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THERMODYNAMICS OF SODIUM CARBONATE-BASED SLAGS CONTAINING As, Sn, OR Fe-OXIDE

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Synopsis: Thermodynamic properties of sodium carbonate-based slags, containing As-, Sn-, or Fe-oxide were studied at 1423 K to 1523 K by the following experiments: (1)Activity measurements of $NaO_{0.5}$ by EMF technique, (2)Activity measurements of these oxides by slag/metal equilibrium technique, (3)Solubility measurements of CO_2, (4)Redox equilibrium measurements of these oxides, and (5)Determination of phase diagrams. Based on the results, the equilibrium distribution ratios of these elements between the slags and molten copper were estimated as a function of partial pressures of CO_2 and O_2 and the slag composition.

Key words: thermochemistry, thermodynamic activity, distribution ratio, sodium carbonate-based slag, $NaO_{0.5}$, $AsO_{2.5}$, SnO_2, $FeO_{1.5}$, CO_2, electromotive force method, beta"-alumina, high purity copper

1. Introduction

In view of the application of sodium carbonate slag not only to the fire-refining of crude copper but also to the production of high purity copper, authors have been conducting a series of fundamental studies to estimate the equilibrium distribution ratio of various impurity elements between sodium carbonate-based slags and molten copper [1]-[6]. In the present study, the thermodynamic properties of sodium carbonate-based slags containing As-, Sn-, or Fe-oxide were studied to estimate the distribution behavior of these impurity elements between the slags and molten copper.

2. Experimental principle

The distribution reaction of impurity element X between the slag and molten copper may be represented by:

$$X(\text{in metal}) + \nu/4O_2 = XO_{\nu/2}(\text{in slag}) \qquad (1)$$

when X predominantly exists as ν-valent oxide in the slag. The equilibrium distribution ratio of X, L_X defined by (%X in slag)/[%X in metal], can be derived as:

$$L_X = \frac{(\%X)}{[\%X]} = \frac{K\cdot(n_T)\cdot\gamma_X}{[n_T]\cdot\gamma_{XO_{\nu/2}}}\cdot P_{O_2}{}^{\nu/4} \qquad (2)$$

where K is the equilibrium constant of Eq. (1), $[n_T]$ and (n_T) the molar amount of 100 g metal and slag, respectively, γ_i Raoultian activity coefficient of component i, and P_{O_2} the oxygen partial pressure at the slag-metal interface. From this equation, it is known that thermodynamic properties of slags and metals are required to determine the distribution ratio. Since the thermodynamic properties of molten copper alloys have been relatively well established, then the ones of the slags such as the values of (n_T) and $\gamma_{XO_{\nu/2}}$ should be determined experimentally.

In the present study, following measurements were conducted to determine the thermodynamic properties of sodium carbonate-based slags, containing the oxide of various impurity elements (As, Sn, or Fe) in crude copper, at 1423 K to 1523 K:

(1) Electrochemical measurements of activity of $NaO_{0.5}$,
(2) Activity measurements of impurity oxides by slag/metal equilibrium technique,
(3) Solubility measurements of CO_2,
(4) Redox equilibrium measurements of impurity oxides,
(5) Determination of phase diagrams.

Fig.1 shows the flow chart for calculating the distribution ratio. Combination of the results of (1) and (2) enabled us to calculate the activity of the impurity oxides from the activity of $NaO_{0.5}$ by the Gibbs–Duhem integration. The slag compositions were determined from the solubility measurements of CO_2. The measurements (4) were required as the impurity element might change the valence depending on the experimental conditions. In the case of the slags containing Sn– or Fe–oxide, there exist stable solid compounds, Na_2SnO_3 and $NaFeO_2$, therefore the measurements (5) were required to establish the (solid + liquid) two phase regions. Thus, the distribution ratios could be finally estimated as a function of partial pressures of CO_2 and O_2 and the slag composition N ($\equiv n_{Na_2O}/(n_{Na_2O} + n_{\text{Impurity oxide}})$, n: the number of moles).

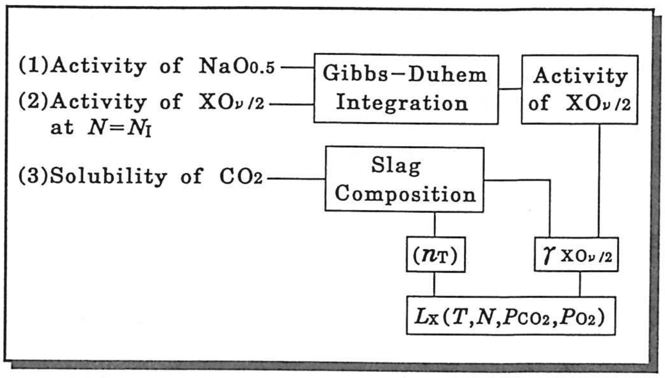

Fig.1 Flow chart for calculating the distribution ratio.

3. Activity of $NaO_{0.5}$

Activities of $NaO_{0.5}$ in the slags were determined by EMF method, using beta"–alumina as a solid electrolyte, for various partial pressures of CO_2 at 1423 to 1523 K. The electrochemical cell used in the present work may be represented as:

Pt, $O_2(g, P_{O_2}{}^*)$	Na^+	$CO_2(g, P_{CO_2})$, $O_2(g, P_{O_2})$, Pt
$NaO_{0.5}$–SiO_2–$FeO_{1.5}$ ref. melt	beta"–Al_2O_3	Sodium carbonate–based sample melt

The activity of $NaO_{0.5}$ in the sample melt was evaluated by the following equation [4]:

$$\log a_{NaO_{0.5}(l)} = -5039E/T + \log a_{NaO_{0.5}(l)}{}^* - (1/4)\log(P_{O_2}{}^*/P_{O_2}) \qquad (3)$$

where E is the electromotive force, T the absolute temperature, and the superscript, *, denotes the values for the reference melt.

The activity of $NaO_{0.5}$ in the $NaO_{0.5}$–CO_2–$AsO_{2.5}$ system at 1523 K is shown in Fig.2. Partial pressure of CO_2 has a great influence on the activity.

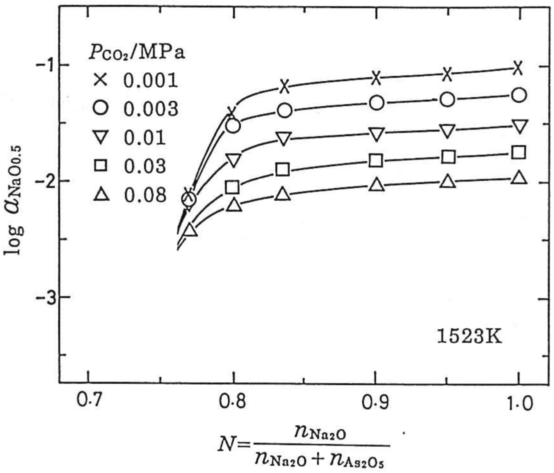

Fig.2 Activity of $NaO_{0.5}$ in the $NaO_{0.5}$–CO_2–$AsO_{2.5}$ system at 1523 K.

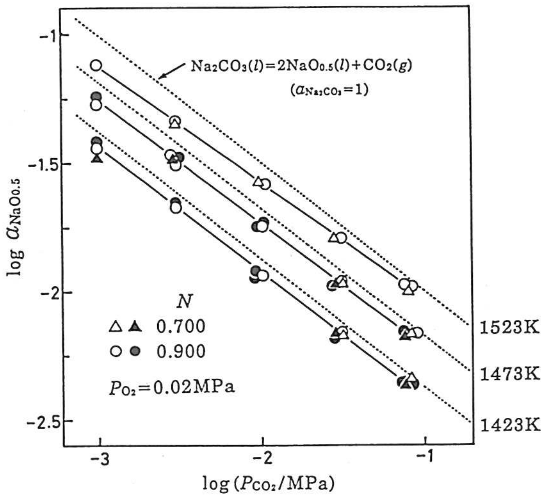

Fig.3 Effect of partial pressure of CO_2 on the activity of $NaO_{0.5}$ in the $NaO_{0.5}$–CO_2–$FeO_{1.5}$ system.

The activity of $NaO_{0.5}$ in the $NaO_{0.5}-CO_2-FeO_{1.5}$ system is shown in Fig.3. With decreasing P_{CO_2} the activity of $NaO_{0.5}$ increases, but does not show any dependence on the slag composition. The similar results were also obtained in the $NaO_{0.5}-CO_2-SnO_2$ system. By the X-ray diffraction analysis of the slag specimens taken after the experiments, $NaFeO_2$ and Na_2CO_3, Na_2SnO_3 and Na_2CO_3, were identified, respectively. Therefore, it was considered that these slags were saturated with $NaFeO_2(s)$ or $Na_2SnO_3(s)$, respectively. Then the solubility measurements of Na_2SnO_3 and $NaFeO_2$ into sodium carbonate melt were conducted.

4. Solubility measurement

4.1 Solubility of Na_2SnO_3 and $NaFeO_2$ into sodium carbonate melt

A synthesized and sintered Na_2SnO_3 or $NaFeO_2$ block was placed in a bottom of an alumina crucible and fixed by using an alumina tube. Sodium carbonate powder was also charged on the sintered compound. Then the sample in the crucible was heated at 1523 K. The CO_2-O_2-(or CO)$-$Ar gas mixture was continuously flushed over the sample melt to control the partial pressures of oxygen and CO_2. A sample was withdrawn from the upper melted part by careful dipping a stainless steel rod at given time intervals. Obtained samples were subjected to chemical analyses.

The results of the solubility measurement of $NaFeO_2$ are shown in Fig.4. With decreasing the partial pressure of CO_2 the solubility increased, but the partial pressure of oxygen had no effect. The experimental points are on the line connecting sodium carbonate with Na_3FeO_3. This implies that the dissolution reaction proceeds according to the following reaction and Fe exists as FeO_3^{3-} anion in the sodium carbonate-based melt.

$$2NaO_{0.5}(l) + NaFeO_2(s) = \underset{(3Na^+,\ FeO_3^{3-})}{Na_3FeO_3(l)} \qquad (4)$$

Quite similar results were obtained by the solubility measurements of Na_2SnO_3, and it is also presumed that the dissolution reaction proceeds according to the following reaction:

$$2NaO_{0.5}(l) + Na_2SnO_3(s) = \underset{(4Na^+,\ SnO_4^{4-})}{Na_4SnO_4(l)} \qquad (5)$$

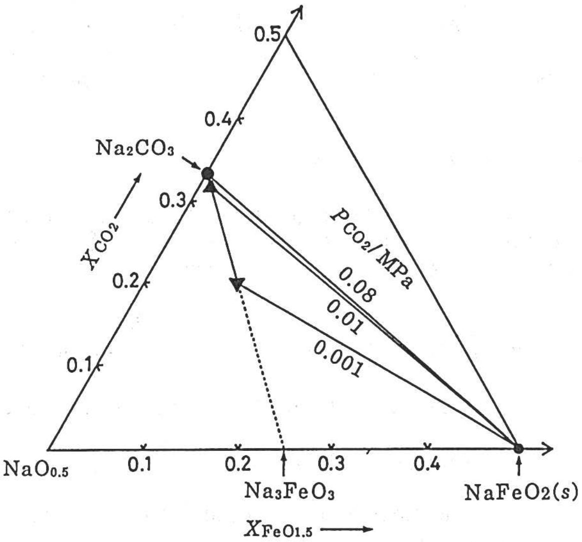

Fig.4 Solubility of $NaFeO_2(s)$ into sodium carbonate melt at 1523K.

4.2 Solubility of CO_2 into $NaO_{0.5}-AsO_{2.5}$ melt [6]

The solubilities of CO_2 in $NaO_{0.5}-AsO_{2.5}$ melts were measured by equilibrating the melts with $CO_2-CO-Ar$ gas mixtures at 1523 K or 1423 K. After the experiments, the CO_2 as well as other components in the melts were chemically analyzed. In order to confirm the applicability of Eq. (1), the contents of trivalent and pentavalent As were also determined by chemical analysis.

The solubility values of CO_2 were plotted on the $NaO_{0.5}-CO_2-AsO_{2.5}$ ternary diagram and it was found that all the experimental points were distributed along the straight line connecting sodium carbonate with Na_3AsO_4 in spite of different partial pressures of oxygen and CO_2. This implies that arsenic exists in the form of pentavalent anion AsO_4^{3-} in the slags. The trivalent/pentavalent arsenic ratio was very small in the range of the present experimental conditions. The redox reaction of arsenic had, therefore, almost no effect on the CO_2 solubility in the melts.

5. Oxide activity of As, Sn and Fe in sodium carbonate-based slags

5.1 Activity of $AsO_{2.5}$

The activity of $AsO_{2.5}$ in $NaO_{0.5}-CO_2-AsO_{2.5}$ melt was calculated from the activity of $NaO_{0.5}$ by integrating the Gibbs-Duhem relation. Under the condition of a constant P_{CO_2}, the Gibbs-Duhem relation for the $NaO_{0.5}-CO_2-AsO_{2.5}$ system [4] is given as:

$$N\, d\ln a_{NaO_{0.5}} + (1 - N)\, d\ln a_{AsO_{2.5}} = 0 \quad ; \; N \equiv n_{Na_2O}/(n_{Na_2O} + n_{As_2O_5}) \qquad (6)$$

In order to calculate the activity of $AsO_{2.5}$, the initial values of the integration were needed. To determine the initial values, distribution equilibrium measurements of As between this slag and molten copper were conducted. The experimental procedure of the distribution measurements was almost the same as reported in the previous paper [3]. The thermodynamic data used for the evaluation of the distribution equilibrium are summarized in Table 1, together with those for Sn and Fe. The calculated activity of $AsO_{2.5}$ is shown in Fig.5, together with the experimentally obtained points. In the Gibbs–Duhem calculation, the points at N=0.85 were used as the initial values of the integration. The partial pressure of CO_2 has great influence on the activities of the components in the $NaO_{0.5}$–CO_2–$AsO_{2.5}$ system.

Table 1 Thermodynamic data used for the evaluation of distribution equilibrium at 1523 K.

Free enrgy change of reaction		
$As(s) + 5/4O_2(g) = AsO_{2.5}(s)$:	$\Delta G° = -93.9$ kJ [7]	
$Sn(l) + O_2(g) = SnO_2(s)$:	$\Delta G° = -260.4$ kJ [7]	
$Fe(s) + 3/4O_2(g) = FeO_{1.5}(s)$:	$\Delta G° = -215.7$ kJ [7]	
Activity coefficient in molten copper alloy		
$\gamma^{\circ}_{O(g)} = 0.25$ [8],	$\gamma^{\circ}_{As(s)} = 3.6 \times 10^{-3}$ [9]	
$\gamma^{\circ}_{Sn(l)} = 6.5 \times 10^{-2}$ [10],	$\gamma^{\circ}_{Fe(s)} = 31.5$ [11]	
Interaction parameter in molten copper alloy		
$\varepsilon_{As}^{As}{}_{(1423K)} = 10$ [12],	$\varepsilon_{Sn}^{Sn}{}_{(1593K)} = 11$ [13]	
$\varepsilon_{Fe}^{Fe} = -20$ [14],	$\varepsilon_{O}^{O} = -7$ [8],	$\varepsilon_{O}^{As} = 0$ [15]
$\varepsilon_{O}^{Sn} = -2$ [16],	$\varepsilon_{O}^{Fe} = -141$ [present authors]	

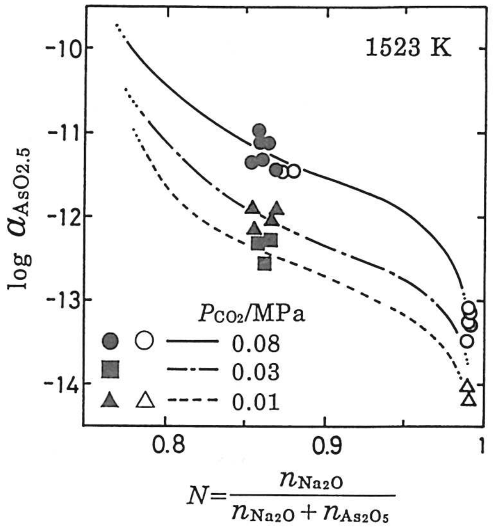

Fig.5 Activity of $AsO_{2.5}$ in the $NaO_{0.5}$–CO_2–$AsO_{2.5}$ system at 1523 K.

5.2 Activity of $FeO_{1.5}$

The activity of $FeO_{1.5}$ in the (solid + liquid) two phase region can be calculated from the activity of $NaO_{0.5}$ by using the following equilibrium relation:

$$NaO_{0.5}(l) + FeO_{1.5}(s) = NaFeO_2(\gamma) \qquad (7)$$

In order to determine the free energy change of this reaction, EMF measurements were conducted by using the following electrochemical cells:

$$\begin{array}{l|c|ll} \text{Pt, } CO_2(g, P_{CO_2}^{*}),\ O_2(g, P_{O_2}^{*}) & Na^{+} & O_2(g, P_{O_2}),\ \text{Pt} & \\ \quad \text{Reference} & & \text{Sample mixture} & FeO_{1.5}(s) + Na_3Fe_5O_9(s) \\ \qquad\qquad Na_2CO_3(\text{s or l}) & \text{beta}''\text{–}Al_2O_3 & \qquad\qquad \text{or} & Na_3Fe_5O_9(s) + NaFeO_2(\gamma) \end{array}$$

and

$$5/3FeO_{1.5}(s) + NaO_{0.5}(s) = 1/3Na_3Fe_5O_9(s):$$

$$\Delta G°/\text{J} = RT\ln a_{NaO_{0.5}} = -\ 85950 + 2.20T \; (\,973\text{–}1403 \text{ K}\,) \qquad (8)$$

$$1/2Na_3Fe_5O_9(s) + NaO_{0.5}(s) = 5/2NaFeO_2(\gamma):$$

$$\Delta G°/\text{J} = RT\ln a_{NaO_{0.5}} = -\ 71300 - 6.88T \; (\,1293\text{–}1423 \text{ K}\,) \qquad (9)$$

were obtained. Combining above two equations with

$$NaO_{0.5}(s) = NaO_{0.5}(l) : \Delta G°/\text{J} = 34940 + 10.33T\ln T - 99.75T \; [7] \qquad (10)$$

the following free energy values were finally obtained:

$$NaO_{0.5}(l) + FeO_{1.5}(s) = NaFeO_2(\gamma): \Delta G°/J = -115000 - 10.33T\ln T + 98.32T \quad (7\text{-}1)$$

Distribution equilibrium measurements for Fe were also conducted to determine the activity of $FeO_{1.5}$ in the liquid region. As shown in Fig.6, the activity coefficient of $FeO_{1.5}$ in $NaO_{0.5}$–CO_2–$FeO_{1.5}$ melts has a constant value for a constant P_{CO_2}, independent of the concentration. The oxide species were, therefore, expressed with mono-nuclear atom base in the present paper. The activity of $FeO_{1.5}$ is shown in Fig.7.

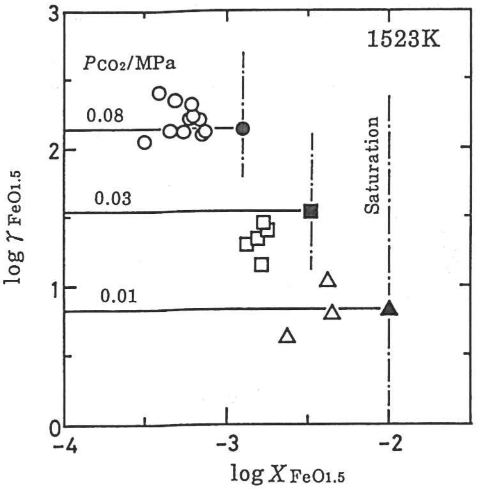

Fig.6 Activity coefficient of $FeO_{1.5}$ in $NaO_{0.5}$–CO_2–$FeO_{1.5}$ melts at 1523 K.

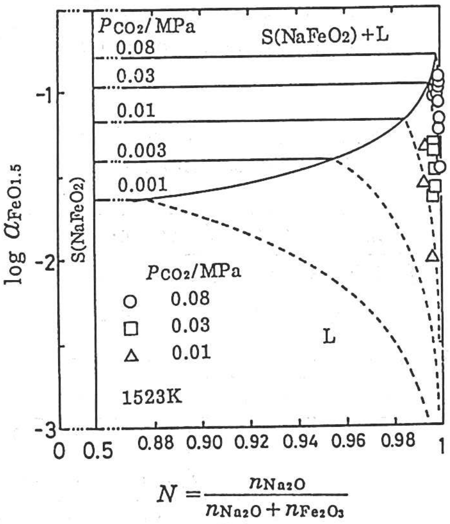

Fig.7 Activity of $FeO_{1.5}$ in the $NaO_{0.5}$–CO_2–$FeO_{1.5}$ system at 1523 K.

5.3 Activity of SnO_2

The activity of SnO_2 in the (solid + liquid) two phase region can be also calculated from the activity of $NaO_{0.5}$ by using the following equilibrium relation:

$$2NaO_{0.5}(l) + SnO_2(s) = Na_2SnO_3(s) \quad (11)$$

Some distribution equilibrium measurements for Sn were also conducted between the saturated slag and molten copper alloy, and from the determined activity of SnO_2 and that of $NaO_{0.5}$, the free energy change of the above reaction was determined as $\Delta G° = -163$ kJ (1523 K). Then the activity of SnO_2 for different P_{CO_2} was evaluated.

The activity of SnO_2 in the liquid region was also evaluated from the distribution measurements, and it was found that the activity coefficient of SnO_2 in the $NaO_{0.5}$–CO_2–SnO_2 system had also a constant value for a constant P_{CO_2}. The activity of SnO_2 is shown in Fig.8.

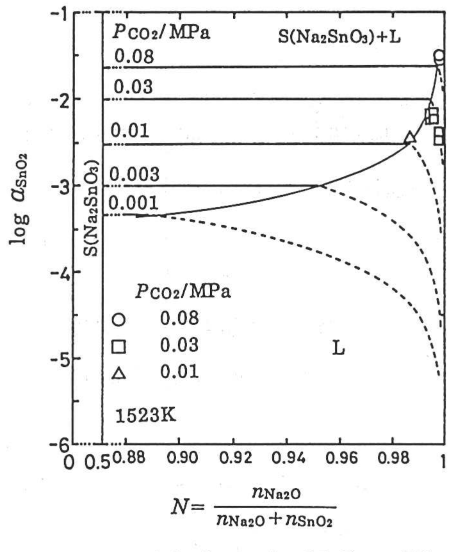

Fig.8 Activity of SnO_2 in the $NaO_{0.5}$–CO_2–SnO_2 system at 1523 K.

6. Estimation of equilibrium distribution ratio

The distribution ratios of As, Sn, and Fe were estimated by the above mentioned method and are shown in Fig.9. New value of the interaction parameter of Fe on O in molten copper, shown in Table 1, was determined from the equilibrium measurements between the $NaFeO_2$ saturated slag and molten copper alloy, and was used in the calculation of the distribution ratio of Fe. The details will be presented in a separate paper.

The distribution ratio of As increases with increasing the value of the slag composition N, whereas that of Fe and Sn decreases because of the coexistence of the stable solid compound. The higher oxygen partial pressure and the lower CO_2 partial pressure are more preferable for the removal of these impurity elements from molten copper. The distribution ratios of them have considerably large values. It is, therefore, presumed that the contents of them in the molten copper can be easily reduced down to the impurity level of high purity copper by using sodium carbonate slag.

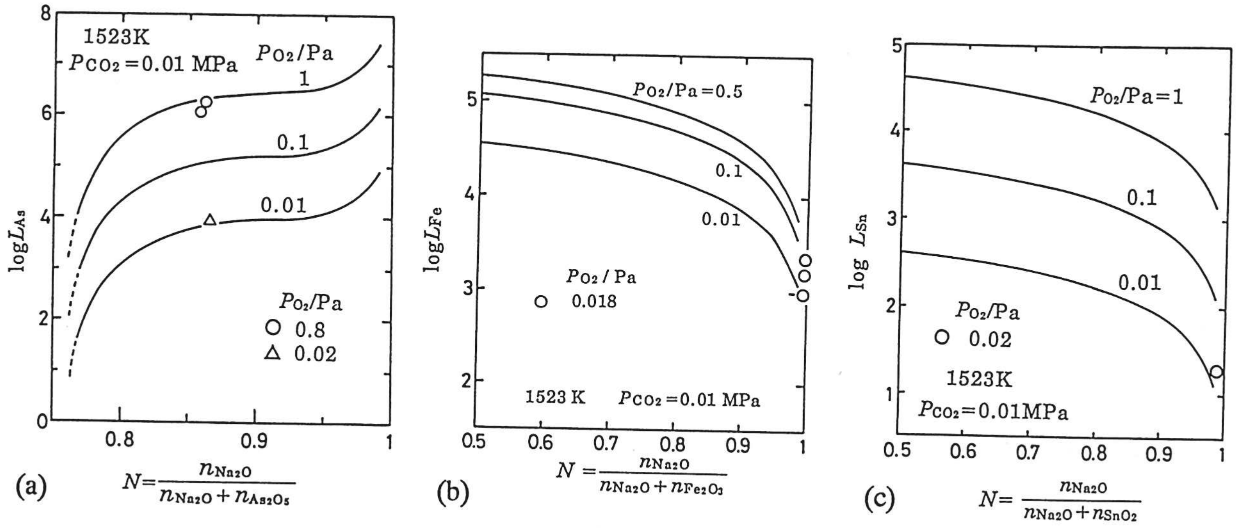

Fig.9 Estimated distribution ratios of (a) As, (b) Fe and (c) Sn for P_{CO_2} = 0.01 MPa at 1523 K.

7. Conclusion

Experimental study was conducted on the thermodynamics of sodium carbonate-based slags containing As–, Sn–, or Fe–oxide. Based on the results, the equilibrium distribution ratios of these elements between the slags and molten copper could be successfully estimated as a function of partial pressures of CO_2 and O_2 and the slag composition.

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