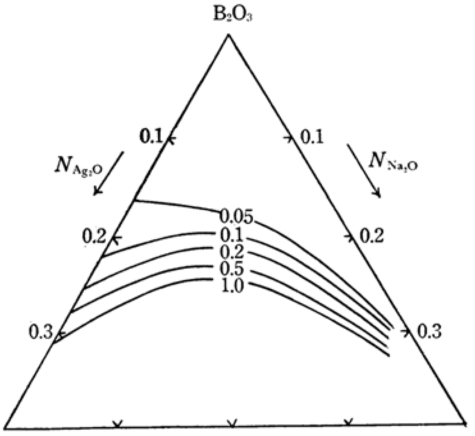

Fig. 7. The iso-activity lines of Ag_2O in Ag_2O-Na_2O-B_2O_3 ternary composition diagram at 850°C.
The standard state for Ag_2O is the melt in equilibrium with silver and oxygen at 1 atm.

increase in the Na_2O contents. This indicates that the silver oxide is a weaker base than sodium oxide. This is due to the fact that, while the silver ion and the sodium ion are both monovalent and are comparable in their ionic radii, the silver ion has a large polarizability and its bond to oxygen shows a somewhat covalent character. From Fig. 7 the following fact is shown: when the Ag_2O contents are small, the a_{Ag_2O} value increases with the increase in the Ag_2O contents at a constant composition of B_2O_3, but on the Ag_2O-rich side the inverse relation occurs. This might be explained by a possible strong negative interaction among silver ions when the Ag_2O contents increase. However, this idea is not acceptable in view of the fact that in the Ag_2O-B_2O_3 binary system Ag_2O behaves much like Na_2O. In molten oxide systems, it has been proposed that the strength of the base can be expressed in terms of the oxygen ion activity. This is an idea similar to that of the hydrogen ion concentration in aqueous solutions. An acid-base equilibrium was porposed by Lux and Flood to result from the following reaction;

$$\text{Base} = \text{Acid} + O^= \tag{8}$$

Therefore, the higher the oxygen ion activity in a melt, the stronger its basicity. The basicity of the melts will change with the relative contents of Ag_2O and Na_2O due to the difference in the oxygen-ion activity of the two components, even in the melts with an equal composition of total basic oxides. Thus Fig. 7 shows that the oxygen-ion activity of Ag-borate is smaller than that of Na-Borate. If Ag_2O and Na_2O dissociate perfectly in the melts, the following relations hold;

$$a_{Ag_2O} = a^2_{Ag^+}\cdot a_{O^=} = N^2_{Ag^+}\cdot\gamma^2_{Ag^+}\cdot a_{O^=} = N^2_{Ag^+}\cdot A \tag{9}$$

Here the A quantity is defined by;

$$A = a_{Ag_2O}/N_{Ag_2O} = \gamma^2_{Ag^+}\, a_{O^=} \tag{10}$$

where;

$$N_{Ag^+} = N_{Ag_2O}/(N_{Ag_2O} + N_{Na_2O}) \tag{11}$$

Figure 8 shows the relation between A and N_{Ag} at a constant composition of basic oxides. From Fig. 8 it may be seen that, even at a constant basic oxide composition, A increases with the increase in the proportion of Na_2O to Ag_2O. If

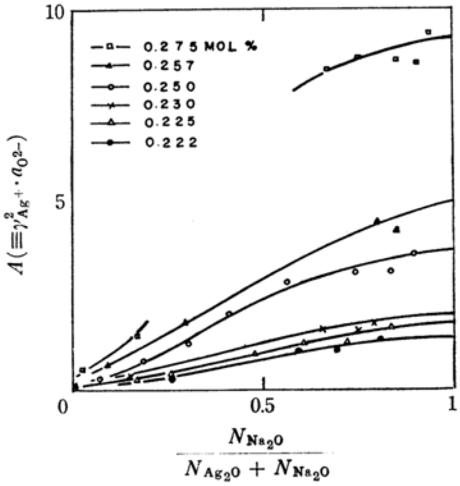

Fig. 8. The quantity $A(=\gamma^2_{Ag^+}\cdot a_{O^{2-}})$ as a function of $N_{Na}(=N_{Na_2O}/(N_{Ag_2O}+N_{Na_2O})$ at constant basic oxide concentration at 850°C.

it is assumed that γ_{Ag^+} is independent of the composition. A becomes proportional to $a_{O^=}$. γ_{Ag^+} will be assumed to be constant at the lower limits

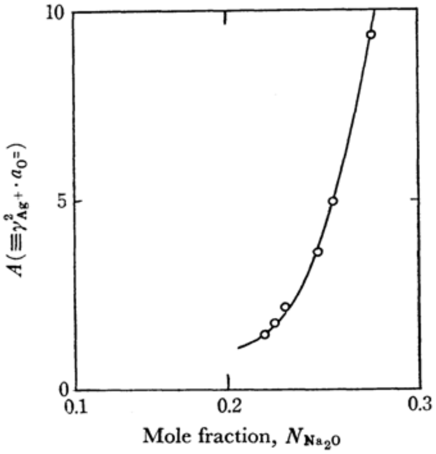

Fig. 9. The oxygen ion activity in arbitrary unit in Na_2O-B_2O_3 binary melt at 850°C.

of the Ag_2O concentration, even though this assumption is not acceptable over the complete range of the compositions. Therefore, the value of A extraporated to $N_{Ag_2O}=0$ indicates a quantity proportional to the activity of oxygen ions in the Na_2O-B_2O_3 binary system. This relation is plotted in Fig. 9. The oxygen-ion activity increases rapidly with an increese in the Na_2O contents.

(3) **Metallic Silver.** It has long been considered that the silver in a glass is in a metallic colloidal state, and that this causes the coloration. However, the fact that the definite solubility exists as a function of the temperature, the oxygen pressure, and the Na_2O content shows that the silver mostly dissolves in a glass as Ag_2O as far as a thermodynamic treatment is concerned. Another piece of evidence to support this view is the electric conductivity of this system, which will be reported on a separate paper. The electrical conductance of Ag-borate is similar to that of Na-borate in its absolute value as well as in its activation energy.

The color of this glass is yellow; it turns red with the increase in the Ag_2O content. This coloration is probably due to the covalent character of the Ag–O bond.