Solubility of Platinum in Molten Fluxes as a Measure of Basicity

SHIGEKO NAKAMURA and NOBUO SANO

The solubility of platinum in the molten BaO-Al$_2$O$_3$, BaO-SiO$_2$, CaO-Al$_2$O$_3$, CaO-SiO$_2$, Na$_2$O-SiO$_2$, and CaO-Al$_2$O$_3$-SiO$_2$ systems has been measured in order to seek a new measure of basicity. The solubility of platinum increases with increasing content of basic oxide. The correlations among the solubility of platinum, carbonate, sulfide, and phosphate capacities, basic oxide activities, and theoretical optical basicity are discussed.

I. INTRODUCTION

THE basicity of a flux is one of the most important factors in the refining of metals. Although it is most appropriate to be defined by the activity of an oxide ion, it cannot be experimentally measured in principle. Therefore, a variety of measures, such as gas solubility in molten fluxes, redox equilibria of transition metal ions, and theoretical optical basicity have been proposed for expressing flux basicity. The authors studied the redox equilibria of copper ions in molten silicate fluxes for this purpose.[1] The results demonstrate that the ratio of cuprous and cupric may be a good indicator of silicate flux basicity. However, this is not applicable to fluxes containing transition metals or highly basic fluxes. In the former case, the ratio of cuprous and cupric is influenced by the presence of transition metals. It is well known that platinum dissolves in highly basic oxide melts such as BaO or Na$_2$O. It may be used as a measure of basicity of highly basic fluxes containing transition metals. The purpose of this study is to seek a measure of flux basicity by investigating the solubility of platinum as a function of composition in BaO-Al$_2$O$_3$, BaO-SiO$_2$, CaO-Al$_2$O$_3$, CaO-SiO$_2$, Na$_2$O-SiO$_2$, and CaO-Al$_2$O$_3$-SiO$_2$ melts.

Platinum may exist in these melts as metallic platinum or platinum cation or platinate ion. The solubility of metallic platinum may be independent of oxygen partial pressure and that of platinum cation probably decreases with increasing activity of oxide ion, while the platinate ion may have several oxidation states depending on the prevailing activity of an oxide ion and oxygen partial pressure as follows:

$$\text{Pt} + m\text{O}_2 + n\text{O}^{2-} = \text{PtO}_{(2m+n)}^{2n-} \qquad [1]$$
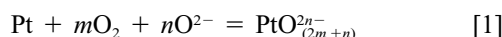
Equation [1] suggests that the solubility of platinate increases with increasing oxide ion activity and oxygen partial pressure.

In the present study, the dependences of the solubility of platinum on flux composition, oxygen partial pressure, and temperature have been investigated. In addition, the correlations among the platinum solubility, carbonate, sulfide, and phosphate capacities, basic oxide activities, and theoretical optical basicity are discussed.

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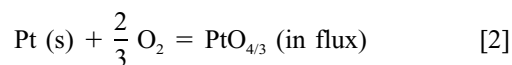
II. EXPERIMENTAL

An electric furnace was used for equilibration. The temperature was controlled at 1873 K within ± 2 K using a Pt-6 pct Rh/Pt-30 pct Rh thermocouple and a PID controller. The flux sample was prepared using reagent grade BaCO$_3$, Al$_2$O$_3$, and SiO$_2$ and CaO calcined from CaCO$_3$ in air.

Four grams of flux samples were held in a platinum crucible in air for equilibration. For examining the dependence of oxygen partial pressure, the desired P_{O_2} was obtained by mixing O$_2$ and Ar. A gas train for air, Ar, and O$_2$ gas mixtures consisted of sulfuric acid and magnesium perchlorate for dehydration. The time for equilibration varying from 5 to 15 hours was preliminarily determined for each flux system. After equilibration, the sample was quenched and crushed for chemical analysis. The platinum content was determined by ICP.

III. RESULTS AND DISCUSSION

A. Dependence of the Solubility of Platinum on Temperature in the CaO-Al$_2$O$_3$ and Na$_2$O-SiO$_2$ Systems and on Oxygen Partial Pressure in the CaO-Al$_2$O$_3$ System

Dependence of the solubility of platinum on temperature in the 65.5 (mol pct)CaO-Al$_2$O$_3$ and 47.5 (mol pct)Na$_2$O-SiO$_2$ melts is shown in Figure 1. In both melts, the solubility of platinum increases very slightly with increasing temperature. Assuming that the solubility is low enough for Henry's law to hold at any temperatures employed in the present study, the enthalpy changes for dissolution of solid platinum in the 65.5 (mol pct)CaO-Al$_2$O$_3$ and 47.5 (mol pct)Na$_2$O-SiO$_2$ melts are calculated from the slopes of Figure 1 as 20.7 and 37.1 kJ/mol, respectively, indicating that the dissolution is a slightly endothermic reaction. This can be explained as follows. Thermodynamic data for platinum oxide are available only for Pt$_3$O$_4$[2] in the solid state at 298 K with some uncertainty. Nevertheless, assuming that the platinum oxide exists as Pt$_3$O$_4$, the reaction of platinum dissolution may be written as follows:

$$\text{Pt (s)} + \frac{2}{3}\text{O}_2 = \text{PtO}_{4/3} \text{ (in flux)} \qquad [2]$$

Equation [2] is composed of the following steps:
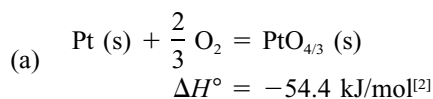
$$(a) \quad \text{Pt (s)} + \frac{2}{3}\text{O}_2 = \text{PtO}_{4/3} \text{ (s)}$$
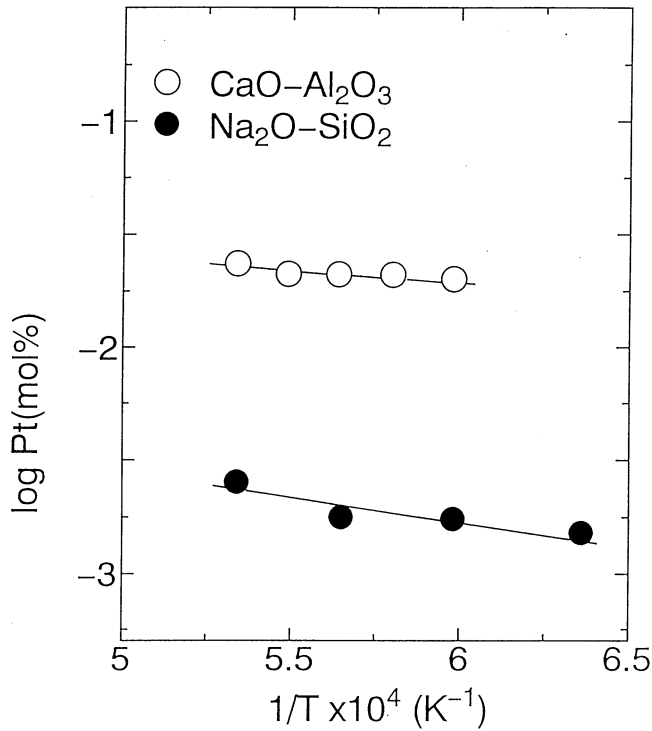$$\Delta H^\circ = -54.4 \text{ kJ/mol}^{[2]}$$

Fig. 1—Dependence of Pt solubility on temperature for the 65.5(mol pct)CaO-Al$_2$O$_3$ and 47.5(mol pct)Na$_2$O-SiO$_2$ melts.
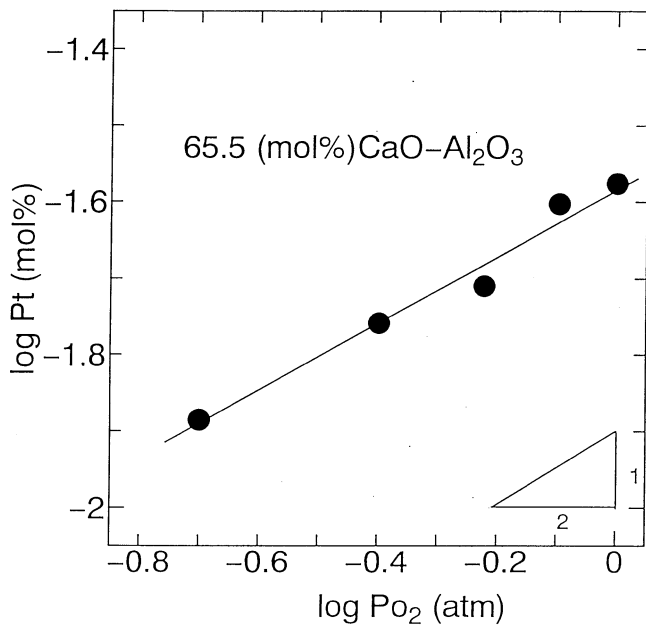
Fig. 2—Dependence of Pt solubility on oxygen partial pressure for the 65.5(mol pct)CaO-Al$_2$O$_3$ melt at 1873 K.

(b) PtO$_{4/3}$ (s) = PtO$_{4/3}$ (1)

(c) PtO$_{4/3}$ (1) = PtO$_{4/3}$ (in flux)
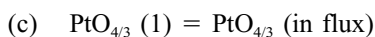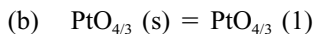
If the sum of the absolute values for the enthalpy changes of steps b and c is larger than 54.4 kJ/mol, the enthalpy change for Eq. [2] will be positive, as shown in the present study. Although the enthalpy change for step b is not available, it is definitely positive. If the value for step a is less negative than −54.4 kJ/mol, because of the noble nature of
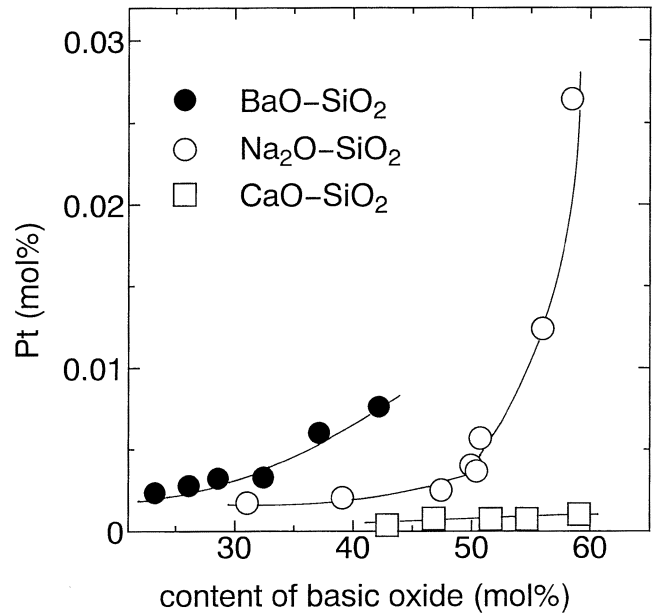

Fig. 3—Dependence of Pt solubility on content of basic oxides for the BaO-SiO$_2$, Na$_2$O-SiO$_2$, and CaO-SiO$_2$ systems in air at 1873 K.

platinum, the trend for the solubility to increase with increasing temperature would become stronger as a singular example.

The equilibrium constant for Eq. [1], $K_{[1]}$, is expressed by Eq. [3].

$$K_{[1]} = \frac{a_{PtO_{(2m+n)}^{2n-}}}{a_{Pt} \cdot (a_{O^{2-}})^n \cdot (P_{O_2})^m}$$ [3]

where a_i is the activity of i.

In this study, the activity of platinum is unity because a platinum crucible was used.

Thus,

$$\log (\text{mass pct } PtO_{(2m+n)}^{2n-}) = n \log a_{O^{2-}} + m \log P_{O_2}$$
$$- \log f_{PtO_{(2m+n)}^{2n-}} + \log K_{[1]}$$ [4]

where $f_{PtO_{(2m+n)}^{2n-}}$ is the activity coefficient of $PtO_{(2m+n)}^{2n-}$.

When the solubility of platinum is measured with changing oxygen partial pressure for a flux of fixed composition at constant temperature, the oxide ion activity, $a_{O^{2-}}$, and the activity coefficient, $f_{PtO_{(2m+n)}^{2n-}}$, may be constant. The solubility of platinum is then expected to have a linear relationship with the oxygen partial pressure in logarithmic form and the slope of the line will be m. The solubility of platinum at 1873 K is plotted against oxygen partial pressure in logarithmic form for the 65.5 (mol pct)CaO-Al$_2$O$_3$ melt in Figure 2. As expected, they show a good linear correlation. A slope of 0.41 was determined by the method of least squares. This value is close to 0.5, indicating that the coefficient of the oxygen term in Eq. [1], m, is 1/2.

B. *Dependence of the Solubility of Platinum on the Flux Composition*

In Figure 3, the solubilities of platinum at 1873 K in the CaO-SiO$_2$, Na$_2$O-SiO$_2$, and BaO-SiO$_2$ systems in air are plotted as a function of the basic oxide content on a molar
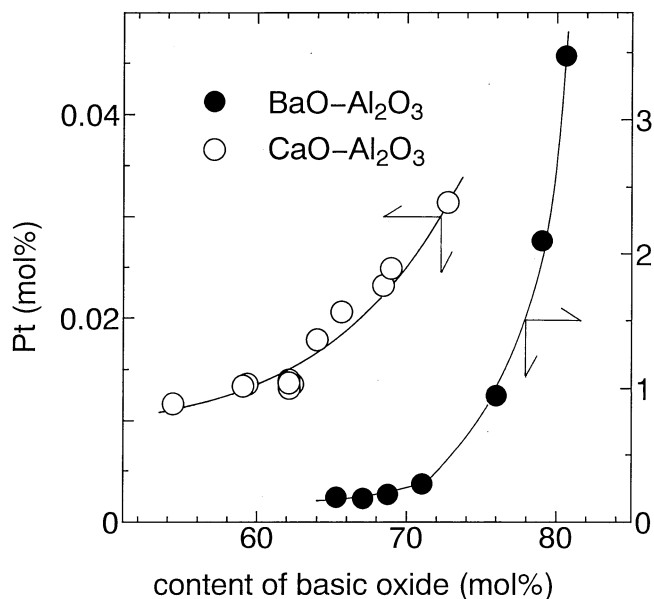
Fig. 4—Dependence of Pt solubility on content of basic oxides for the BaO-Al$_2$O$_3$ and CaO-Al$_2$O$_3$ systems in air at 1873 K.
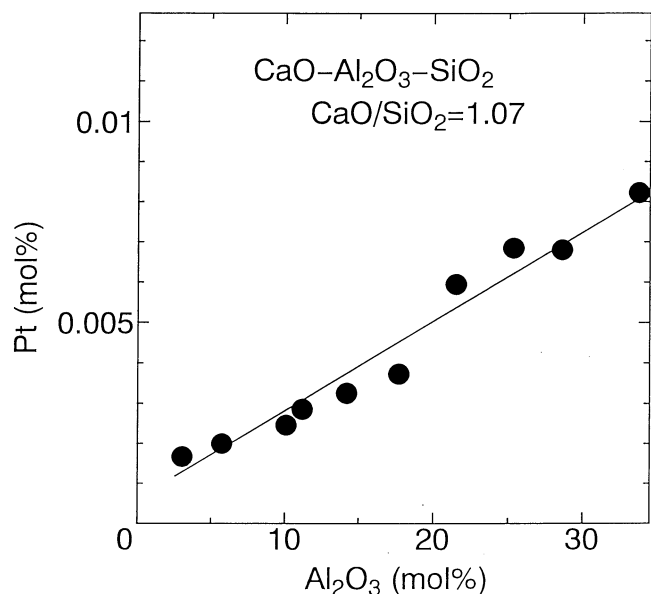

Fig. 5—Dependence of Pt solubility on content of Al$_2$O$_3$ addition to the 51.7(mol pct)CaO-SiO$_2$ melt at 1873 K.
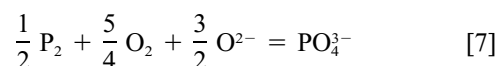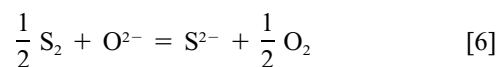
basis. The solubility of platinum in these systems increases with increasing content of basic oxide, and at the same basic oxide content, barium silicates have the highest solubility followed by sodium silicates and then calcium silicates. As can be seen in Figure 4, Al$_2$O$_3$ is confirmed to behave as an acidic oxide for the CaO-Al$_2$O$_3$ and BaO-Al$_2$O$_3$ systems.

Comparing the solubility of platinum in silicate systems with that in aluminate having a common basic oxide, the latter is about 100 times larger than the former, indicating that Al$_2$O$_3$ is less acidic than SiO$_2$. Figure 5 shows the effect of Al$_2$O$_3$ addition to the 51.7 (mol pct)CaO-SiO$_2$ melt on its solubility of platinum. The solubility of platinum increases with increasing Al$_2$O$_3$ content, and Al$_2$O$_3$ is considered to behave as a basic oxide in this case. Since aluminum

oxide is amphoteric, it behaves as an acidic oxide in the BaO-Al$_2$O$_3$ and CaO-Al$_2$O$_3$ systems and behaves as a basic oxide in the CaO-Al$_2$O$_3$-SiO$_2$ system due to the presence of SiO$_2$ which is a more acidic component.

C. Correlations among the Solubility of Platinum, Carbonate, Sulfide, and Phosphate Capacities and the Basic Oxide Activity

The dissolution of CO$_2$, S$_2$, and P$_2$ into molten fluxes may be expressed by Eqs. [5] through [7], respectively.

$$CO_2 + O^{2-} = CO_3^{2-} \qquad [5]$$

$$\frac{1}{2} S_2 + O^{2-} = S^{2-} + \frac{1}{2} O_2 \qquad [6]$$

$$\frac{1}{2} P_2 + \frac{5}{4} O_2 + \frac{3}{2} O^{2-} = PO_4^{3-} \qquad [7]$$

The carbonate, sulfide, and phosphate capacities are defined according to the preceding reactions.[3]

$$C_{CO_3^{2-}} = \frac{(\text{mass pct } CO_3^{2-})}{P_{CO_2}} = K_{[5]} \frac{a_{O^{2-}}}{f_{CO_3^{2-}}} \qquad [8]$$

$$C_{S^{2-}} = \frac{(\text{mass pct } S^{2-}) \cdot (P_{O_2})^{1/2}}{(P_{S_2})^{1/2}} = K_{[6]} \frac{a_{O^{2-}}}{f_{S^{2-}}} \qquad [9]$$

$$C_{PO_4^{3-}} = \frac{(\text{mass pct } PO_4^{3-})}{(P_{P_2})^{1/2} \cdot (P_{O_2})^{5/4}} = K_{[7]} \frac{(a_{O^{2-}})^{3/2}}{f_{PO_4^{3-}}} \qquad [10]$$

where C_i is the capacity of i. Eliminating the $a_{O^{2-}}$ term from Eqs. [4] and [8] and using $m = 1/2$, the relationship between the solubility of platinum and carbonate capacity is derived as follows:

$$\log (\text{mass pct } PtO_{(1+n)}^{2n-}) = n \log C_{CO_3^{2-}} + \log \frac{(f_{CO_3^{2-}})^n}{f_{PtO_{(1+n)}^{2n-}}} \qquad [11]$$
$$+ \frac{1}{2} \log P_{O_2} + \log \frac{K_{[1]}}{K_{[5]}^n}$$

The activity coefficients of the platinate ion, $f_{PtO_{(1+n)}^{2n-}}$, and carbonate ion, $f_{CO_3^{2-}}$, are dependent upon the flux composition. However, the second term on the right-hand side of Eq. [11] will be constant if the two activity coefficients have the same dependence on flux composition. In the same manner, the relationships between the solubility of platinum and sulfide capacity or phosphate capacity are derived from Eqs. [4] and [9] or [10] as follows:

$$\log (\text{mass pct } PtO_{(1+n)}^{2n-}) = n \log C_{S^{2-}} + \log \frac{(f_{S^{2-}})^n}{f_{PtO_{(1+n)}^{2n-}}} \qquad [12]$$
$$+ \frac{1}{2} \log P_{O_2} + \log \frac{K_{[1]}}{K_{[6]}^n}$$

$$\log (\text{mass pct } PtO_{(1+n)}^{2n-}) = \frac{2}{3} n \log C_{PO_4^{3-}} + \log \frac{(f_{PO_4^{3-}})^{2n/3}}{f_{PtO_{(1+n)}^{2n-}}} \qquad [13]$$
$$+ \frac{1}{2} \log P_{O_2} + \log \frac{K_{[1]}}{K_{[7]}^{2n/3}}$$

Thus, the solubility of platinum may be expected to have a linear relationship with carbonate, sulfide, and phosphate
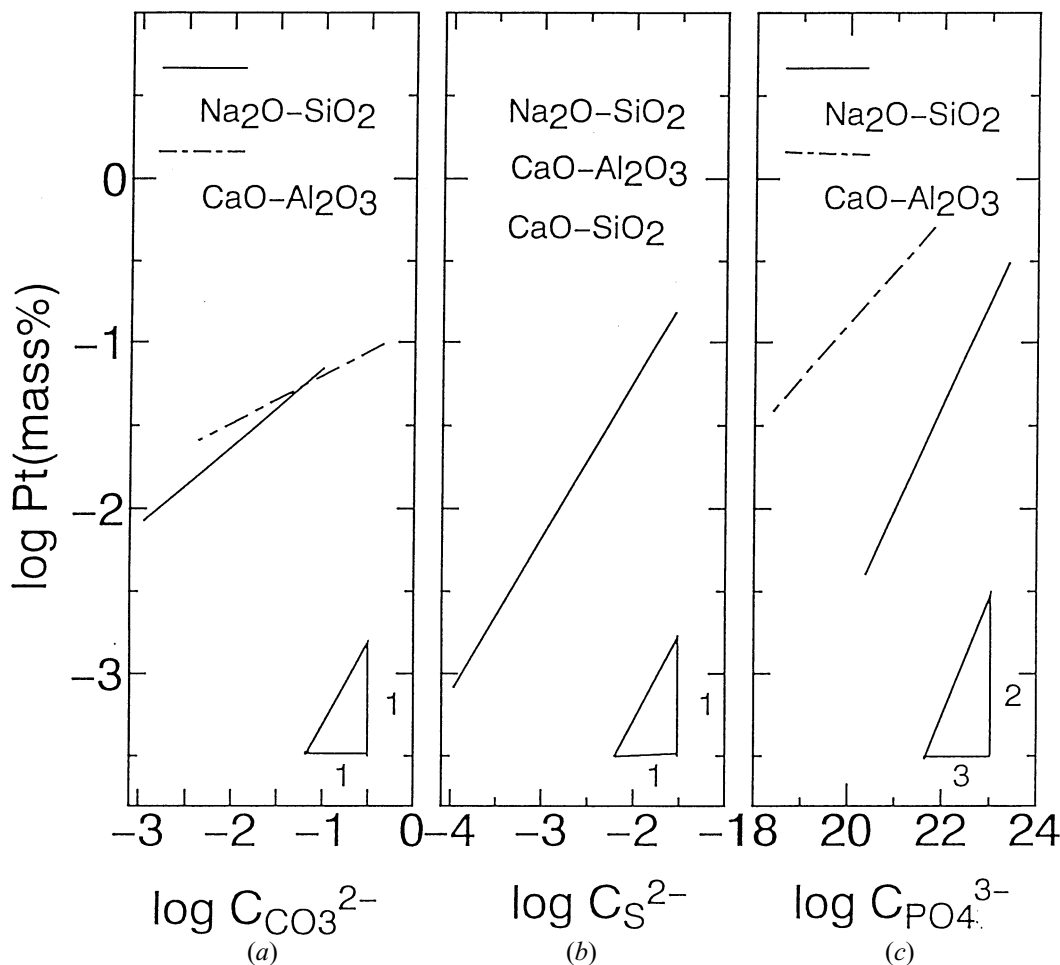
Fig. 6—Relationship between (*a*) carbonate, (*b*) sulfide, and (*c*) phosphate capacities and Pt solubility.

capacities in logarithmic form, and the slope of the former two will be n and the latter will be $2n/3$.

Kawahara *et al.*[4] measured the carbonate capacities of the $CaO-Al_2O_3$ and Na_2O-SiO_2 systems at 1773 and 1473 K, respectively. The effect of the composition on the partial molar enthalpy change for the dissolution of CO_2 in the Na_2O-SiO_2 system was studied by Maeda *et al.*[5] and Iwase *et al.*[6] According to their results, it decreases with increasing Na_2O content and it varies from 220 (30 mass pct Na_2O) to 20 kJ/mol (60 mass pct Na_2O). In Figure 6(a), the solubility of platinum from the present study at 1873 K is plotted against the carbonate capacities of the $CaO-Al_2O_3$ and Na_2O-SiO_2 systems at the same temperature in logarithmic form, which are extrapolated using the aforementioned temperature dependence. Straight lines are shown with slopes 0.35 and 0.49 for the $CaO-Al_2O_3$ and Na_2O-SiO_2 systems, respectively, which are far lower than the expected value of unity.

The sulfide capacities for the $CaO-Al_2O_3$ and $CaO-SiO_2$ systems at 1923 K were measured by Fincham and Richardson.[7] Inoue and Suito[8] measured the sulfur partition between carbon saturated iron melts and Na_2O-SiO_2 fluxes at 1523 and 1623 K and concluded that temperature has little effect on the sulfur partition. Figure 6(b) shows the solubility of platinum against sulfide capacity in logarithmic form for the $CaO-Al_2O_3$, $CaO-SiO_2$, and Na_2O-SiO_2 systems. All the plots are on a common straight line with

a slope of 0.93, which is close to one. Even if the sulfide capacity depends on temperature, the slope of the Na_2O-SiO_2 system may remain constant and the line would be only shifted to the right.

Tsukihashi *et al.*[9,10] measured the phosphate capacities of the $CaO-Al_2O_3$ and Na_2O-SiO_2 systems at 1773 and 1573 K. Figure 6(c) shows the solubility of platinum against phosphate capacity at 1873 K in logarithmic form for the $CaO-Al_2O_3$ and Na_2O-SiO_2 systems, the latter being extrapolated using the partial molar enthalpy change for dephosphorization reported by Tsukihashi *et al.* Both systems show linear relationships. The slope for the former is 0.35, and that for the latter is 0.71, which is close to the expected value of 2/3.

From those experimental findings, it is suggested that the coefficient of O^{2-}, n, in Eq. [1] is unity, although the determination of n is rather uncertain. Equation [1] can then be written as follows:

$$Pt + \frac{1}{2} O_2 + O^{2-} = PtO_2^{2-} \qquad [14]$$
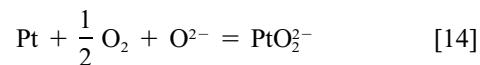
According to this equation, the platinum ion has a valence of +2 in the fluxes investigated in the present study. Although quantitative analysis of Pt^{2+} has not been established, strong evidence of the presence of Pt^{2+} in the $CaO-Al_2O_3$ system was confirmed by extracting Pt^{2+} into
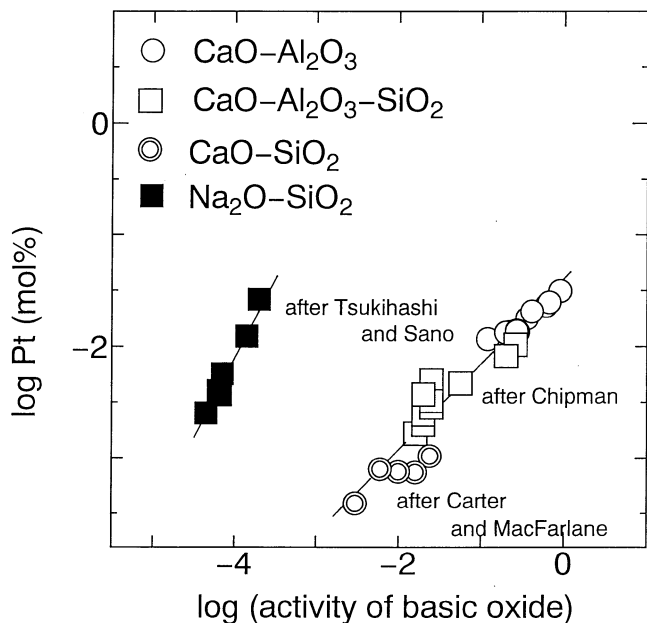
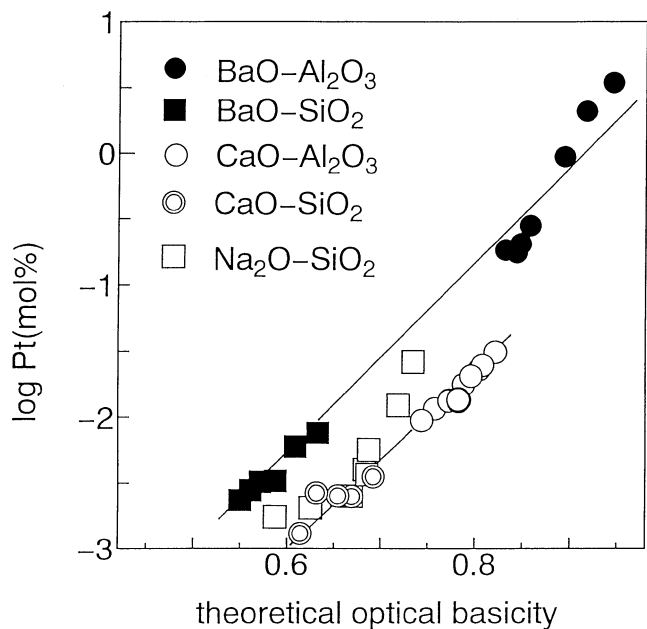Fig. 7—Dependence of Pt solubility on the activity of basic oxide.

Fig. 8—Relationship between theoretical optical basicity and Pt solubility.

carbon tetrachloride followed by color change of dithizon from green to red violet.[11]

D. *Relationship between the Solubility of Platinum and the Activity of the Basic Oxides*

In Figure 7, the solubility of platinum is plotted against the activity of the basic oxides. The activity of CaO in the CaO-Al_2O_3 and CaO-Al_2O_3-SiO_2 systems was measured by Chipman[12] at 1873 K and that in the CaO-SiO_2 system was measured by Carter and MacFarlane[13] at 1773 K. In the case of the Na_2O-SiO_2 system, the activity of Na_2O is estimated by extrapolating the temperature dependence of the activity of Na_2O reported by Tsukihashi and Sano.[14] For all cases, the platinum solubility increases with increasing

activity of the basic oxides. The activity of Na_2O for the Na_2O-SiO_2 system is about three orders of magnitude smaller than that of CaO at a constant platinum solubility. This demonstrates that Na_2O is a more basic oxide than CaO.

E. *Relationship between the Solubility of Platinum and the Theoretical Optical Basicity*

Duffy and Ingram[15] proposed the optical basicity as a measure of basicity of glasses. In their approach, the basicity is expressed in terms of electron donor power of the oxide ion, and it was measured by probe ion spectroscopy, such as Pb or Tl. Theoretical optical basicity, Λ_{th}, for several compounds containing transition metals and halides was derived by Nakamura *et al.*[16] and Duffy.[17,18] The equation proposed by Nakamura *et al.* is based on the concept of the average electron density, whereas Duffy's is based on molar polarization. In Figure 8, the solubility of platinum in logarithmic form is plotted against the optical basicity defined by Nakamura *et al.* for the BaO-Al_2O_3, CaO-Al_2O_3, BaO-SiO_2, CaO-SiO_2, and Na_2O-SiO_2 systems. All of these systems have a linear relationship and solubility of platinum increases with increasing theoretical optical basicity. The BaO-Al_2O_3 and BaO-SiO_2 systems approximately fit on the same line, in spite of the difference in an accompanying acidic oxide. The same is true with the CaO-Al_2O_3 and CaO-SiO_2 systems. The slopes of the two lines are approximately identical, as shown in Figure 8. Since the solubility of platinum in BaO-containing systems is about 100 times larger than that of CaO-containing systems, it does not fit on a single line. The relationship between the solubility of platinum and optical basicity after Duffy was found not to fit on a single line.

IV. CONCLUSIONS

The solubility of platinum increases with increasing content of basic oxide, such as BaO, Na_2O, and CaO, in the BaO-Al_2O_3, CaO-Al_2O_3, BaO-SiO_2, CaO-SiO_2, and Na_2O-SiO_2 systems, suggesting that it may be a good indicator of the basicity of highly basic fluxes.

The enthalpy change of Eq. [1] is positive because of the noble nature of platinum.

The correlations among the solubility of platinum, other refining indexes (such as carbonate, sulfide, and phosphate capacities), basic oxide activity, and theoretical optical basicity have been investigated. The solubility of platinum has a linear relationship with carbonate, sulfide, and phosphate capacities, the basic oxide activity, and theoretical optical basicity in logarithmic form.

The ionic form of platinum in molten fluxes is suggested as PtO_2^{2-} by examining the dependence of the solubility of platinum on the oxygen partial pressure and relationship between the solubility of platinum and other refining indexes, such as carbonate, sulfide, and phosphate capacities.

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