Activities of Lead Oxide in the Melts $\text{PbO-B}_2\text{O}_3$ and $\text{PbO-B}_2\text{O}_3\text{-Me}_2\text{O}(\text{Me}=\text{Li, Na, K})$

By Hideaki Suito*, Youji Yamada** and Masayasu Ohtani*

Thermodynamic properties of the binary melt $\text{PbO-B}_2\text{O}_3$ and the ternary melts $\text{PbO-B}_2\text{O}_3\text{-Li}_2\text{O}(\text{Na}_2\text{O, K}_2\text{O})$ have been studied by measuring the emf of the following cell:

The activities of lead oxide have been calculated in the temperature range from 800 to 1000°C. The partial and integral molar properties of the system $\text{PbO-B}_2\text{O}_3$ have been calculated at 1000°C. The results obtained are compared with previous experimental data. It was found in the ternary melts $\text{PbO-B}_2\text{O}_3\text{-Li}_2\text{O}(\text{Na}_2\text{O, K}_2\text{O})$ that at constant boron trioxide mole fraction, alkali metal oxide raises the activity coefficient of lead oxide in the range of compositions investigated.

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I. Introduction

The phase diagram for the $\text{PbO-B}_2\text{O}_3$ system has been determined by Geller and Bunting⁽¹⁾ and shows a wide liquid region at reasonably low temperature. Thermodynamic properties of the system $\text{PbO-B}_2\text{O}_3$ have been studied by the emf's measurement of cell: $\text{Pb}|\text{PbO-B}_2\text{O}_3|\text{ZrO}_2\cdot\text{CaO}|\text{O}_2(\text{Pt})$ between 750 and 1050°C⁽²⁾. Sridhar and Jeffes⁽³⁾ have measured activities of PbO in the binary poly-anionic melts such as PbO-SiO_2 , $\text{PbO-B}_2\text{O}_3$ and $\text{PbO-P}_2\text{O}_5$. Their experiment has been carried out by constructing the following type of the cell:

The activity of PbO in melts is then obtained from the equation,

$$-\ln a_{\text{PbO}} = \frac{nF(E_2 - E_1)}{RT}. \quad (2)$$

Where

a_{PbO} : the activity of PbO in the melt.

n : the valency ($n=2$).

F : the Faraday's constant

(23060 cal. v.⁻¹equiv.⁻¹).

R : the gas constant (cal. mol.⁻¹. K.⁻¹).

T : the absolute temperature (K).

E_1 : the emf of cell using PbO as electrolyte.

E_2 : the emf of cell using melts containing PbO as electrolyte.

Holm and Kleppa⁽⁴⁾ have measured the partial molar enthalpies of the components in lead borate melts at 800°C by means of a high-temperature calorimeter. In the present work, the activities of PbO in the binary melt $\text{PbO-B}_2\text{O}_3$ and the ternary melts $\text{PbO-B}_2\text{O}_3\text{-Li}_2\text{O}(\text{Na}_2\text{O, K}_2\text{O})$ have been measured by the cell given by eq. (1). From the results of the binary system, the thermodynamic properties are compared with those of other workers^{(2)~(4)}. Thermodynamic information on the ternary system $\text{PbO-B}_2\text{O}_3\text{-Li}_2\text{O}(\text{Na}_2\text{O, K}_2\text{O})$ is of theoretical interest when the ionic structure of the poly-anionic melts such as silicates, borates and phosphates is considered.

II. Experimental

The experiments were conducted in a silicon carbide resistance furnace and the temperature was controlled within $\pm 1^\circ\text{C}$ by a Chino proportional band controller. The Pt/Pt-13%Rh thermocouple was used for the measurement of temperature calibrated against copper (1083°C). Borate slags were prepared from weighed amounts of reagent-grade lead oxide, boron trioxide and alkali metal carbonate in a

* Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Sendai 980, Japan.

** Graduate School, Tohoku University, Sendai 980, Japan.

platinum crucible by heating to about 800~1000°C. The melts were quenched by pouring onto a nickel plate and these samples were stored in a desiccator before use. About 50 g of lead (99.99%Pb) was placed in a recrystallized alumina crucible (40 mm I.D and 50 mm in height), to which about 30 g (PbO-low melt) to 60 g (PbO-rich melt) of powdered slag of the desired composition was poured. When the crucible contents had melted and attained a fixed temperature, the stainless steel pre-oxidized wire (3 mm ϕ) protected by an alumina tube was lowered to the molten lead and the oxygen electrode having the platinum wire (0.5 mm ϕ) of ring shape (4 mm ϕ) as shown in Fig. 1 was slowly lowered until it came into contact with the surface of the melt. Dry oxygen gas was passed through the inner alumina tube with a dimension of 3.5 mm ϕ (outer alumina tube: 8 mm ϕ). Argon was passed through the furnace tube during the experiment. The effect of the flow rate of oxygen, the oxygen potential in furnace atmosphere and the weight ratio of metal/slag on the emf's value was discussed in detail in the following section. After the emf measurement, the melts were subjected to chemical analysis to determine the dissolved amount of alumina, since it was found that the alumina of the cell material were considerably attacked. Consequently, the time for measurement was limited within 1~1.5 hr after the sample was melted. The emf between the electrodes was measured with a high-impedance of 1 M Ω electrometer reading to ± 1 mV. When the cell temperature was changed and attained a fixed temperature, the steady emf was ob-

tained immediately, but it took a few minutes when the temperature was low and the PbO content in slag was small. The emf was measured when the cell temperature was attained both from higher or lower sides. The cell emf was corrected for the thermo-emf due to Pt-stainless steel contact.

III. Results and Discussion

Ditschenko and Rochow⁽⁵⁾ first suggested the use of an oxygen electrode in silicate melts consisting of oxygen gas bubbling around a platinum wire. It has successfully been applied to PbO-SiO₂⁽⁶⁾⁽⁷⁾, PbO-B₂O₃⁽³⁾⁽⁸⁾ and PbO-P₂O₅⁽³⁾ systems. A more detailed study of the oxygen electrode was made by Jeffes and Sridhar⁽⁹⁾. The oxygen electrode used by them, in which the oxygen tube dips into the melt and oxygen gas at 1 atm. is bubbling around a platinum wire, was also used in our preliminary experiment, but it was found that the steady emf was not obtained probably because the slag melt was considerably oscillated by bubbling oxygen gas into the melt.

In order to obtain the steady emf, a platinum wire must be in contact with both oxygen gas at 1 atm. and the melt as electrolyte. In other words, the oxygen potential on the surface of a platinum wire should be 1 atm. oxygen pressure. Actually, however, a gradient of the oxygen potential even near the top of the melt is considered to be high, since the oxygen potential at the Pb/(PbO) interface is much lower than that at the surface of the melt ($P_{O_2}=1$). i.e., the oxygen potential in which pure PbO is equilibrated with Pb at 1000°C is calculated to be 3.41×10^{-8} atm. and the depth of the slag layer is about 10~15 mm. Accordingly, the exact position of the end of a platinum wire which depended on the slag composition and temperature was one of the most critical conditions to obtain the proper and steady emf.

1. Preliminary experiment

The influence of the size, shape and depth of a platinum wire and the flow rate of oxygen on emf has been examined in our preliminary experiment. The steady emf was found to be

Fig. 1 Configuration of Pt-O₂ electrode.

independent of the size of a platinum wire and the flow rate of oxygen as far as the oxygen gas is passed at a certain flow rate. The use of the ring-shaped platinum wire shown in Fig. 1 proved to be effective for obtaining the steady emf. The reason why the ring-shaped platinum wire was used seems to be the increase of the contact area between slag and oxygen gas at 1 atm. due to the film formed in the ring. The platinum wire is raised from the position where it touches the surface of the melt and stable emf appears. At this position, a Pt ring is probably covered by the melt due to creeping.

Figure 2 shows the effect of the distance from this position upon emf. As shown in Fig. 2, the emf increases with the raising of a Pt wire, but the plateau region which shows the maximum emf appears depending on the slag composition and temperature. The depth "0 mm" in Fig. 2 denotes the position at which the platinum wire come into contact with the melt. This plateau region tends to decrease with increasing lead oxide content. Therefore, in the present work, the dependence of the distance on the emf has been checked in each measurement. The effect of the oxygen potential in furnace atmosphere on the emf has been studied under a stream of oxygen gas or argon

gas. Although it was found that the emf obtained was not influenced by the oxygen potential in furnace atmosphere during the course of the present experiment, argon gas was passed through the furnace tube to prevent oxidation of the lead which may change the slag composition. The effect of slag/metal ratio on the emf was not observed in the time interval of 1~1.5 hr, although lead is expected to be oxidized with decreasing depth of the slag layer.

In the preliminary experiments, both a stainless steel wire and a pure iron wire as the anode lead have been used, but the extensive oxidation of these wires was observed, since the oxygen potential in equilibration with Pb and the PbO-low melt was higher than that in equilibration with Fe and FeO. Richardson et al.⁽¹⁰⁾ and Charette et al.⁽¹¹⁾ used successfully the iridium wire. The preoxidized nickel wire⁽¹²⁾ and stainless steel wire⁽¹³⁾ with a dense coherent oxide layer have also been used. In the present measurement, the preoxidized stainless steel wire was found to be appreciably effective for protection against the oxidation of anode lead.

2. Pure PbO melts

The emf of the cell with pure PbO as the electrolyte was measured from the temperature just above the melting point to 1000°C. The standard free energy of the formation of liquid lead oxide from liquid lead and oxygen was calculated by $\Delta G^\circ = -2FE_1$ cal/mol PbO. These values are plotted against temperature in Fig. 3. The emf E_1 (V) and the standard free

Fig. 2 Relationship between the distance of a Pt wire and EMF. (EMF is corrected for thermo-emf). (1) Pure PbO at 962°C (2) 0.70PbO-0.30Li₂O·2B₂O₃ at 1003°C.

Fig. 3 Free energies of the formation of liquid PbO.

Table 1 Results for weight pct. alumina.

PbO (mol%)	PbO-B ₂ O ₃	PbO-Li ₂ O·2B ₂ O ₃	PbO-Na ₂ O·2B ₂ O ₃	PbO-K ₂ O·2B ₂ O ₃
100	1.05, 0.90			
90	2.05	2.19	1.60	1.66
80	2.39	2.74	4.49	1.76
70	2.96	3.43	3.09	1.11
60	3.40	4.35	5.08	0.88
50		5.48	5.49	2.16
40	3.00			
30				2.05
20	1.22			

energy of formation ΔG° (cal/mol) as a function of temperature are calculated by least squares method and represented as follows:

$$E_1 = 1.008 - 0.000421T(K), \quad (3)$$

$$\Delta G^\circ = 46480 - 19.43T(K) \pm 230. \quad (4)$$

As shown in Fig. 3 together with other investigators values, our experimental values obtained are in good agreement with those of Shridhar et al.⁽³⁾ who carried out the emf measurement using a similar type of cell given by eq. (1). Our values are about 1.4 kcal/mol more positive than the maximum negative value of Kapoor et al.⁽²⁾ All values by other workers were obtained by the emf method except for those by Richardson et al.⁽¹⁰⁾, who obtained the free energy of the formation of liquid lead oxide by determining the oxygen content of molten lead in equilibrium with PbO. The contamination of the melt by alumina is shown in Table 1. One may see that the slag was contaminated with about 1 wt % alumina.

3. PbO-B₂O₃ melts

The emf of the cell of various PbO contents corrected for the thermo-emf between stainless steel and platinum, is plotted against temperature between 800 and 1000°C in Fig. 4.

Activities of PbO were calculated by eq. (2), using the values of E_1 determined from the present work. Activities of B₂O₃ were calculated by the Gibbs-Duhem integration. These values at 1000°C are plotted in Fig. 5 together with other values⁽²⁾⁽³⁾⁽⁸⁾. Figure 5 shows that the present activity data are in fair agreement with those of Sridhar et al.⁽³⁾ and Kapoor et al.⁽²⁾ The data obtained by Lepinskikh and

Fig. 4 EMF of cells containing PbO-B₂O₃ melts.

Esin⁽⁸⁾ are considerably higher than those of the present work. The reasons for this anomaly may be an unsatisfactory oxygen electrode configuration and the use of a platinum electrode in contact with the liquid lead.

The integral molar free energy of mixing ΔG^M in the system PbO-B₂O₃ is given by the following equation:

$$\Delta G^M = N_{\text{PbO}} \Delta \bar{G}_{\text{PbO}}^M + N_{\text{B}_2\text{O}_3} \Delta \bar{G}_{\text{B}_2\text{O}_3}^M. \quad (5)$$

Here, $\Delta \bar{G}_{\text{PbO}}^M$ and $\Delta \bar{G}_{\text{B}_2\text{O}_3}^M$ are the partial molar free energies of mixing of PbO and B₂O₃, respectively. N_{PbO} and $N_{\text{B}_2\text{O}_3}$ are the mole fractions of PbO and B₂O₃, respectively. The

Fig. 5 Activities in PbO-B₂O₃ melts.

partial molar enthalpy of mixing of PbO, $\Delta\bar{H}_{\text{PbO}}^{\text{M}}$ and the entropy of mixing of PbO, $\Delta\bar{S}_{\text{PbO}}^{\text{M}}$ are calculated according to the following equations:

$$\Delta\bar{H}_{\text{PbO}}^{\text{M}} = \frac{\partial(\Delta\bar{G}_{\text{PbO}}^{\text{M}}/T)}{\partial(1/T)} = \frac{R\partial(\ln a_{\text{PbO}})}{\partial(1/T)}, \quad (6)$$

$$\Delta\bar{S}_{\text{PbO}}^{\text{M}} = (\Delta\bar{H}_{\text{PbO}}^{\text{M}} - \Delta\bar{G}_{\text{PbO}}^{\text{M}})/T. \quad (7)$$

The above partial molar properties of B₂O₃ are calculated by the activities of B₂O₃ obtained by the Gibbs-Duhem equation. The integral molar enthalpy of mixing ΔH^{M} and the entropy of mixing ΔS^{M} are given by the following relations:

$$\Delta H^{\text{M}} = N_{\text{PbO}}\Delta\bar{H}_{\text{PbO}}^{\text{M}} + N_{\text{B}_2\text{O}_3}\Delta\bar{H}_{\text{B}_2\text{O}_3}^{\text{M}}, \quad (8)$$

$$\Delta S^{\text{M}} = N_{\text{PbO}}\Delta\bar{S}_{\text{PbO}}^{\text{M}} + N_{\text{B}_2\text{O}_3}\Delta\bar{S}_{\text{B}_2\text{O}_3}^{\text{M}}, \quad (9)$$

where $\Delta\bar{H}^{\text{M}}$ and $\Delta\bar{S}^{\text{M}}$ are the partial molar enthalpy and entropy of mixing, respectively.

Figures 6 and 7 show the values of $\Delta\bar{H}_{\text{PbO}}$, $\Delta\bar{H}_{\text{B}_2\text{O}_3}$, ΔH^{M} and ΔS^{M} calculated from the activities of PbO and B₂O₃ in the temperature range between 800 and 1000°C. $\Delta\bar{H}_{\text{PbO}}$ and $\Delta\bar{H}_{\text{B}_2\text{O}_3}$ obtained by high-temperature calorimetric measurements⁽⁴⁾ are included in Fig. 6 for comparison. The values of $\Delta\bar{H}_{\text{PbO}}$ by the present authors and Sridhar et al.⁽³⁾ show positive values of about 0.8 and 4 kcal/mol respectively at the composition of $N_{\text{PbO}} =$

Fig. 6 Partial molar heats of solution in PbO-B₂O₃ melts. $\Delta\bar{H}_{\text{PbO}}^{\text{M}}$: 1, 2, 3, 4, $\Delta\bar{H}_{\text{B}_2\text{O}_3}^{\text{M}}$: 1', 2', 3', 4'. Fig. 7 Integral molar entropies and enthalpies of mixing in PbO-B₂O₃ melts.

0.8~0.7. It may be seen from Fig. 7 that the change of ΔH^{M} with composition is in better agreement with the results of Kapoor et al.⁽²⁾, but is not in agreement with the results of Holm et al.⁽⁴⁾ and Sridhar et al.⁽³⁾ The ΔS^{M} shows its maximum at the composition $N_{\text{PbO}} =$

0.8~0.7, except for the results of Kapoor et al.⁽²⁾ and the present result of ΔS^M is intermediate among the other results. The change in melt composition due to the evaporation loss was found to be negligible⁽¹⁵⁾. Contamination of the melt by the alumina refractories was analyzed and given in Table 1. The alumina content increases with increasing B_2O_3 content and reaches a maximum value of about 3.4 wt% Al_2O_3 at $N_{PbO}=0.6$. On the other hand, the results of Sridhar et al.⁽³⁾ indicate that no serious contamination of the melts by refractories takes place. Kapoor et al.⁽²⁾, did not examine this contamination.

4. $PbO-B_2O_3-Li_2O(Na_2O, K_2O)$ melts

Activities of PbO in the ternary melts $PbO-B_2O_3-Li_2O$, $PbO-B_2O_3-Na_2O$ and $PbO-B_2O_3-K_2O$ have been measured in the temperature range of 800~1000°C along the constant ratio of $N_{B_2O_3}/N_{M_2O}=2$ ($M=Li, Na, K$). The emf values of the cells corrected for the thermo-emf are plotted against temperature in Fig. 8, Fig. 9 and Fig. 10, respectively.

Fig. 8 EMF of cells containing $PbO-Li_2O \cdot 2B_2O_3$ melts.

Fig. 9 EMF of cells containing $PbO-Na_2O \cdot 2B_2O_3$ melts.

Fig. 10 EMF of cells containing $PbO-K_2O \cdot 2B_2O_3$ melts.

The composition N'_{PbO} denotes the mole fraction of the component PbO in the pseudo-binary system $\text{PbO-M}_2\text{O} \cdot 2\text{B}_2\text{O}_3$. Table 1 gives the results of contamination by Al_2O_3 contents. In Fig. 11, the activities of PbO calculated from eq. (2) at 1000°C are shown in the section of the ternary diagram $\text{PbO-B}_2\text{O}_3\text{-M}_2\text{O}$. To our knowledge, the only work on these systems was made by Russian workers⁽¹⁶⁾ who measured the activity of PbO in the $\text{PbO-B}_2\text{O}_3\text{-Na}_2\text{O}$ melt. Their results are also shown in Fig. 11 for comparison. It may be clear that their results are in better agreement with the present result. From the pattern of the behavior of the activities of PbO as shown in Fig. 11, alkali metal oxides tend to raise the activity coefficient of PbO at constant B_2O_3 mole fraction in the composition range studied. These iso-activities contours observed in the borate system are similar to those of the silicate system⁽¹⁷⁾ CaO-FeO-SiO_2 at 1600°C , in which the addition of CaO raises the activity

Fig. 11 Iso-activities curves for PbO in the ternary systems, (a) $\text{PbO-B}_2\text{O}_3\text{-Li}_2\text{O}$, (b) $\text{PbO-B}_2\text{O}_3\text{-Na}_2\text{O}$ and (c) $\text{PbO-B}_2\text{O}_3\text{-K}_2\text{O}$, at 1000°C . Solid circles denote the data from Delimarskii and Nazarenko⁽¹⁶⁾.

Fig. 12 Plots of $RT \ln \gamma_{\text{PbO}}$ against $N_{\text{B}_2\text{O}_3}$ in the ternary borate system at 1000°C .

coefficient of FeO at constant silica mole fraction. This can be interpreted in the following way. When alkali metal oxide is added to the $\text{PbO-B}_2\text{O}_3$ melt, the activity of PbO will increase as a result of a stronger interaction between B_2O_3 and alkali metal oxide which is more basic than PbO. This can be seen from Fig. 12 in which $RT \ln \gamma_{\text{PbO}}$ (at 1000°C) is plotted against the mole fraction of B_2O_3 for the constant 0.1 mol fraction of alkali metal oxide. Although the effect of the addition of Li_2O and Na_2O on the activity coefficient of PbO is not distinguishable, the activity coefficient of PbO tends to increase in the order of $\text{K}_2\text{O} > \text{Na}_2\text{O} > \text{Li}_2\text{O}$. Richardson and Pillay⁽¹⁸⁾ measured the activity of PbO in the ternary silicate melts PbO-CaO-SiO_2 and PbO-MgO-SiO_2 and found that at constant silica mole fraction, CaO and MgO raise the activity coefficient of PbO. Moreover, the effect of the addition of CaO on the activity coefficient of PbO was found to be more than that of MgO. A marked similarity in iso-activity contours was observed between ternary silicate and borate melts.

The ideal mixing of silicate model proposed by Richardson⁽¹⁹⁾ has been found to be very useful in permitting the prediction of the thermodynamic properties of a ternary silicate melt from a knowledge of the properties of the constituent binary silicate. The model is based on the assumption that the free energy of mixing two binary silicates of the same metal oxide/silica ratio arises solely from the entropy

of randomly mixing the cations in a constant silicate anionic matrix. This model has been applied to the present ternary borate system. Then, the activity of PbO in the ternary borate system is given by

$$a_{\text{PbO}}^t = a_{\text{PbO}(\text{B}_2\text{O}_3)}^b \left(\frac{x_{y\text{PbO} \cdot \text{B}_2\text{O}_3}}{2 - x_{y\text{PbO} \cdot \text{B}_2\text{O}_3}} \right) \times \left[\frac{a_{\text{B}_2\text{O}_3(\text{PbO})}^b}{a_{\text{B}_2\text{O}_3(\text{M}_2\text{O})}^b} \right] \frac{1 - x_{y\text{PbO} \cdot \text{B}_2\text{O}_3}}{y} \quad (10)$$

where the subscripts *t* and *b* indicate 'ternary' and 'binary' respectively, and $x_{y\text{PbO} \cdot \text{B}_2\text{O}_3}$ is the mole fraction of the $y\text{PbO} \cdot \text{B}_2\text{O}_3$ in the pseudobinary system $y\text{PbO} \cdot \text{B}_2\text{O}_3$ – $y\text{M}_2\text{O} \cdot \text{B}_2\text{O}_3$. Activities of PbO in the ternary borate melt have been calculated from the values of $a_{\text{B}_2\text{O}_3}(a_{\text{B}_2\text{O}_3(\text{M}_2\text{O})}^b)$ in the B_2O_3 – M_2O ($\text{M}=\text{Li}, \text{Na}, \text{K}$) systems obtained by means of concentration cells⁽²⁰⁾ and the values of $a_{\text{B}_2\text{O}_3}(a_{\text{B}_2\text{O}_3(\text{PbO})}^b)$ in the present PbO – B_2O_3 system. The calculated results of iso-activities contours for PbO at 900°C are shown in Fig. 13 in the corner of B_2O_3 in PbO – B_2O_3 – M_2O melts. It is evident from the figure that the activity of PbO at constant B_2O_3 mole fraction increases in the order of Li_2O , Na_2O and K_2O by the addition of alkali metal oxide which is identical with the order found in the experimental results shown in Fig. 11. One may see from Fig. 11 and Fig. 13 that the deviation from the model increases in the order of Li_2O , Na_2O , K_2O .

Recently, Belton and co-workers⁽²¹⁾ have studied the thermodynamics of mixing in the sodium-potassium silicates at disilicate compositions at 1100°C by means of a Knudsen cell-mass spectrometer technique. They concluded that the positive deviation from ideal silicate mixing occurs slightly and this deviation is interpreted in terms of the accommodation of the different size of cations. Although the difference in cation radius in the PbO – B_2O_3 – K_2O system is smaller than that in the PbO – B_2O_3 – Na_2O system (PbO – B_2O_3 – Li_2O system), the deviation from the model in the PbO – B_2O_3 – K_2O system is found to be larger than that in the PbO – B_2O_3 – Na_2O system (PbO – B_2O_3 – Li_2O system). Thus, the observed deviation may not be interpreted in terms of the accommodation of the different size of

Fig. 13 Calculated iso-activities curves for PbO by Richardson's ideal mixing model⁽¹⁹⁾ in the ternary systems, (a) PbO – B_2O_3 – Li_2O , (b) PbO – B_2O_3 – Na_2O and (c) PbO – B_2O_3 – K_2O , at 900°C.

cations in a constant anionic matrix, but in terms of the interaction which occurs with or among the cationic species found in an iron-cobalt orthosilicate melt⁽²²⁾.

IV. Conclusion

(1) The standard free energy of formation of liquid lead oxide from liquid lead and oxygen has been obtained in the temperature range from above the melting point of PbO to 1000°C.

$$\Delta G^\circ = 46,480 - 19.43T(\text{K}) \pm 230 \text{ cal/mol PbO.}$$

(2) Activities of PbO and B_2O_3 in the binary lead borate system has been determined in the temperature range from 800 to 1000°C. The partial and integral molar properties has been calculated at 1000°C. The results were compared with previous experimental data.

(3) In the ternary PbO – B_2O_3 – Li_2O (Na_2O ,

K_2O) system, alkali metal oxide was found to raise the activity coefficient of lead oxide at constant B_2O_3 mole fraction.

(4) Ideal mixing model proposed by Richardson in ternary silicate melt has been applied to the present ternary borate systems to calculate activities of PbO . These calculated activities of PbO have been compared with the experimentally determined activities of PbO in the B_2O_3 corner of the ternary melts.

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