Densities of Melts in the FeO–Fe₂O₃–BaO System

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The densities of melts in the system FeO–Fe₂O₃–BaO and BaO–BaCO₃ have been measured under controlled atmospheres from the liquidus temperature to 1873 K by using the Archimedean method. The molar volumes of melts in the binary system BaO–BaCO₃ satisfy the additive rule. On the other hand, the molar volumes of melts in the ternary system FeO–Fe₂O₃–BaO show a positive deviation from the additive rule and can be reproduced to within ±0.6% by the following equations:

\[
V_M (\text{cm}^3/\text{mol}) = 15.54 N_{\text{FeO}} + 37.16 N_{\text{Fe}_2\text{O}_3} + 31.27 N_{\text{BaO}} + 3.05 N_{\text{Fe}_2\text{O}_3\text{BaO}} / (N_{\text{Fe}_2\text{O}_3} + N_{\text{BaO}}) \text{ at } 1673 \text{ K},
\]

\[
= 15.66 N_{\text{FeO}} + 37.50 N_{\text{Fe}_2\text{O}_3} + 31.40 N_{\text{BaO}} + 2.98 N_{\text{Fe}_2\text{O}_3\text{BaO}} / (N_{\text{Fe}_2\text{O}_3} + N_{\text{BaO}}) \text{ at } 1773 \text{ K},
\]

\[
= 15.80 N_{\text{FeO}} + 37.84 N_{\text{Fe}_2\text{O}_3} + 31.53 N_{\text{BaO}} + 2.91 N_{\text{Fe}_2\text{O}_3\text{BaO}} / (N_{\text{Fe}_2\text{O}_3} + N_{\text{BaO}}) \text{ at } 1873 \text{ K},
\]

A similar positive deviation is not observed for the melts in the system FeO–Fe₂O₃–CaO. This suggests that the addition of Ba²⁺ cation results in the polymerization of ferrite anions as FeO₅⁴⁻.

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I. Introduction

In pyrometallurgical processes, the development of new types of flux having better refining ability for hot metals is required. For this purpose, fluxes containing highly basic components such as sodium oxide, and barium oxide are currently used. However, the behavior of such oxides in metallurgical melts, especially in iron oxide-based melts is not yet well understood. In melts containing iron oxide, the ratio of ferric to ferrous ions, [Fe³⁺]/[Fe²⁺], is a function of the partial pressure of oxygen in the gas phase, for which the position of the oxygen isobars of the melts in the system, FeO–Fe₂O₃–MO (MO: basic oxide) is the most important information. In the ternary systems, FeO–Fe₂O₃–CaO and FeO–Fe₂O₃–2CaO–SiO₂, the authors have determined and reported the positions of the oxygen isobars(1).

For iron oxide-based melts containing barium oxide, Larson and Chipman(2)

measured the effect of barium oxide addition on the ratio [Fe³⁺]/[Fe²⁺] in the melts under the mixed gas of CO₂/CO=11.4 at 1823 K, and Iwase, Yamada, Ichise and Akizuki(3) also measured the ratio [Fe³⁺]/[Fe²⁺] in BaO–FeO and SrO–FeO melt in iron saturation at 1673 K. The oxygen isobars of the melts in the system, FeO–Fe₂O₃–BaO have recently been measured by Kiyohara(4).

On the other hand, the densities of melts in this system have not been measured, except for the melts equilibrated with air by Sumita, Morinaga and Yanagase(5). In the present study, the densities of melts in the system FeO–Fe₂O₃–BaO have been measured under controlled partial pressures from the liquidus temperature to 1873 K by using the Archimedean method.

II. Experimental Procedure

1. The density measurement of the melts

The Archimedean method was used to measure the densities of the melts. The double bob method for buoyancy measurement was applied to eliminate the effect of surface tension on the suspension wire. The volumes of the bobs at high temperature were calculated from those measured at room temperature and

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the thermal expansivity of platinum. The partial pressure of oxygen in the gas phase was controlled by air, CO$_2$ or CO$_2$–H$_2$ mixed gases. The apparatus used for the measurements and the procedure are almost the same as those reported previously for the melts in the systems, FeO–Fe$_2$O$_3$–CaO and FeO–Fe$_2$O$_3$–2CaO–SiO$_2$.

Melts in the FeO–Fe$_2$O$_3$–BaO, contained in a Pt–20 mass%Rh crucible, were held at 1773 K for a period of 24 h under a gaseous atmosphere of known $P_{O_2}$ flowing at a rate of $8 \times 10^{-6}$ m$^3$ s$^{-1}$. The temperature of the melt was changed in sequence to 1873, 1823, 1773, 1673, and 1723 K. Usually, a period of 2 h was allowed after the change in temperature of the melt. For the system BaO–BaCO$_3$, the melt were held at 1673 K for a period of more than 6 h under a gas of fixed $P_{CO_2}$. A period of 2 h was also allowed for the BaO–BaCO$_3$ melts, after any change was made in the temperature of the melts. A period of 6 h was required to establish the melt-gas equilibrium after any change was made in the partial pressure of CO$_2$ in the gas phase.

2. Materials

The melts in the system FeO–Fe$_2$O$_3$–BaO were prepared by melting mixtures of Fe$_2$O$_3$ and BaO (purity up to 99.5 mass%), CERAC Inc.). Hematite (Fe$_2$O$_3$) was made by dissociation of chemical reagent iron (II) oxalate at 1173 K. Barium carbonate (BaCO$_3$) was supplied from Rare Metallic Co. and its purity is better than 99.9 mass%.

3. The compositions of the melts in the system FeO–Fe$_2$O$_3$–BaO

Kiyohara has measured the ferric-ferrous equilibria in melts, in the system FeO–Fe$_2$O$_3$–BaO under controlled gas atmospheres of air, CO$_2$, O$_2$–Ar, or CO$_2$–H$_2$ mixtures using the thermogravimetric method. However, his results for melts containing higher BaO contents equilibrated with CO$_2$–H$_2$ mixtures having higher CO$_2$ partial pressures, are slightly incorrect as shown in the later section, because the melts have a small solubility of CO$_2$. Hence, in this work, the compositions of melts in the system FeO–Fe$_2$O$_3$–BaO equilibrated with given oxygen partial pressures in the gas phase, are estimated from Fig. 1 in which corrections have been made to the results of Kiyohara for the effect of CO$_2$ dissolved into the melt. Kiyohara’s measurements were made at 1773 K, and hence the [Fe$^{3+}$/Fe$^{2+}$] ratios at different temperatures were estimated using the assumption that under a constant $P_{CO_2}/P_{CO}$ of less than 100, the ratio [Fe$^{3+}$/Fe$^{2+}$] in the melt is independent of temperature in the range 1673–1873 K, while under air or CO$_2$, the ratio [Fe$^{3+}$/Fe$^{2+}$] varies with temperature as given by

$$\log ([Fe^{3+}]/[Fe^{2+}]) = A(\log PO_{2}(\text{MPa}) + 29.501/T + 0.994) + B$$

The values of $A$ and $B$ at a given $P_{O_2}$ are calculated from the results shown in Fig. 1 and listed in Table 1.

4. The composition of the melts in the system BaO–BaCO$_3$

Ishida has studied the equilibrium of the
reaction \( \text{BaCO}_3 = \text{BaO} + \text{CO}_2(\text{gas}) \) under controlled \( P_{\text{CO}_2} \) pressures. Figure 2 shows the relationships between \( P_{\text{CO}_2} \) and temperature for the melts containing 30, 40 and 50 mol\% \( \text{BaO} \). These data were used in the present study to maintain the composition of the melt constant when the temperature was changed. In some runs, the densities were measured at 1673 K for various values of \( P_{\text{CO}_2} \) in which the compositions of the melts were changed in a stepwise manner.

5. The source of experimental error

The major sources of experimental error in the determination of the density are (1) determination of the \( \text{BaO} \) content, (2) determination of the \( \text{FeO} \) content, (3) the accuracy of the volumes of the bobs, (4) weight changes of the bobs during the run, (5) the influence of surface tension on the suspension wire, (6) accuracy of temperature determination, and (7) the accuracy of the balance.

The contribution of these factors to the error are listed below:

| Factor              | Error in determination | Error in density |
|---------------------|------------------------|-----------------|
|                     | \( \text{BaO} - \text{FeO} - \text{Fe}_2\text{O}_3 \) | \( \text{BaO} - \text{BaCO}_3 \) |
| \( \text{BaO} \) content | \( \pm 0.2 \text{ mol}\% \) | \( \pm 0.05\% \) | \(-\) |
|                     | \( \pm 1.0 \text{ mol}\% \) | \(-\) | \( \pm 0.26\% \) |
| \( \text{FeO} \) contents | \( \pm 1.0 \text{ mol}\% \) | \( \pm 0.07\% \) | \(-\) |
| Volume of bobs      | \( \pm 5 \times 10^{-4} \text{ cm}^3 \) | \( \pm 0.07\% \) | \( \pm 0.07\% \) |
| Change of bobs      | \( +4.0 \text{ mg} \) | \( +0.07\% \) | \(-\) |
|                     | \( -10.0 \text{ mg} \) | \(-\) | \(-0.30\% \) |
| Surface tension     | \( \pm 1.0 \text{ mg} \) | \( \pm 0.04\% \) | \( \pm 0.04\% \) |
| Temperature         | \( \pm 5 \text{ K} \) | \( \pm 0.03\% \) | \( \pm 0.09\% \) |
| Balance             | \( \pm 0.5 \text{ mg} \) | \( \pm 0.02\% \) | \( \pm 0.02\% \) |

Total \( \pm 0.35\% \) \( \pm 0.78\% \)
### Densities of Melts in the FeO–FeO$_2$–BaO System

#### Table 2  The densities of melts in the system FeO–FeO$_2$–BaO.

| Temp. (T/K) | $-\log (P_{O_2}/\text{MPa})$ | Density ($\rho/10^3$ kg m$^{-3}$) | Temp. (T/K) | $-\log (P_{O_2}/\text{MPa})$ | Density ($\rho/10^3$ kg m$^{-3}$) |
|------------|-------------------------------|-----------------------------------|------------|-------------------------------|-----------------------------------|
| FeO–FeO$_1.5$–11.5 mol%BaO |                               |                                    |            |                               |                                    |
| under air  |                               |                                    |            |                               |                                    |
| 1771       | 1.67                          | 4.387                             | 1670       | 6.03                          | 4.499                             |
| 1771       | 1.67                          | 4.388                             | 1726       | 5.45                          | 4.484                             |
| 1823       | 1.67                          | 4.378                             | 1771       | 5.02                          | 4.471                             |
| 1870       | 1.67                          | 4.366                             | 1773       | 5.00                          | 4.470                             |
| under CO$_2$/H$_2$=20 |     |                                  | 1822       | 4.55                          | 4.457                             |
| 1724       | 5.43                          | 4.458                             | 1868       | 4.16                          | 4.443                             |
| 1773       | 5.00                          | 4.440                             |            |                               |                                    |
| 1773       | 5.00                          | 4.442                             |            |                               |                                    |
| 1821       | 4.56                          | 4.426                             |            |                               |                                    |
| 1869       | 4.15                          | 4.411                             |            |                               |                                    |
| FeO–FeO$_1.5$–18.3 mol%BaO |                               |                                    |            |                               |                                    |
| under air  |                               |                                    |            |                               |                                    |
| 1721       | 1.67                          | 4.407                             | 1673       | 1.67                          | 4.493                             |
| 1772       | 1.67                          | 4.397                             | 1723       | 1.67                          | 4.481                             |
| 1773       | 1.67                          | 4.398                             | 1772       | 1.67                          | 4.472                             |
| 1821       | 1.67                          | 4.388                             | 1774       | 1.67                          | 4.475                             |
| 1868       | 1.67                          | 4.380                             | 1824       | 1.67                          | 4.460                             |
| under CO$_2$ |                               |                                    | 1870       | 1.67                          | 4.451                             |
| 1721       | 2.90                          | 4.435                             |            |                               |                                    |
| 1770       | 2.74                          | 4.419                             |            |                               |                                    |
| 1770       | 2.74                          | 4.421                             |            |                               |                                    |
| 1823       | 2.58                          | 4.407                             |            |                               |                                    |
| 1873       | 2.44                          | 4.391                             |            |                               |                                    |
| under CO$_2$/H$_2$=20 |     |                                  | 1670       | 6.03                          | 4.483                             |
| 1721       | 5.50                          | 4.468                             | 1672       | 3.10                          | 4.573                             |
| 1773       | 5.00                          | 4.451                             | 1719       | 3.10                          | 4.560                             |
| 1820       | 4.57                          | 4.437                             | 1773       | 3.10                          | 4.547                             |
| 1870       | 4.14                          | 4.421                             | 1775       | 3.10                          | 4.546                             |
| FeO–FeO$_1.5$–25.8 mol% BaO |                               |                                    |            |                               |                                    |
| under air  |                               |                                    |            |                               |                                    |
| 1673       | 1.67                          | 4.442                             | 1671       | 3.08                          | 4.575                             |
| 1718       | 1.67                          | 4.435                             | 1720       | 2.91                          | 4.561                             |
| 1721       | 1.67                          | 4.435                             | 1773       | 2.73                          | 4.548                             |
| 1778       | 1.67                          | 4.423                             | 1774       | 2.73                          | 4.550                             |
| 1822       | 1.67                          | 4.415                             | 1824       | 2.58                          | 4.534                             |
| 1870       | 1.67                          | 4.405                             | 1868       | 2.45                          | 4.522                             |
| under CO$_2$ |                               |                                    | 1673       | 5.99                          | 4.587                             |
| 1674       | 3.07                          | 4.472                             | 1726       | 5.45                          | 4.572                             |
| 1721       | 2.90                          | 4.461                             | 1773       | 5.00                          | 4.558                             |
| 1771       | 2.74                          | 4.448                             | 1774       | 4.99                          | 4.557                             |
| 1774       | 2.73                          | 4.447                             | 1822       | 4.55                          | 4.544                             |
| 1823       | 2.58                          | 4.435                             | 1870       | 4.14                          | 4.528                             |
| 1874       | 2.43                          | 4.421                             |            |                               |                                    |
| under CO$_2$/H$_2$=50 |     |                                  | 1674       | 5.17                          | 4.487                             |
| 1726       | 4.64                          | 4.474                             |            |                               |                                    |
| 1772       | 4.20                          | 4.462                             |            |                               |                                    |
| 1774       | 4.18                          | 4.460                             |            |                               |                                    |
| 1824       | 3.70                          | 4.447                             |            |                               |                                    |
| 1872       | 3.38                          | 4.435                             |            |                               |                                    |
The total error in the determination of the densities is thus estimated as being less than ±0.35% for the system, BaO–FeO–Fe₂O₃ and ±0.78% for the system, BaO–BaCO₃, respectively.

### 6. Results

The experimental results for the system BaO–FeO–Fe₂O₃ are listed in Table 2. In all cases, the densities of the melts equilibrated with a fixed gaseous atmosphere varied linearly with temperature. The results for the system BaO–BaCO₃ are listed in Tables 3 and 4. The density of the BaO–BaCO₃ melts varied non-linearly with temperature.

### III. Discussion

1. **The molar volume of the system BaO–BaCO₃**

The molar volumes of binary melts are generally defined by the following relation:

\[ V_M = \frac{M_1 N_1 + M_2 N_2}{\rho} \]  

(2)

where \( V_M \) is the molar volume of the melt, \( \rho \) its density, and \( M \) and \( N \) denote the molecular weight and the mole fractions of the components, respectively. The molar volumes of the BaO–BaCO₃ melts at 1673 K are shown in Fig. 3 as a function of composition. Within the experimental accuracy, a linear relationship between the molar volume and the composition was obtained.

The densities of the BaO–BaCO₃ melts, \( \rho (\text{kgm}^{-3}) \) at 1673 K can be reproduced to within ±0.3% by the following equation:

\[ 10^5/\rho = (1/4.903) \times (\text{mass}\% \text{BaO}) + (1/3.665) \times (\text{mass}\% \text{BaCO}_3) \]  

(3)

Assuming that the additive rule for molar volume can be applied to the system BaO–BaCO₃, the molar volumes of hypothetical liquid BaO and BaCO₃ can be estimated, respectively to be 31.28 and 53.84 cm³ mol⁻¹ at 1673 K. From the measurement of the densities of CaF₂-BaO melts at 1823 K, the authors estimated the molar volume of the hypothetical BaO melt to be 34.15 cm³ mol⁻¹. However, the CaF₂–BaO system should be treated as the CaF₂–BaF₂–CaO ternary system, because equilibrium in the reaction \( \text{CaF}_2 + \text{BaO} = \text{CaO} + \text{BaF}_2 \) lies to the right side. In this case, the apparent molar volume of BaO should be higher than the true value, since it

### Table 3 Densities of BaO–BaCO₃ melts.

| Temp. (K) | \( P_{\text{CO}_2} \) (MPa) | Density (\( \rho/10^3 \text{kgm}^{-3} \)) | Temp. (K) | \( P_{\text{CO}_2} \) (MPa) | Density (\( \rho/10^3 \text{kgm}^{-3} \)) | Temp. (K) | \( P_{\text{CO}_2} \) (MPa) | Density (\( \rho/10^3 \text{kgm}^{-3} \)) |
|----------|----------------|-----------------|----------|----------------|-----------------|----------|----------------|----------------|
| 1582     | 0.0274         | 3.954           | 1612     | 0.0172         | 4.029           | 1642     | 0.0118         | 4.138           |
| 1613     | 0.0371         | 3.945           | 1643     | 0.0243         | 4.016           | 1673     | 0.0167         | 4.118           |
| 1642     | 0.0507         | 3.927           | 1671     | 0.0331         | 4.001           | 1704     | 0.0243         | 4.098           |
| 1674     | 0.0719         | 3.906           | 1702     | 0.0452         | 3.989           | 1733     | 0.0346         | 4.071           |
| 1706     | 0.1013         | 3.887           | 1734     | 0.0628         | 3.962           | 1765     | 0.0495         | 4.049           |
| 1762     | 0.0932         | 3.933           |          |                |                 |          |                |                 |

### Table 4 Densities of BaO–BaCO₃ melts at 1673 K.

| \( P_{\text{CO}_2} \) (MPa) | Composition(mol%) BaO | Density (\( \rho/10^3 \text{kgm}^{-3} \)) | \( P_{\text{CO}_2} \) (MPa) | Composition(mol%) BaO | Density (\( \rho/10^3 \text{kgm}^{-3} \)) |
|----------------|-----------------|-----------------|----------------|-----------------|----------------|
| 0.1013        | 25.5            | 74.5            | 3.869          | 0.0394          | 41.0           | 59.0           | 4.032           |
| 0.1013        | 25.5            | 74.5            | 3.873          | 0.0203          | 47.0           | 53.0           | 4.092           |
| 0.0507        | 34.0            | 66.0            | 3.955          | 0.0167          | 50.0           | 50.0           | 4.115           |
was observed that the volume of a CaF$_2$-BaF$_2$ melt was slightly higher than that calculated from the ideal mixing law for the pure components\(^{(10)}\). On the other hand, from measurements in the system BaO-SiO$_2$, the molar volume of BaO was estimated by Tomlinson \textit{et al.}\(^{(11)}\) to be 27.50 cm$^3$ mol$^{-1}$ which is lower than that estimated in the present work from the BaO–BaCO$_3$ system.

2. The effect of dissolution of CO$_2$ on the densities of melts in the system BaO–FeO–Fe$_2$O$_3$

Kiyohara\(^{(4)}\) measured the effect of oxygen partial pressure in gas phase on the ratio [Fe$^{3+}$]/[Fe$^{2+}$] in melts in the system FeO$_x$–BaO at 1773 K using the thermogravimetric method. Some of the results are shown in Fig. 4. According to the results, the apparent [Fe$^{3+}$]/[Fe$^{2+}$] ratios in the melt increased when the gaseous atmosphere was changed from air to pure CO$_2$, although this change decreases the oxygen partial pressure in the gas phase. Kiyohara concluded that the dissolution of CO$_2$ in the melts is very small, since the ratio [Fe$^{3+}$]/[Fe$^{2+}$] in FeO$_x$–43.9 mol\% BaO melt equilibrated with the gas mixture of CO$_2$/H$_2=50$ did not change when the gas was diluted with Ar gas and for FeO$_x$–43.9 mol\% BaO and FeO$_x$–18.3 mol\% BaO melts, weight change of the samples was scarcely observed when the gas phase was changed from pure CO$_2$(log $P_{O_2}$(MPa) = −3.72 at 1773 K) to the mixed gas of O$_2$/Ar=1/99(log $P_{O_2}$(MPa) = −2.99). From the results, it is considered that the oxygen partial pressures in the range $-1.67 > \log P_{O_2}$(MPa) $>-3.99$ do not affect the ratio [Fe$^{3+}$]/[Fe$^{2+}$] in FeO$_x$–BaO melts. In the present work, density of the FeO$_x$–43.9 mol\% BaO melt was measured under pure CO$_2$ and O$_2$/Ar=4/496 mixed gas. Figure 5 which shows the results at 1773 K indicates that the solubility of CO$_2$ in the melt is very small. As the density of BaCO$_3$ (3.665 $\times$ 10$^{-3}$ kg m$^{-3}$ at 1673 K) is less than that of hypothetical liquid BaO (4.903 $\times$ 10$^{-3}$ kg m$^{-3}$ at 1673 K), the density of the melt equilibrated with pure CO$_2$ should be less than that measured under the mixed gas if CO$_2$ dissolves in the melt. Figure 5 also indicates that a decrease in oxygen partial pressure in the gas, i.e. an increase in the concentration of ferric ions in the melts, increases the density.
Assuming that the ratio $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ in FeO$_x$-BaO melts does not change with the variation of log $P_{O_2}$(MPa) from $-1.67$ to $-3.99$, the density of the melt should not be affected by the oxygen partial pressure in this range. The observation of density shows that this is not the case. From the thermogravimetric measurements, small amount of CO$_2$ dissolution affects the ratio $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ in the melts, especially for the melts of having lower Fe$^{2+}$ content. Assuming that the relation between log $P_{O_2}$ and log ($[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$) can be represented by the full lines in Fig. 4, which is similar to the behavior in the FeO$_x$-CaO system\(^{(1)}\), the computed contents of BaCO$_3$ in FeO$_x$-43.9 mass%BaO and FeO$_x$-18.3 mass%BaO melts equilibrated with pure CO$_2$ are 0.9 and 1.5 mol%, respectively. Consequently, the effect of CO$_2$ dissolution on the measured densities considered to be negligibly small.

### 3. The molar volume of the system BaO–FeO–Fe$_2$O$_3$

The molar volumes of ternary melts are defined by the equation,

$$V_M = \frac{(M_1N_1 + M_2N_2 + M_3N_3)}{\rho}$$  \hspace{1cm} (4)

The molar volumes calculated from the measured densities and the compositions are listed in Table 5. It has been found previously that, for the FeO–FeO$_{1.5}$–CaO ternary system, the simple additive rule for molar volume can be applied, and hence on the assumption that a similar relationship exists in the system FeO–FeO$_{1.5}$–BaO, the application of the method of least squares to the observed values gives the following equations:

$$V_M(\text{cm}^3/\text{mol}) = 15.88N_{\text{FeO}} + 18.74N_{\text{FeO}_{1.5}} + 32.15N_{\text{BaO}} \quad \text{at 1673 K,} \hspace{1cm} (5)$$

$$V_M = 16.03N_{\text{FeO}} + 18.82N_{\text{FeO}_{1.5}} + 32.38N_{\text{BaO}} \quad \text{at 1773 K,} \hspace{1cm} (6)$$

$$V_M = 16.20N_{\text{FeO}} + 18.83N_{\text{FeO}_{1.5}} + 32.62N_{\text{BaO}} \quad \text{at 1873 K.} \hspace{1cm} (7)$$

Those relations reproduce the densities of FeO–FeO$_{1.5}$–BaO melts to within ±0.7%, but following difficulties arise: (1) the values of the density of hypothetical liquid FeO and FeO$_{1.5}$ are lower than those estimated from measurements in the system FeO–FeO$_{1.5}$–CaO, hence (2) the density of liquid FeO$_2$ in iron saturation is less than the measured value, and (3) the differences between the measured and the calculated densities from eqs. (5), (6) and (7)

### Table 5 Molar volumes of BaO–BaCO$_3$ melts at 1673 K.

| $P_{CO_2}$ (MPa) | Composition (mol%) | Molar volume (cm$^3$/mol) | $P_{CO_2}$ (MPa) | Composition (mol%) | Molar volume (cm$^3$/mol) |
|------------------|--------------------|--------------------------|------------------|--------------------|--------------------------|
| 0.1013           | 25.5               | 74.5                     | 48.11            | 0.0304             | 41.0                     | 59.0 | 44.47 |
| 0.1013           | 25.5               | 74.5                     | 48.06            | 0.0203             | 47.0                     | 53.0 | 43.17 |
| 0.0719           | 30.0               | 70.0                     | 47.13            | 0.0167             | 50.0                     | 50.0 | 42.61 |
| 0.0507           | 34.0               | 66.0                     | 46.11            | 0.0167             | 50.0                     | 50.0 | 42.58 |
| 0.0331           | 40.0               | 60.0                     | 44.94            |                    |                          |      |      |
are negative in the BaO-rich region and are positive in the intermediate region. From those facts, it is concluded that the equations cannot be applied to the calculation of the molar volume.

The molar volume of the ternary melt, defined by eq. (4), may be written in terms of the partial molar volumes \( \bar{V}_i \),

\[
V_M = N_{FeO} \bar{V}_{FeO} + N_{FeO_{1.5}} \bar{V}_{FeO_{1.5}} + N_{BaO} \bar{V}_{BaO} \quad (8)
\]

The molar volume of BaO–FeO\(_{1.5}\) binary melt, \( V_M^* \) is also defined as,

\[
V_M^* = \left( \frac{N_{BaO}}{N_{BaO} + N_{FeO_{1.5}}} \right) \cdot \bar{V}_{BaO} + \left( \frac{N_{FeO_{1.5}}}{N_{BaO} + N_{FeO_{1.5}}} \right) \cdot \bar{V}_{FeO_{1.5}} \quad (9)
\]

Assuming that the partial molar volume of FeO, \( \bar{V}_{FeO} \) is equal to the molar volume of hypothetical liquid FeO, \( \bar{V}_{FeO} \) estimated from measurements of the densities of FeO–Fe\(_2\)O\(_3\)–CaO melts and that the value does not depend on composition of the melts, then, the molar volume, \( V_M^* \) can be expressed by the following equation:

\[
V_M^* = \left( V_{M(FeO-FeO_{1.5}-BaO)} - \bar{V}_{FeO} N_{FeO} \right) / (1 - N_{FeO})
\]

\[
= N_{BaO}^* \bar{V}_{BaO} + N_{FeO_{1.5}}^* \bar{V}_{FeO_{1.5}}, \quad (10)
\]

where

\[
N_{BaO}^* = N_{BaO} / (1 - N_{FeO})
\]

\[
= N_{BaO} / (N_{BaO} + N_{FeO_{1.5}})
\]

and

\[
N_{FeO_{1.5}}^* = N_{FeO_{1.5}} / (1 - N_{FeO})
\]

\[
= N_{FeO_{1.5}} / (N_{BaO} + N_{FeO_{1.5}}).
\]

The molar volumes of the BaO–FeO\(_{1.5}\) pseudo-binary melts at 1773 K are shown in Fig. 6 in which the molar volumes of melts in the CaO–FeO\(_{1.5}\) pseudo-binary system are also included. The molar volumes for the CaO–FeO\(_{1.5}\) pseudo-binary melts satisfy the additive rule, while those of the BaO–FeO\(_{1.5}\) melts show a positive deviation from the additive rule when the molar volume of hypothetical liquid BaO is estimated from the measurements made on BaO–BaCO\(_3\) melts. The maximum deviation is observed at \( N_{FeO_{1.5}} \approx 0.67 \) which is the composi-

\[
\text{Fig. 6 Molar volumes of the pseudo-binary system BaO}^{*}–\text{FeO}^{*}_{1.5} \text{ at 1773 K.}
\]

\[
V_{M}^{**} = (V_{M(FeO-FeO_{1.5}-BaO)} - \bar{V}_{FeO} N_{FeO}) / (1 - N_{FeO})
\]

\[
= N_{BaO}^* \bar{V}_{BaO} + N_{FeO_{1.5}}^* \bar{V}_{FeO_{1.5}}, \quad (11)
\]

\[
N_{BaO}^{**} = N_{BaO} / (1 - N_{FeO}),
\]

\[
N_{FeO_{1.5}}^{**} = N_{FeO_{1.5}} / (1 - N_{FeO}). \quad (12)
\]

The molar volumes of Fe\(_2\)O\(_3\)–BaO binary melts calculated from eq. (11) at 1773 K are shown in Fig. 7. Those at 1673, 1773 and 1873 K are represented by the following relations:

\[
V_{M}^{**} = \text{(cm}^3/\text{mol}) = 31.27 N_{BaO} + 37.16 N_{FeO_{1.5}} + 3.05 N_{BaO} N_{FeO_{1.5}} \quad \text{at 1673 K} \quad (13)
\]
The molar volumes for FeO-Fe$_2$O$_3$-BaO ternary melts can be calculated from the following relations:

\[ 31.40 N_{\text{BaO}}^* + 37.50 N_{\text{FeO}}^* + 2.98 N_{\text{BaO}}^* N_{\text{FeO}}^* \]
\[ \text{at } 1773 \text{ K} \quad (14) \]
\[ 31.53 N_{\text{BaO}}^* + 37.84 N_{\text{FeO}}^* + 2.91 N_{\text{BaO}}^* N_{\text{FeO}}^* \]
\[ \text{at } 1873 \text{ K} \quad (15) \]

The molar volumes for FeO-Fe$_2$O$_3$-BaO ternary melts can be calculated from the following relations:

\[ V_{\text{M(FeO-Fe$_2$O$_3$-BaO)}}(\text{cm}^3/\text{mol}) = \]
\[ 31.27 N_{\text{BaO}} + 15.54 N_{\text{FeO}} + 37.16 N_{\text{FeO}_3} + 3.05 N_{\text{BaO}} N_{\text{FeO}_3} \]
\[ \text{at } 1673 \text{ K} \quad (13') \]
\[ 31.40 N_{\text{BaO}} + 15.66 N_{\text{FeO}} + 37.50 N_{\text{FeO}_3} + 2.98 N_{\text{BaO}} N_{\text{FeO}_3} \]
\[ \text{at } 1773 \text{ K} \quad (14') \]
\[ 31.53 N_{\text{BaO}} + 15.80 N_{\text{FeO}} + 37.84 N_{\text{FeO}_3} + 2.91 N_{\text{BaO}} N_{\text{FeO}_3} \]
\[ \text{at } 1873 \text{ K} \quad (15') \]

Sumita et al.\(^{(5)}\) measured the densities and the compositions of melts in the system FeO-Fe$_2$O$_3$-SrO under air. On the same assumption applied to FeO-Fe$_2$O$_3$-BaO melts (see eq. (11)), the molar volumes $V_M^*$ of pseudo-binary melts in the system Fe$_2$O$_3$-SrO at 1773 K are computed as shown in Fig. 7.

Figure 8 shows the molar volumes of $V_M^*$ at 1773 K for the melts of MO·Fe$_2$O$_3$ composition (M: Fe, Ca, Sr, Ba) as a function of the cube of the ionic radius of the cation $r_c^3$. Assuming that the molar volumes of the MO·Fe$_2$O$_3$ melt are the sum of volumes for the cations and the anions, a linear relation between the volume, $V_M^*$ and $r_c^3$ could be expected. The volume of the BaO·Fe$_2$O$_3$ melt is, however, lower than that expected from the linear relation as shown in Fig. 8, which suggests that polymerization of ferrite anions as FeO$_5^-$ occurs, when larger cation as Ba$^{2+}$ is added to magnetite liquid.

4. Comparison of the measured and calculated densities in the system FeO-Fe$_2$O$_3$-BaO

The densities of FeO-Fe$_2$O$_3$-BaO melts, $\rho$ is computed from the division of the molecular weight, $W_M$ by the molar volume $V_M$, as

\[ \rho(10^{-3}\text{kgm}^{-3}) = \frac{W_M}{V_M} \]
\[ = (0.15334 N_{\text{BaO}} + 0.07185 N_{\text{FeO}} + 0.1597 N_{\text{FeO}_3})/V_M \quad (16) \]

Figure 9 shows the iso-density curves for FeO-Fe$_2$O$_3$-BaO melts at 1773 K. For FeO-Fe$_2$O$_3$-BaO melts, the differences between the measured densities and those calculated from
eqs. (13'), (14') and (15') are less than ±0.6%, except for the case of FeOx-11.5 mol%BaO melt under air where the error is 0.9%.

5. The densities of FeO-Fe₂O₃-BaO melts under air

Figure 10 shows the measured densities of FeOₓ-BaO melts under air at 1773 K. The full line, calculated from eq. (14'), shows good agreement with the measurements of Sumita et al. (5) as well as those obtained in the present work. However, the densities of melts containing more than 50 mol%BaO, reported by Sumita et al., are higher than those calculated from eq. (14'). In the present work, the measurements in the region were very difficult, because the melts is very corrosive to the Pt-20 mass%Rh crucible and the deposition of the suspended platinum particles in the melts on the bobs disturbed the measurements of the buoyancies of the platinum bobs.

6. The densities of FeOₓ-BaO melts at iron saturation

The densities of FeOₓ-BaO melts at iron saturation have not yet been reported. The previous report on the densities of FeOₓ-CaO melts shows that the results obtained under higher oxygen partial pressure can be used for the estimation of the densities near iron saturation. Iwase et al. (3) and Kiyohara (4) have measured the variation of the ratio [Fe³⁺]/[Fe²⁺] at iron saturation with BaO addition and their results are shown in Fig. 11. The densities of FeOₓ-BaO melts at 1673 K can be computed from combination of the results with eq. (13'). These are shown in Fig. 12 in comparison with those of FeOₓ-CaO melts at iron saturation at 1673 K.

7. The thermal expansivity of melts in the system FeO-Fe₂O₃-BaO

The apparent thermal expansivities of the melts at 1773 K are shown in Fig. 13. Since the compositions of the melts equilibrated with air and pure CO₂ gas vary with the temperature, it
should be noted that the apparent values under these atmospheres include the effect of temperature on composition and hence the values are lower than the true values at constant compositions, while the values obtained under CO$_2$/H$_2$<100 give the true values. Generally, the effects of the variation of the ratio [Fe$^{3+}$]/[Fe$^{2+}$] and BaO content on the expansivity are very small. The thermal expansivities are estimated to be 7±2×10$^{-5}$/K which are almost the same as those obtained for FeO–Fe$_2$O$_3$–CaO melts.

IV. Conclusion

From measurements of the densities of melts in the systems FeO–Fe$_2$O$_3$–BaO and BaO–BaCO$_3$, the following conclusions are obtained:

(1) The molar volumes of the binary BaO–BaCO$_3$ system obey a simple additive rule at 1673 K and the density $\rho$ (kgm$^{-3}$) can be reproduced to within ±0.3% by the following equation:

$$10^5/\rho = (1/4.903)\text{(mass\% BaO)} + (1/3.665)\text{(mass\% BaCO$_3$)}.$$  

(2) The molar volumes of the ternary system deviate positively from the additive rule and can be reproduced to within ±0.6% by the following equation:

$$V_M(\text{cm}^3/\text{mol}) =
\begin{align*}
15.54N_{FeO} + 37.16N_{Fe_2O_3} + 31.27N_{BaO} &+ 3.05N_{Fe_2O_3}N_{BaO}/(N_{Fe_2O_3} + N_{BaO}) \\
&\text{at 1673 K} \\
15.66N_{FeO} + 37.50N_{Fe_2O_3} + 31.40N_{BaO} &+ 2.98N_{Fe_2O_3}N_{BaO}/(N_{Fe_2O_3} + N_{BaO}) \\
&\text{at 1773 K} \\
15.80N_{FeO} + 37.84N_{Fe_2O_3} + 31.53N_{BaO} &+ 2.91N_{Fe_2O_3}N_{BaO}/(N_{Fe_2O_3} + N_{BaO}) \\
&\text{at 1873 K}
\end{align*}$$  

(3) The volume of the hypothetical BaO•Fe$_2$O$_3$ melt at 1773 K is lower than that expected from the linear relation between the molar volumes of $V^*_{**}$ and the cube of the ionic radius of the cation $r_i^3$ for the melts of Mo•Fe$_2$O$_3$ composition (M: Fe, Ca, Sr, Ba). This suggests that polymerization of ferrite anions as FeO$_4$$^-_4$ occurs, when larger cations as Ba$^{2+}$ are added to magnetite liquid.

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APPENDIX

Estimation of the values of A and B in eq. (1)

When the equilibrium of the reaction (1A) is established between iron oxide-based melts and gas phase,

\[
\text{FeO}_1 \text{(in FeO}_x\text{-MO)} = \text{FeO}_1 \text{(in FeO}_x\text{-MO)} + 1/4 \text{O}_2 \text{(gas)} \quad (1A)
\]

The equilibrium constant \( K_1 \) is defined as,

\[
K_1 = \frac{a_{\text{FeO}_1}}{a_{\text{FeO}_1}} \frac{P_{\text{O}_2}^{1/4}}{P_{\text{O}_2}^{1/4}} = \frac{\gamma_{\text{FeO}_1}}{\gamma_{\text{FeO}_1}} \frac{N_{\text{FeO}_1}}{N_{\text{FeO}_1}} \frac{P_{\text{O}_2}^{1/4}}{P_{\text{O}_2}^{1/4}} \quad (2A)
\]

where \( \gamma \) and \( a \) are the activity coefficient and the activity of the i-component, respectively. From eq. (2A), the following relation is deduced:

\[
\log \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) = \log \left( \frac{N_{\text{FeO}_1}}{N_{\text{FeO}_1}} \right) = \frac{1}{4} \log P_{\text{O}_2} - \log K_1 + \log \left( \frac{\gamma_{\text{FeO}_1}}{\gamma_{\text{FeO}_1}} \right) \quad (3A)
\]

Assuming that the equilibrium constant changes with temperature, and the ratio \( \gamma_{\text{FeO}_1}/\gamma_{\text{FeO}_1} \) is not affected by the composition and temperature, eq. (3A) becomes

\[
\log \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) = \log \left( \frac{N_{\text{FeO}_1}}{N_{\text{FeO}_1}} \right) = \frac{1}{4} \log P_{\text{O}_2} + K(T) + B' \quad (4A)
\]

When the melt is equilibrated with a CO₂–CO mixed gas, the oxygen potential is calculated from the equilibrium of the reaction,

\[
\text{CO}_2 \text{(gas)} = \text{CO(gas)} + 1/2 \text{O}_2 \text{(gas)}
\]

\[
\log P_{\text{O}_2} \text{(MPa)} = 2 \log \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right) -29501 \frac{T}{T + 8.075} \quad (5A)
\]

If the initial \( P_{\text{CO}_2}/P_{\text{CO}} \) ratio in a mixed gas is less than 100, the ratio is nearly equal to that in the equilibrated gas at \( T \) K.

When eq. (5A) is substituted in eq. (4A), the following relation can be obtained:

\[
\log \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) = \frac{1}{4} \left( 2 \log \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right) -29501 \frac{T}{T + 8.075} + K(T) + B' \right) \quad (6A)
\]

If the initial ratio, \( P_{\text{CO}_2}/P_{\text{CO}} \) is kept constant, it is known that \( [\text{Fe}^{3+}]/[\text{Fe}^{2+}] \) is independent of temperatureⁿ(12)(13) and hence, \( K(T) \) is 7375.3/\( T \). Consequently, the following relation can be derived:

\[
\log \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) = \frac{1}{4} \left( \log P_{\text{O}_2} + \frac{7375.3}{T} + B' \right) \quad (7A)
\]

However, the relation is not satisfied practically. This suggests that the ratio of activity coefficient, \( \gamma_{\text{FeO}_1}/\gamma_{\text{FeO}_1} \), which relates to the term \( B' \), is influenced by the composition of melts, and hence the following relation is assumed:

\[
\log \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) = A \left( \log P_{\text{O}_2} + \frac{29501}{T} + 0.994 \right) + B \quad (8A)
\]

where \( A \) and \( B \) change with the composition of the melt, but do not change with temperature.
From gradient of a tangential line at a given point on the curves, which are shown in Fig. 1, the value of $A$ is calculated and then the value of $B$ is also computed from the datum point at 1773 K.

Table 6: Molar volumes of melts in the system BaO-FeO$_x$.

| Atmosphere | Temp. (°C) | $-\log (P_{O_2}/MPa)$ | Composition (mol%) | Molar volumes (cm$^3$/mol) | Measured | Calculated |
|------------|------------|------------------------|-------------------|-----------------------------|----------|------------|
|            |            |                        | BaO    | FeO    | FeO$_{1.5}$ |            |            |
| air        | 1673       | 1.67                   | 43.9   | 2.4    | 53.7       | 24.48     | 24.58      |
| O$_2$/Ar=4/496 | 1673       | 3.10                   | 43.9   | 4.1    | 52.0       | 24.45     | 24.52      |
| CO$_2$     | 1673       | 5.05                   | 43.9   | 5.8    | 50.3       | 24.40     | 24.46      |
| CO$_2$/H$_2$=22 | 1673       | 6.90                   | 43.9   | 14.8   | 41.3       | 24.18     | 24.13      |
| air        | 1673       | 1.67                   | 34.2   | 5.4    | 60.4       | 23.27     | 23.24      |
| air        | 1673       | 1.67                   | 25.8   | 9.7    | 64.5       | 22.07     | 21.99      |
| CO$_2$     | 1673       | 5.05                   | 25.8   | 12.2   | 62.0       | 21.87     | 21.91      |
| CO$_2$/H$_2$=50 | 1673       | 6.18                   | 25.8   | 23.5   | 50.7       | 21.60     | 21.53      |
| CO$_2$/H$_2$=20 | 1673       | 6.99                   | 25.8   | 30.8   | 43.4       | 21.42     | 21.27      |
| air        | 1673       | 1.67                   | 18.3   | 13.6   | 68.1       | 20.88*    | 20.85      |
| CO$_2$     | 1673       | 5.05                   | 18.3   | 16.6   | 65.1       | 20.68*    | 20.75      |
| CO$_2$/H$_2$=20 | 1673       | 6.99                   | 18.3   | 34.7   | 47.0       | 20.20     | 20.16      |
| air        | 1673       | 1.67                   | 11.5   | 11.6   | 76.9       | 19.82*    | 19.95      |
| CO$_2$/H$_2$=20 | 1673       | 6.99                   | 11.5   | 40.4   | 48.1       | 19.01*    | 19.05      |
| air        | 1773       | 1.67                   | 43.9   | 3.5    | 52.6       | 24.61     | 24.69      |
| O$_2$/Ar=4/496 | 1773       | 3.10                   | 43.9   | 5.9    | 50.2       | 24.55     | 24.60      |
| CO$_2$     | 1773       | 3.72                   | 43.9   | 7.4    | 48.7       | 24.52     | 24.54      |
| CO$_2$/H$_2$=22 | 1773       | 3.91                   | 43.9   | 14.8   | 41.3       | 24.34     | 24.27      |
| air        | 1773       | 1.67                   | 34.2   | 6.6    | 92.2       | 23.36     | 23.35      |
| air        | 1773       | 1.67                   | 25.8   | 10.8   | 63.4       | 22.14     | 22.10      |
| CO$_2$     | 1773       | 3.72                   | 25.8   | 14.6   | 59.6       | 21.96     | 21.98      |
| CO$_2$/H$_2$=50 | 1773       | 5.19                   | 25.8   | 23.5   | 50.7       | 21.73     | 21.67      |
| CO$_2$/H$_2$=20 | 1773       | 6.00                   | 25.8   | 30.8   | 43.4       | 21.55     | 21.41      |
| air        | 1773       | 1.67                   | 18.3   | 14.8   | 66.9       | 20.94     | 20.96      |
| CO$_2$     | 1773       | 3.72                   | 18.3   | 19.0   | 62.7       | 20.76     | 20.82      |
| CO$_2$/H$_2$=20 | 1773       | 6.00                   | 18.3   | 34.7   | 47.0       | 20.34     | 20.30      |
| air        | 1773       | 1.67                   | 11.5   | 13.6   | 74.9       | 19.88     | 20.05      |
| CO$_2$/H$_2$=20 | 1773       | 6.00                   | 11.5   | 40.4   | 48.1       | 19.15     | 19.19      |
| air        | 1873       | 1.67                   | 43.9   | 4.9    | 51.2       | 24.73     | 24.78      |
| O$_2$/Ar=4/496 | 1873       | 3.10                   | 43.9   | 8.0    | 48.1       | 24.65     | 24.66      |
| CO$_2$     | 1873       | 3.43                   | 43.9   | 9.0    | 47.1       | 24.64     | 24.62      |
| CO$_2$/H$_2$=22 | 1873       | 5.03                   | 43.9   | 14.8   | 41.3       | 24.50     | 24.40      |
| air        | 1873       | 1.67                   | 34.2   | 7.8    | 58.0       | 23.45     | 23.45      |
| air        | 1873       | 1.67                   | 25.8   | 11.8   | 62.4       | 22.22     | 22.22      |
| CO$_2$     | 1873       | 3.43                   | 25.8   | 17.0   | 57.2       | 22.04     | 22.04      |
| CO$_2$/H$_2$=50 | 1873       | 4.33                   | 25.8   | 23.5   | 50.7       | 21.86     | 21.81      |
| CO$_2$/H$_2$=20 | 1873       | 5.11                   | 25.8   | 30.8   | 43.4       | 21.69     | 21.56      |
| air        | 1873       | 1.67                   | 18.3   | 16.0   | 65.7       | 21.01     | 21.07      |
| CO$_2$     | 1873       | 3.43                   | 18.3   | 21.2   | 60.5       | 20.86     | 20.90      |
| CO$_2$/H$_2$=20 | 1873       | 5.11                   | 18.3   | 34.7   | 47.0       | 20.48     | 20.44      |
| air        | 1873       | 1.67                   | 11.5   | 15.7   | 72.8       | 19.93     | 20.14      |
| CO$_2$/H$_2$=20 | 1873       | 5.11                   | 11.5   | 40.4   | 48.1       | 19.29     | 19.34      |

* supercooled liquid