Determination of CO₂ Contents in Slags and Molten Salts by B₂O₃ Fusion and KBF₄ Fusion Methods*

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Two methods have been developed for the determination of the CO₂ contents (carbonate ion contents) in oxide-containing melts. They are the B₂O₃ fusion method and the KBF₄ fusion method. The latter is applicable to chloride melts. The methods consist of two simple procedures: (1) fusion of a sample with B₂O₃ or KBF₄ to evolve CO₂ from the sample, and subsequently (2) determination of the amount of the evolved CO₂ by the weight loss method or using a commercially available carbon analyzer. The present methods have been used to determine the solubility of CO₂ in the Na₂O-SiO₂ system at 1473 K under 101325 Pa of CO₂ and in the NaCl-Na₂O system at 1073 K under 101325 Pa of CO₂. The present methods were found to be successfully applicable even to melts where the thermobalance method is inapplicable because of the low solubilities of CO₂ or the evaporation losses of the melts.

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I. Introduction

Slags, glasses, and oxide-containing molten salts have O²⁻ ion as a common ion species. In most cases, O²⁻ ion participates in various reactions which take place in such melts. Therefore, it is very important to know the activity of the O²⁻ ion. The basicity of such a melt can be rationally defined in terms of log [activity of O²⁻]. Thus, relative activity of O²⁻ in several melts have been determined by the electromotive force method(1)-(9). At present, however, this method is difficult to apply to all melts. In this context, the concentrations of substances or properties which relate directly to the activity of O²⁻ in melts have been used as measures of the basicity of the melts. Masuko(10), Goto and Matsushita(11), Iwamoto(12)(13), and Yokokawa(14) have reviewed such measures, which can be determined by the H₂O solubility method(15), the CO₂ solubility method(16)-(20), the SO₂ solubility method(21)(22), the redox ion pair method(23)-(25), the UV spectrum method (optical basicity method)(26)(27), etc. Also, the relative basicity or acidity of oxides may be obtained by comparing the solubility products of the oxides in the melts(28)-(30), the dissociation energies of the oxides(31), the heats of reaction of the oxides(31), the attractive forces between the cations and oxygen ion(11)(25), and standard Gibbs energies of formation of the carbonates or sulfates(11)(32). Furthermore, the potentiometric titration can determine the relative basicity or acidity of oxyanions, oxides and salts in molten salts(33)-(39).

The CO₂ solubility method can be applied to almost all slags, glasses, and oxide-containing molten salts and its experimental procedure for determining the CO₂ solubility is simple. Table 1 lists the methods used for the determination of the CO₂ amounts absorbed in melts. Methods 1, 2, 3, and 4 were applied to the melts which were considered to absorb CO₂ gas in a molecular form, that is, for determining the so-called “physical solubility” of CO₂ gas. Moreover, their applications were limited to temperatures below about 1273 K. On the other hand, methods 5 and 6 were applied to the melts which were considered to absorb CO₂ gas chemically according to the following equation.

\[ \text{CO}_2(\text{g}) + \text{O}^{2-}(\text{melt}) = \text{CO}_3^{2-}(\text{melt}). \]
They were used for determining the so-called "chemical solubility" of CO₂ gas. The carbonate capacity, which Wagner⁵⁸ has proposed as a measure for the basicity of slags, is a quantity that relates directly to this chemical solubility of CO₂ gas. The determination of the carbonate capacity premises that (1) the CO₂ which has been physically absorbed is evolved from the melt on freezing, or (2) the physical solubility of CO₂ gas is negligibly small compared with the chemical solubility of CO₂ gas. The former is generally satisfied, and the latter is satisfied for the melts with strong basicity. Method 5 can be applied only to the melts which have negligibly small amounts of evaporation in comparison with the absorption amounts of CO₂ or to the melts which have large solubilities of CO₂.

In method 6, method 6-3 is the fundamental method and may be widely used because of the simple apparatus. However, it cannot be applied to the substances which are difficult to dissolve in aqueous acid solutions. Thus, we undertook this work to find a method which can determine chemical CO₂-solubilities of almost all melts by a simple process. The principle of our method consists of (1) quenching a melt sample which has absorbed CO₂ gas, (2) adding a solid strong acid to the quenched sample, (3) fusing it at a low temperature to expel...
the CO₂ which has been absorbed as carbonate ions, and (4) determining the CO₂ evolved. Boron oxide and P₂O₅(P₄O₁₀) seemed to be strong acids suitable for procedure (3) as judged by their dissociation energies, their heats of formation, interactive forces between the cations and the oxygen ion, and standard Gibbs energies of the carbonates. Phosphorous pentoxide was presumed to be more acidic than B₂O₃ in the light of their dissociation energies which may be regarded as a measure of basicity, but B₂O₃ was assumed to be more acidic than P₂O₅ in the light of their heats of formation which may be regarded as a measure of acidity. Furthermore, P₂O₅ is very deliquescent and has high vapor pressures (the sublimation point is about 623 K) while B₂O₃ is not as deliquescent as P₂O₅ and has low vapor pressures (the boiling point is about 2073 K) and a favorably low melting point (723 K). For these reasons, B₂O₃ was selected as the strong acid to expel the CO₂ from CO₂-containing substances. 

Boron oxide is partially miscible with chloride melts at low temperatures, causing liquid immiscibility. Therefore, B₂O₃ is inappropriate as a strong acid to determine CO₂ contents in chloride melts. KBF₄ was then selected as the strong acid to determine CO₂ contents in the chloride melts.

A textbook on analytical chemistry describes a weight loss method for determining CO₂ contents in carbonate ores by adding Na₂B₄O₇ (mp: 1014 K) or NaPO₃ (mp: 900 K) to a sample, fusing it, and then measuring the weight loss. Thus, we also used Na₂B₄O₇ and NaPO₃ as agents to expel the CO₂ from a CO₂-containing substance. We then examined the accuracies of the obtained analytical values.

II. Experimental

1. Analytical procedure

Figure 1 shows schematic diagrams of the experimental procedures. Experimental series I was carried out to examine the extent to which B₂O₃, KBF₄, Na₂B₄O₇, and NaPO₃, which were selected as the acids, were able to expel the CO₂ from the samples. Sodium carbonate (Na₂CO₃) was used as a substance having a known content of CO₂. One of the solid acids described previously was added to a given amount of Na₂CO₃. The mixture of the Na₂CO₃ and one of the solid acids was fused to expel the CO₂. Finally, the amount of the expelled CO₂ was determined by coulometric titration or gravimetry which measured the weight loss. In

Fig. 1 Experimental procedures for CO₂ determination.
experimental series II, the strong acids which experimental series I showed to be promising for determining CO₂ contents were actually applied to the determinations of the CO₂ solubilities in two types of melts (Na₂O–SiO₂ and NaCl–Na₂O systems). Samples were allowed to absorb CO₂ gas and then quenched. The strong acids were then added to the quenched samples to expel the CO₂. Lastly, the amount of the expelled CO₂ was determined by coulometric titration.

2. Reagents

Sodium carbonate (standard reagent for volumetric analysis; purity: 99.98%; mp: 1124 K) was dried for 2.7 ks at 923 K in air before use. Carbon dioxide (99.99%, Seiitetu Chemical Co., Ltd.) was purified through active carbon and magnesium perchlorate. Boron oxide, KBF₄, and Na₂B₄O₇ were guaranteed grade reagents. Sodium metaphosphate was prepared by heating NaH₂PO₄·2H₂O (guaranteed grade reagent) at 723 K for 24 h. The boron oxide to be used for the weight loss method should be as free from water as possible; therefore, it was dried at given high temperatures and prescribed periods of time, which will be specified later, in a stream of the oxygen gas which was dehydrated through magnesium perchlorate. On the other hand, the B₂O₃ to be used for coulometric titration can contain a small amount of water; therefore, it was dried at a low temperature of 473 K for 3.6 ks. Potassium tetrafluoride, NaPO₃, and Na₂B₄O₇ were fused in air before use to remove carbonates and sulphates which might be included in the reagents.

Samples of the Na₂O–SiO₂ system were prepared from Na₂CO₃ and SiO₂ (guaranteed grade reagent); SiO₂ was dried at 673 K for 3.6 ks. Samples of the NaCl–Na₂O system were prepared from NaCl (guaranteed grade reagent) and Na₂CO₃ or Na₂O (98% purity); Na₂O was dried at 473 K for 3.6 ks.

3. Container for melt samples

In experimental series I, a platinum crucible (inside diameter, 10 mm; height, 16 mm) or a platinum boat (width, 4 mm; length, 35 mm; height, 8 mm) was used as the container for the melt samples. In experimental series II, a platinum boat (width, 4 mm; length, 35 mm; height, 8 mm) was used as the container for the melt samples.

4. Apparatus for CO₂ absorption

Figure 2 shows a schematic diagram of the apparatus for the CO₂ absorption. The samples were placed in a platinum boat, allowed to absorb CO₂ gas at given temperatures for given periods of time in a stream of CO₂ gas [101325 Pa (1 atm)], quickly withdrawn into a water-cooled copper tube, and quenched. The thermocouple used in this experiment was calibrated with the melting point of copper (mp; 1356.5 K).

5. Gravimetry and coulometric titration

Samples were weighed with an electronic balance with a measurable limit of 0.01 mg. The CO₂ expulsion (evolution) for the weight loss method was carried out in a stream of oxygen gas (flow rate: 40 cm³/min) which was prepared by desiccating commercial oxygen gas (99.99% purity) with magnesium perchlorate, while that for the coulometric titration was carried out in a stream of commercial oxygen gas (99.99% purity; flow rate: 150 cm³/min). The coulometric titration was carried out with a carbon analyzer for metals (Kokusai Electric Co., Ltd., Coulomatic C, Model VK-1C), which was calibrated with CaCO₃ of the primary standard reagent.
Before use, the CaCO₃ was dried at 673 K.

III. Results and Discussion

1. Dehydration of B₂O₃

As-purchased B₂O₃ contains a considerable amount of water because it is deliquescent. Therefore, it must be dehydrated before the use for the weight loss method. Figure 3 shows the relations between the rate of weight loss of the as-purchased B₂O₃ and heating time at three temperatures in air. The rate of weight loss became constant after 12 ks at 1473 K and after 4 ks at 1673 K. Therefore, we judged that the dehydration had almost finished within the above periods of time at the above temperatures, and after those periods of time the evaporation of B₂O₃ mainly took place. On the other hand, we judged that at a lower temperature of 1273 K, the hydration had not yet finished within the experimental time period. On the basis of these results, the B₂O₃ to be used for the weight loss method was dehydrated at 1473 K for 14.4 ks (4 h). The dehydration was carried out in a stream of oxygen gas to avoid the influence of moisture in air.

2. Measurements of evaporation losses of B₂O₃

The above experimental results showed that B₂O₃ evaporates at high temperatures although the evaporation rates were small. Therefore, when B₂O₃ is used as a reagent for the gravimetry (weight loss method) which measures a weight loss of a sample, it is necessary to know the evaporation loss of B₂O₃ at a fusing temperature (a temperature for expelling the CO₂ from the sample) and correct the weight loss of the sample in order to know the true weight loss due to the CO₂ evolution. If only a mixture of a sample and B₂O₃ fuses at a temperature, that temperature can be adopted as the fusing temperature for that sample. When Na₂CO₃ (mp: 1124 K) was used as a standard sample having a known content of CO₂, a temperature of 1123 K was adopted as the fusing temperature; thus, evaporation amounts of B₂O₃ were measured at 1123 K, under the same conditions as those in the gravimetry, which will be described later, by using the B₂O₃ which was dehydrated at 1473 K for 14.4 ks (4 h). In order to minimize errors in correcting the weight losses in the gravimetry, the identical platinum crucible which was used for the gravimetry was used as the sample container. Figure 4 shows the results. The weight losses in the gravimetry were corrected using these results, as will be described later.

3. Gravimetry

Figure 5 shows the results of the gravimetry for the samples of Na₂CO₃ and B₂O₃ mixtures in a molar ratio of 1/3. The apparent percentages of CO₂ evolution in Fig. 5 are the values obtained by assuming that the weight losses were only due to the CO₂ evolution, whereas the corrected percentages of CO₂ evolution are the values which were calculated by assuming that the true amounts of the evolved CO₂ were the weight losses minus the expected evaporation losses of B₂O₃. The evaporation of Na₂O was not taken into account because the Na₂O amounts in the samples were much less than
the B$_2$O$_3$ amounts. The corrected percentage of CO$_2$ evolution was 100.02% while the value obtained by extrapolating linearly the relation between the apparent percentage of CO$_2$ evolution and heating time to the ordinate (zero on the time scale) was 100.01%. Both were in good agreement. Similar experiments were carried out with samples of Na$_2$CO$_3$ and B$_2$O$_3$ mixtures in molar ratios of 1/4 and 1/5. For the molar ratio of 1/4, the extrapolated value was 100.14% and the corrected value was also 100.14%, while for the molar ratio of 1/5, the extrapolated value was 100.10% and the corrected value was 100.14%. The reason why both the extrapolated values and the corrected ones were larger by 0.01% to 0.14% than 100% is probably due to that the dehydration of the B$_2$O$_3$ was not complete, and the evolution of the residual water was probably induced by the evolution of CO$_2$. This presumption is supported by the fact that the use of the B$_2$O$_3$ which was less completely dehydrated gave a larger extrapolated value (100.24%), as will be described later (Fig. 7). From the fact that the percentage of CO$_2$ evolution was from 100.01% to 100.14% as described above, it was found that our gravimetry can determine the CO$_2$ content to three significant figures. Furthermore, owing to the fact that the corrected values were equal or almost equal to the extrapolated values, it was found that one can easily obtain the content of CO$_2$ to three significant figures by extrapolation instead of determining the evaporation amounts of B$_2$O$_3$ and subtracting them from the weight losses. Also, from the fact that the apparent percentages of CO$_2$ evolution at 0.3 ks (5 min) of holding time were 100.09% for the molar ratio of 1/3 (see Fig. 5), 100.20% for 1/4, and 100.23% for 1/5, it was found that if an analytical value with about two and a half significant figures will do, one can adopt the apparent CO$_2$ contents at the holding time of 0.3 ks (5 min) as the CO$_2$ content of the sample.

When the amount of B$_2$O$_3$ was too small, the CO$_2$ evolution was incomplete, as shown in
In the gravimetry described above, the B₂O₃ which was dehydrated at 1473 K was used as an agent for the CO₂ evolution from the samples. The dehydration at such a high temperature needs an electric furnace with a ceramic heating element such as a silicon carbide bar. If B₂O₃ dehydrated at lower temperatures can be used, an inexpensive electric furnace with a less expensive heating element such as nichrome wire can be used. Therefore, the possibility of using the B₂O₃ which was dehydrated at 1173 K (900°C) for 36 ks (10 h) was examined (Fig. 3 shows that the dehydration at that temperature is not complete). The results are shown in Fig. 7. The extrapolated value was 100.24%, and the apparent percentage of CO₂ evolution at 0.3 ks (5 min) of holding time was 100.30%. Therefore, it was found that even the use of the B₂O₃ which has not completely dehydrated may also give an analytical value with two or two and a half significant figures, although the accuracy of the analytical value is lower by 0.1 to 0.2% than that obtained when using the B₂O₃ which is almost completely dehydrated at 1473 K.

Hereinafter, the method which uses B₂O₃ as a strong acid for expelling the CO₂ from a CO₂-containing sample will be referred to as the B₂O₃ fusion method.

### 4. Coulometric titration

In order to confirm the previous conclusions, the percentage of CO₂ evolution from the sample of a Na₂CO₃ and B₂O₃ mixture in a molar ratio of 1/5 was determined by coulometric titration which need not take the evaporation loss of a sample into consideration unlike the already described weight loss method. For the reason described previously (section 1-2), the B₂O₃ was only slightly dehydrated at a low temperature (473 K, 3.6 ks). The percentage of CO₂ evolution, as shown in Table 2, was 100.00±0.07%; therefore, it can be said that the neutralization proceeded quantitatively and the percentage of CO₂ evolution by B₂O₃ was 100.0%.

Therefore, it is concluded that one can determine the content of CO₂ with very high accuracy by using the B₂O₃ fusion method.

The instrumental analysis (such as the coulometric titration method, the thermal conductivity method, and the infrared absorption method, which need expensive apparatuses) or the Askarite absorption method has the advantage of being able to use B₂O₃ in a nearly as purchased state without significant dehydration.

### 5. Percentage of CO₂ evolution by KBF₄

Boron oxide is partially miscible with chloride melts at low temperatures. Therefore, it is important to find a strong acid to expel

<table>
<thead>
<tr>
<th>No.</th>
<th>B₂O₃</th>
<th>KBF₄</th>
<th>Na₂B₄O₇</th>
<th>NaPO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.02</td>
<td>100.14</td>
<td>99.83</td>
<td>97.79</td>
</tr>
<tr>
<td>2</td>
<td>99.90</td>
<td>100.11</td>
<td>99.45</td>
<td>98.83</td>
</tr>
<tr>
<td>3</td>
<td>99.96</td>
<td>100.10</td>
<td>99.58</td>
<td>98.57</td>
</tr>
<tr>
<td>4</td>
<td>100.07</td>
<td>99.95</td>
<td>99.55</td>
<td>98.06</td>
</tr>
<tr>
<td>5</td>
<td>100.05</td>
<td>99.92</td>
<td>99.51</td>
<td>98.93</td>
</tr>
</tbody>
</table>

Average 100.00 100.05 99.58 98.44

Standard deviation 0.07 0.09 0.15 0.49

CO₂ from chloride melts. Since KBF₄ is miscible with chloride melts, it was selected as a strong acid candidate for chloride melts. Its ability to expel the CO₂ from a CO₂-containing sample was examined by coulometric titration using Na₂CO₃ as a standard CO₂-containing sample. The molar ratio of Na₂CO₃ to KBF₄ was 1/10, and the fusing temperature was 873 K (600 °C). The results are included in Table 2. The percentage of CO₂ evolution was 100.05 ± 0.09%. Consequently, it can be said that KBF₄ is a strong acid which can completely (100.0%) remove the CO₂ from CO₂-containing substances. Therefore, it is concluded that the CO₂ content in a CO₂-containing sample can be determined with high accuracy by fusing it with KBF₄, as in the B₂O₃ fusion method. Hereinafter, the method which uses KBF₄ as a strong acid for expelling the CO₂ gas from a melt will be referred to as the KBF₄ fusion method.

6. Percentages of CO₂ evolution by Na₂B₄O₇ and NaPO₃

The percentage of CO₂ evolution by Na₂B₄O₇ and NaPO₃ was determined by coulometric titration. The molar ratios of Na₂CO₃/Na₂B₄O₇ and Na₂CO₃/NaPO₃ were both 1/10 and the fusing temperatures were both 1123 K, the same as in the B₂O₃ fusion method. The results are included in Table 2. The percentage of CO₂ evolution by Na₂B₄O₇ and NaPO₃ was 99.58 ± 0.15% and 98.44 ± 0.49%, respectively. Therefore, both Na₂B₄O₇ and NaPO₃ are inferior to B₂O₃ and KBF₄ with respect to the percentage of CO₂ evolution. The reason for this is probably due to the fact that the acidity of Na₂B₄O₇ and NaPO₃ is lower than that of B₂O₃ and KBF₄ because Na₂B₄O₇ and NaPO₃ contain a basic component, Na₂O. Accordingly, if Na₂B₄O₇ or NaPO₃ is used as an acid for expelling the CO₂ gas from a melt with low basicity, the percentage of CO₂ evolution will become smaller than the previous corresponding value (99.58% for Na₂B₄O₇, 98.44% for NaPO₃), and will be accompanied by a large error. To cite an extreme example, if Na₂B₄O₇ is used as an acid to determine the content of CO₂ in a Na₂B₄O₇ melt, then CO₂ will never be evolved.

7. CO₂ solubilities in the Na₂O-SiO₂ system

Solubilities of CO₂ in the Na₂O-SiO₂ system at 1473 K under a CO₂ pressure of 101325 Pa (1 atm) were determined by coulometric titration by using the B₂O₃ fusion method (fusing temperature: 1123 K). The amounts of CO₂ absorbed in the samples reached saturated values at 1.2 to 2.4 ks. Table 3 lists the CO₂ solubilities determined. The chemical composition (X_{Na₂O}, X_{SiO₂}, X_{CO₂}) of the samples after CO₂ absorption were calculated with respect to the following three cases:

(1) assuming that the evaporating substance is Na₂O,
(2) assuming that the evaporating substance is SiO₂,
(3) assuming that the evaporating substance has the same composition as the as-mixed or initial composition. Assumptions (1) and (2) define the extreme shifts of the composition of a sample by evaporation. The evaporation amount, ΔW, from a sample during CO₂ absorption is calculated by the equation:

\[ ΔW = (W_{Na₂O} + W_{SiO₂} + W_{CO₂}) - W_A, \]  

where \( W_{Na₂O} \) and \( W_{SiO₂} \) are the amounts of Na₂O and SiO₂, respectively, in the sample before CO₂ absorption, \( W_A \) is the mass of the sample after CO₂ absorption, and \( W_{CO₂} \) is the CO₂ amount measured by coulometric titration. When ΔW has been determined by eq. (1), the amounts of Na₂O and SiO₂, \( W'_{Na₂O} \) and \( W'_{SiO₂} \), in the sample after CO₂ absorption can be calculated by simple equations, and subsequently \( X'_{Na₂O}, X'_{SiO₂}, \) and \( X'_{CO₂} \) can be calculated using \( W'_{Na₂O}, W'_{SiO₂}, \) and \( W'_{CO₂} \). The first column in Table 3 lists the values of \( X_{Na₂O}/(X_{Na₂O} + X_{SiO₂}) \) of the as-mixed samples, and the second column lists the values of \( X_{Na₂O}/(X_{Na₂O} + X_{SiO₂}) \) of the samples in the two limiting states which are defined by assumptions (1) and (2) described previously. Because the changes in \( X_{Na₂O} \) and \( X_{SiO₂} \) with evaporation were small as can be seen from the values in the second column, the CO₂ solubilities were calculated on the basis of assumption 3 and are listed in the third column. For comparison, the solubilities determined by thermogravimetry(19) and the
vacuum extraction method\(^{(16)}\) are also listed in the fourth and fifth columns. For high basicity, that is, in the large solubilities of CO₂, the results of the present method are in good agreement with those of the thermogravimetry; for example, at 0.9 of \(X_{\text{Na}_2\text{O}}/(X_{\text{Na}_2\text{O}}+X_{\text{SiO}_2})\), the solubility obtained by the present method was 0.424 while that obtained by thermogravimetry was also 0.424. However, as the basicity was reduced and the CO₂ solubility, in turn, became smaller, the discrepancies between our results and those obtained by thermogravimetry became larger; for example, at 0.5 of \(X_{\text{Na}_2\text{O}}/(X_{\text{Na}_2\text{O}}+X_{\text{SiO}_2})\), the thermogravimetry only gave half of our value. The reason for this is considered as follows. The weight gain measured by thermogravimetry is the difference between the weight gain due to CO₂ absorption and the weight loss due to evaporation during the measurement. This corresponds to the amount (\(W_{\text{CO}_2} - \Delta W\)) in our method. The apparent CO₂ solubility which is calculated on the basis of this amount, (\(W_{\text{CO}_2} - \Delta W\)), is 0.0078 at 0.5 of \(X_{\text{Na}_2\text{O}}/(X_{\text{Na}_2\text{O}}+X_{\text{SiO}_2})\). This is in good agreement with the value of 0.0074 which was obtained by thermogravimetry (see the fourth column in Table 3). Therefore, the reason why the CO₂ solubilities obtained by thermogravimetry were much smaller than those obtained by our method in the compositional region having small solubilities of CO₂ is that the evaporation losses were too large to neglect in comparison with the amounts of CO₂ absorbed. Therefore, the present method can be said to be superior to thermogravimetry with respect to accuracy when the CO₂ solubility is small. Also, as can be seen from Table 3, the vacuum extraction method\(^{(16)}\) is inferior to the present method and thermogravimetry.

In order to use the carbonate capacity as a measure of the activity of the oxygen ion in a melt, the concentration of the carbonate ion in the melt should be dilute. Therefore, the CO₂ solubility should be determined under low CO₂ pressures. Thermogravimetry is difficult to apply under such conditions. Also, in the case of slags for iron making and steel making, it is desirable to determine carbonate capacities (CO₂ solubilities) at temperatures where the slags are actually utilized. At such high temperatures, the evaporation losses of the slags cannot be neglected, and therefore, thermogravimetry is difficult to apply. On the other hand, the present method determines the CO₂ content directly, and furthermore the CO₂ solubility can be corrected, if necessary, by determining the evaporation loss of the sample. Therefore, we believe that the present method can determine solubilities of CO₂ in melts under the conditions of high temperatures and low CO₂ pressures where thermogravimetry is difficult to apply.

**8. CO₂ solubilities in NaCl-Na₂O system**

Solubilities of CO₂ in the NaCl-Na₂O system at 1073 K under a CO₂ pressure of 101325 Pa (1 atm) were determined by coulometric titration using the KBF₄ fusion method (fusing temperature: 873 K). The chemical composition \(X_{\text{NaCl}}, X_{\text{Na}_2\text{O}}, X_{\text{CO}_2}\) of the samples after CO₂ absorption were corrected by determining the evaporation losses which took place during CO₂ absorption, just as in the preceding section. The amounts of CO₂ absorbed in the samples reached saturated values at 1.2 ks to 2.4 ks. Table 4 lists the CO₂ solubilities determined. The amounts of the CO₂ absorbed were equimolar with those of the Na₂O in the samples.

<table>
<thead>
<tr>
<th>(X_{\text{Na}<em>2\text{O}}/(X</em>{\text{Na}<em>2\text{O}}+X</em>{\text{SiO}_2}))</th>
<th>(X_{\text{CO}_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 0.497-0.503</td>
<td>0.15 0.0074</td>
</tr>
<tr>
<td>0.55 0.549-0.552</td>
<td>0.053 0.021</td>
</tr>
<tr>
<td>0.60 0.600-0.601</td>
<td>0.104 0.082</td>
</tr>
<tr>
<td>0.65 0.650-0.650</td>
<td>0.164 0.206</td>
</tr>
<tr>
<td>0.70 0.698-0.708</td>
<td>0.239 0.333</td>
</tr>
<tr>
<td>0.80 0.796-0.816</td>
<td>0.339 0.333</td>
</tr>
<tr>
<td>0.90 0.899-0.916</td>
<td>0.424 0.424</td>
</tr>
<tr>
<td>1.00 0.498 0.498</td>
<td></td>
</tr>
</tbody>
</table>

**IV. Conclusions**

Two methods have been developed which simply and accurately determine CO₂ contents.
(carbonate ion contents) of slags, glasses, and oxide-containing molten salts. They are the \( \text{B}_2\text{O}_3 \) fusion method and the \( \text{KBF}_4 \) fusion method. The latter is applicable to chloride molten salts.

(1) These methods consist of two simple procedures in principle: (1) addition of \( \text{B}_2\text{O}_3 \) or \( \text{KBF}_4 \) to a \( \text{CO}_2 \)-containing sample followed by fusion of the sample for \( \text{CO}_2 \) expulsion, and then (2) determination of the amount of the expelled \( \text{CO}_2 \) by the weight loss method (for the \( \text{B}_2\text{O}_3 \) fusion method) or using a commercially available carbon analyzer (for the \( \text{B}_2\text{O}_3 \) fusion method and the \( \text{KBF}_4 \) fusion method).

(2) The \( \text{CO}_2 \) evolution by \( \text{B}_2\text{O}_3 \) or \( \text{KBF}_4 \) proceeded quantitatively and the percentage of \( \text{CO}_2 \) evolution was 100.0% when \( \text{Na}_2\text{CO}_3 \) was used as a \( \text{CO}_2 \)-containing sample.

(3) Solubilities of \( \text{CO}_2 \) in the \( \text{Na}_2\text{O}-\text{SiO}_2 \) system at 1473 K under 101325 Pa (1 atm) of \( \text{CO}_2 \) were determined by the \( \text{B}_2\text{O}_3 \) fusion method and compared with the literature values. In the high concentrations of \( \text{Na}_2\text{O} \), the present method gave \( \text{CO}_2 \) solubilities in good agreement with the values determined by thermogravimetry, whereas in the low concentrations of \( \text{Na}_2\text{O} \) (that is, in low solubilities of \( \text{CO}_2 \)), the present method gave \( \text{CO}_2 \) solubilities with higher accuracies than the thermogravimetry and the vacuum extraction method.

(4) Solubilities of \( \text{CO}_2 \) in the \( \text{NaCl}-\text{Na}_2\text{O} \) system at 1073 K under 101325 Pa (1 atm) of \( \text{CO}_2 \) were determined by the \( \text{KBF}_4 \) fusion method. The amounts of \( \text{CO}_2 \) absorbed were equimolar with the \( \text{Na}_2\text{O} \) amount in the melts.

(5) The present methods are believed to be a useful means to determine \( \text{CO}_2 \) solubilities of melts under the conditions of high tempera-

<table>
<thead>
<tr>
<th>( X_{\text{Na}<em>2\text{O}} / (X</em>{\text{NaCl}} + X_{\text{Na}_2\text{O}}) )</th>
<th>( X_{\text{NaCl}} )</th>
<th>( X_{\text{Na}_2\text{O}} )</th>
<th>( X_{\text{CO}_2} )</th>
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<td>Corrected</td>
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<td></td>
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<tr>
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<td>0.497–0.506</td>
<td>0.333</td>
<td>0.333</td>
</tr>
</tbody>
</table>

REFERENCES

(1) W. Stegmaier and A. Dietzel: Glastechnol. Ber., 18 (1940), 353.
Determination of CO₂ Contents in Slags and Molten Salts by B₂O₃ Fusion and KBF₄ Fusion Methods