Volatility and Vapor Pressure Measurements of Antimony and Arsenic Components in CaO-SiO₂-FeO₁.₅ Slags at 1,573 K by Transpiration Method*

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As a fundamental study for treating fused oxides containing antimony and arsenic components relating to metallurgical and recycling processes, volatility, α, and vapor pressure of the oxide species evaporating from the CaO-SiO₂-FeO₁.₅ slags with Q (\%CaO / (\%CaO + \%SiO₂)) of 0.37, 0.53 and 1 were determined at 1,573 K in a range of mole fraction, N, of SbO₁.₅, SbO₂.₅ and AsO₂.₅ in the slag between 0.005 and 0.05 by using the transpiration method with a vertical volatilization chamber. It was found that the volatility of the antimony and arsenic components in each slag increases with decreasing Q and suggested that control and adjustment of the slag basicity are very important for eliminating these components from the slag by means of volatilization. The log α versus log N plots represented a nearly straight line with a gradient, which is very close to that predicted by the thermodynamic consideration, and it was concluded that Sb₂O₃ and As₂O₅ are the predominant gas species evaporating from the slags. Raoultian activity coefficients, \(γ_{\text{SbO}_1.5}\), SbO₂.₅ and \(γ_{\text{AsO}_2.5}\) in the slags, which were derived from the measured volatility, decrease with increasing Q, and \(γ_{\text{SbO}_2.5}\) and \(γ_{\text{AsO}_2.5}\) are less than unity for the slags with Q of 0.53 and 1.

KEY WORDS: Antimony Oxide, Arsenic Oxide, CaO-SiO₂-FeO₁.₅ Slag, Volatility, Vapor Pressure, Transpiration Method

1. Introduction
Volatilization of the antimony and arsenic components in fused oxides is of great concern in production of metals as well as treatment of secondaries such as residues, dusts and ashes from the incinerator for eliminating these detrimental elements or controlling their behavior. The vapor pressure and activity data for these components in the fused oxides will provide very useful information for thermodynamically evaluating and discussing their behavior in the practical operations or developing a new process for eliminating them by means of volatilization.

Nevertheless, there exist very few data on the thermodynamic properties of the antimony and arsenic components in the fused oxides. As for pure trivalent and pentavalent oxides and their some double oxides, the vapor pressures were determined by Shigematsu¹ with transpiration, dew point and Knudsen methods and Lau et al.² with a torsion-effusion method. One of the authors³ reported the dissociation of various double oxides composing of pentavalent antimony or arsenic oxide. However, no data have been reported on the vapor pressure of the antimony and arsenic components in the molten slag though Vancon and Guerin⁴ observed the volatilization of the arsenic components in the As₂O₅-CaO-FeO-FeO₁.₅ slag at 1,823 K.

Hence, in the present study, the volatility and vapor pressure of the antimony and arsenic components in the molten CaO-SiO₂-FeO₁.₅ slags with Q(\%CaO / (\%CaO + \%SiO₂)) of 0.37, 0.53 and 1 have been determined at 1,573 K by using a transpiration apparatus with a vertical volatilization chamber, when Sb₂O₃, Sb₂O₅ or As₂O₅ was included as a component.

2. Experiments

2·1 Transpiration method
The principle of the transpiration method is described in a reference book⁵. The equilibrium vapor pressure can be determined by measuring the weight of condensate in a condenser, \(W_i\) which is brought with a given amount of carrier gas passing through a volatilization chamber in which the sample is held and the carrier gas is saturated with the evaporated components. The equilibrium partial pressure of a gaseous component of i, \(P_i\), is given by the following equation:

\[P_i = n_i / (n_i + n_e)\]

Here, \(n_i\) is the mole amount of the i component collected in the condenser, \(n_e\) the mole amount of the carrier gas passing through the volatilization chamber, \(P_t\) the total pressure in the chamber (it was set at 1 atm in the present experiments) and \(n_i\) is total mole amount of all the evaporated species collected in the condenser.

In case that the species existing in the gas phase are plural, \(P_i\) can be determined from eq. (1) by measuring the weight of the condensate and combining the equilibrium constants for the reactions between the concerning gas species. However, the information on the gas species of antimony and arsenic components evaporating from the slag is extremely lacking. Furthermore, the equilibrium constants for these components at high temperature are not well known. To avoid these difficul-

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ties encountered in the transpiration study, first of all, an experimental condition must be looked for in the present study so that a singular species may possibly exist in the gas phase.

When elemental, trivalent and pentavalent antimony or arsenic components are assumed, it is considered that their stability in the slag phase is dependent on the ratio of ferrous to ferric iron (Fe^{2+}/Fe^{3+}) in the slag, in other words, the partial pressure of oxygen because the chemical affinity to oxygen is very similar between iron and antimony or arsenic. To evaluate the stability of the antimony components in the slag, the activity ratios of $a_s$ against total activity of $a_t$ in relation to oxygen potential at 1,573 K.

Based on the above considerations, the following slags were selected in the present study: (a) 25 mass % CaO-43%SiO$_2$-32%Fe$_2$O$_3$ ($Q$=42.5°CaO/(%CaO+%SiO$_2$=0.37), (b) 33%Cao-29%SiO$_2$-38%Fe$_2$O$_3$ ($Q$=0.53) and (c) 23%Cao-77%Fe$_2$O$_3$ ($Q$=1), which are fusible at 1,573 K. The similar tendency against the partial pressure of oxygen was also observed for the activity ratios of the arsenic components.

Information on the chemical formulae of the gaseous antimony and arsenic oxide species evaporating from the slag, which is necessary to derive the vapor pressure from eq. (1), have not been fully clarified either. Some studies reported that polymeric Sb$_2$O$_5$ and As$_2$O$_5$ are stable as the species evaporating from pure Sb$_2$O$_3$ and As$_2$O$_3$, respectively, while Lynch reported that the stability of the oxide species is strongly dependent on temperature and partial pressure of oxygen as well as their concentrations in the solid or liquid bulk phase. Hence, in the present study, to avoid the uncertain specification of the chemical formulae, which leads to $n_i$ ($n_i = W/M$ with $M$ of molecular weight of the $i$ species) in eq. (1), volatility, $\alpha$, as defined by eq. (2), was firstly introduced and derived in the present study.

$$\alpha = W/V (g/l) \quad (2)$$

Here, $W$ is the weight of the condensate (gram) and $V$ is the volume of the carrier gas (normal liter). Once the chemical formula of the $i$ species, and accordingly $M$, is fixed, the vapor pressure can be given by eq. (3).

$$p_i = (22.4/M)\alpha \quad (3)$$

in case that molar quantity of the condensate is very small compared with that of the carrier gas ($n_i > n_v$), as in the present study where $n_i$ is 200 ~ 1,000 times larger than $n_v$.

### 2.2 Experimental apparatus and procedure

An essential requisite for the transportation method is that the carrier gas is to be saturated with the sample vapor. For a liquid sample, bubbling of the carrier gas into it is of great help to enlarge the interfacial area between the sample and the carrier gas and resultantly to attain the saturation of vapor. For enabling the bubbling operation, a construction of a vertical volatilization chamber is required, in which the carrier gas passing through a vertical nozzle is blown into the liquid sample.

Hence, in the present study, the transpiration method with the volatilization chamber was selected and an apparatus was constructed as shown in Fig.2. It is mainly composed of a sys-

![Fig.2 Construction of an experimental apparatus with a vertical volatilization chamber.](image-url)
tem for controlling the carrier gas, a volatilization chamber, a gas-condenser and a heating furnace. Argon with the purity of more than 99.9995 % was used as the carrier gas and its flow rate was controlled precisely by using a mass flow controller with a sensor for detecting the change in thermal conductivity of the flowing gas. The volatilization chamber is constructed with a MgO crucible, which has an inner diameter of 24 mm and height of 40 mm, and a lid made from a MgO plate with a thickness of 5 mm. After putting about 15 g of the slag sample including the antimony or arsenic oxide, the lid was air-tightly bound with the crucible by using a zirconia paste. The lid has two holes in it. A MgO tube with an inner diameter of 6 mm is inserted in one of the holes and the length of the tube was adjusted so that its outlet was located at a position about 2 mm below a surface of the liquid slag. In another hole of the lid, a capillary tube with an inner diameter of 0.8 mm is inserted, through which the carrier gas is supplied by bypassing passages. The capillary is connected to the gas condenser which is made from an alumina tube of an inner diameter of 6 mm and a length of 40 mm with silica wool stuffed in it. A small space is made between the capillary and the gas-condenser so that the connection between them can be freely made during the experimental run. In order to prevent the carrier gas from leaking out through the space, another argon gas was introduced into an alumina reaction tube, in which the measuring assembly is set, and it acted effectively as a gas-shield. The volatilization chamber is located in a region of uniform temperature (± 2 K) in the heating furnace which is made from a spiral SiC element.

It is pointed out that the vapor pressure calculated from eq. (1), which is independent of the flow rate of the carrier gas, is to be the equilibrium one. Hence, in the preliminary experiment, the adoptable flow rate of the carrier gas was examined. From the results, the adoptable flow rate of the carrier gas was found to be the equilibrium one. Hence, in the preliminary experiment, the adoptable flow rate of the carrier gas was examined. Therefore, 150 cm$^3$/min was selected as the flow rate in the present experiments.

The antimony and arsenic oxides in the form of calcium compounds, Ca(SbO$_2$)$_2$, Ca$_2$(SbO$_3$)$_3$ and Ca$_3$(AsO$_4$)$_2$, respectively, were put in the volatilization chamber along with the starting slag sample to avoid their loss by evaporation during heating the sample up to the experimental temperature. Their amounts were adjusted so that their mole fraction, $N_{SbO_{1.5}}$ or $N_{AsO_{3.5}}$, in the slag may be about 0.005 and 0.05. Ca(SbO$_2$)$_2$ and Ca$_2$(SbO$_3$)$_3$ were synthesized pyrometallurgically from Ca and Sb$_2$O$_3$ or Sb$_3$O$_5$ while Ca$_3$(AsO$_4$)$_2$ hydro-metallurgically from CaCl$_2$ and NaHAsO$_4$. They were confirmed by X-ray diffraction to be the corresponding compounds. It was found that, by adjusting the period of the experimental run, change in the antimony and arsenic concentrations in the slag during the runs could be kept small at less than 0.002 mole fraction. The solubility of MgO in the slags was found to be small at less than 3 mass % because the period of the experimental run was short at 5–30 min.

Antimony and arsenic in the slags after the transpiration experiments were analyzed by inductively-coupled-plasma spectrometry to determine their concentrations in the slags. The condensate in the condenser was analyzed by X-ray diffraction.

3. Results and Discussions

3.1 Volatility and vapor pressure

When Ca(Sb$_2$O$_3$)$_2$ was put in the CaO-SiO$_2$-FeO$_{1.5}$ slags with $Q$ (%CaO/(%CaO+%SiO$_2$)) of 0.37, 0.53 and 1, the volatility of the antimony component at 1,573 K is shown in Fig.3, in relation to the atomic fraction of SbO$_{1.5}$ in the slag, as calculated by $N_{SbO_{1.5}}$ = $n_{SbO_{1.5}}$ / ($n_{CaO} + n_{SbO_{3}} + n_{FeO_{1.5}} + n_{SbO_{1.5}}$) with $n$ of the molar quantities of the slag components. It is noted that the volatility increases exponentially with $N_{SbO_{1.5}}$ and, at a given mole fraction, decreases with increasing $Q$. In order to prevent the carrier gas from leaking out through the space, another argon gas was introduced into an alumina reaction tube, in which the measuring assembly is set, and it acted effectively as a gas-shield. The volatilization chamber is located in a region of uniform temperature (± 2 K) in the heating furnace which is made from a spiral SiC element.

It is pointed out that the vapor pressure calculated from eq. (1), which is independent of the flow rate of the carrier gas, is to be the equilibrium one. Hence, in the preliminary experiment, the adoptable flow rate of the carrier gas was examined and it was found that the calculated vapor pressures are almost constant in the range of the flow rate between 100 and 300 cm$^3$/min. Therefore, 150 cm$^3$/min was selected as the flow rate in the present experiments.

The antimony and arsenic oxides in the form of calcium compounds, Ca(SbO$_2$)$_2$, Ca$_2$(SbO$_3$)$_3$ and Ca$_3$(AsO$_4$)$_2$, respectively, were put in the volatilization chamber along with the starting slag sample to avoid their loss by evaporation during heating the sample up to the experimental temperature. Their amounts were adjusted so that their mole fraction, $N_{SbO_{1.5}}$ or $N_{AsO_{3.5}}$, in the slag may be about 0.005 and 0.05. Ca(SbO$_2$)$_2$ and Ca$_2$(SbO$_3$)$_3$ were synthesized pyrometallurgically from Ca and Sb$_2$O$_3$ or Sb$_3$O$_5$ while Ca$_3$(AsO$_4$)$_2$ hydro-metallurgically from CaCl$_2$ and NaHAsO$_4$. They were confirmed by X-ray diffraction to be the corresponding compounds. It was found that, by adjusting the period of the experimental run, change in the antimony and arsenic concentrations in the slag during the runs could be kept small at less than 0.002 mole fraction. The solubility of MgO in the slags was found to be small at less than 3 mass % because the period of the experimental run was short at 5–30 min.

Antimony and arsenic in the slags after the transpiration experiments were analyzed by inductively-coupled-plasma spectrometry to determine their concentrations in the slags. The condensate in the condenser was analyzed by X-ray diffraction.
Since the X-ray diffraction analysis for the condensate in the present transpiration experiments clarified that it has a crystal structure of Sb$_2$O$_5$ (senarmotite), no other component being detected, it is considered that the antimony component in the slag evaporates according to eq. (4) or (7).

Hence, the relationship given in Fig.3 has been converted to that between log $\alpha$ and log $N_{SbO_{1.5}}$, as shown in Fig.4. It is obvious in Fig.4 that, for each slag system, log $\alpha$ versus log $N_{SbO_{1.5}}$ plots make a nearly straight line with a gradient close to 4. This strongly suggests that the antimony oxide species in the gas is not Sb$_2$O$_3$ but Sb$_4$O$_6$. Once the gas species may be fixed as Sb$_4$O$_6$, the vapor pressure can be derived from eq. (3) and is shown in Fig.4 with a scale on the right ordinate.

When Ca$_3$(SbO$_4$)$_2$ was put in the slags with $Q$ of 0.37, 0.53 and 1, the logarithmic volatility of the antimony component at 1,573 K is shown in Fig.5, in terms of the linear dependency and its gradient.

The change in the slag mass before and after bubbling argon for the slag after bubbling argon with 150 cm$^3$/min for 60 min when it was made in the same condition as in the first preliminary experiment. The ratio was 0.03. Thirdly, the mass of the slag, which was treated in the same condition as in the second preliminary experiment, was measured by a balance. The change in the slag mass before and after bubbling argon was very small at about 3 mg.

Based on the relationship between (Fe$^{2+}$/Fe$^{3+}$) and $P_{O_2}$ in the CaO-FeO slags, which was reported by Takeda et al.$^8$), the equilibrium partial pressure of oxygen for the present slag with (Fe$^{2+}$/Fe$^{3+}$) of 0.03 was evaluated to be about 0.2 atm. Whenever the slag representing such a high $P_{O_2}$ is exposed in a large amount of carrier gas, (Fe$^{2+}$/Fe$^{3+}$) should increase to much extent. However, the second preliminary experiment clarified that (Fe$^{2+}$/Fe$^{3+}$) did not change at all after bubbling argon of about 0.01 m$^3$. This result, along with that obtained in the third preliminary experiment, suggests that the rate to evolve oxygen from the slag to gas phases, according to the reaction, FeO$_3$ → 2FeO + 1/2O$_2$, is extremely slow and that the carrier gas is very far from the saturation with oxygen.

In case that no iron oxide in the slag pertains to the evolution of oxygen to the gas phase and only the dissociation of the antimony oxide component according to eq. (9) is responsible for the release of oxygen, the dissociation in a neutral gas with a relationship of $P_{O_2} = 2P_{ShbO_4}$ may be applied to eq. (10). With this relationship, the volatility is thermodynamically expressed by eq. (11), on analogy of eq. (6).

$$\log \alpha = \frac{4}{3} \log N_{SbO_{1.5}} + \frac{4}{3} \log \gamma_{SbO_{1.5}} + \log \alpha_o$$ (11)}
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The provision made in the present thermodynamic analysis may be satisfied only when the oxygen liberated from the antimony oxide component in the slag fast moves to the gas phase while the iron oxides in the slag do not actually pertain to the evolution of oxygen into the gas phase. However, a further study will be required to verify the validity of the present provision.

When Ca₆(AsO₄)₂ was put in the slags with Q of 0.37, 0.53 and 1, the logarithmic volatility of the arsenic component at 1,573 K is shown in Fig.6, in relation to the logarithmic mole fraction of AsO₂.₅ in the slag. The log α versus log Nₐs₂o₅ plots make a nearly straight line close to 4/3 for each slag system. Additionally, the X-ray diffraction analysis for the condensate in the transpiration experiments showed that it has a crystal structure of As₂O₅(arsenolite). Therefore, it is suggested that the vaporization of the arsenic component in the slag occurs according to eq. (12) and the volatility is in accord with the thermodynamic expression of eq. (13), on analogy of eq. (11).

\[
4 \text{AsO}_2.₅ (\text{in slag}) = \text{As}_2\text{O}_₅ (g) + 2\text{O}_₂ (g)
\]

\[\log \alpha = \frac{4}{3} \log N_{\text{As}_2\text{O}_₅} + \frac{4}{3} \log \gamma_{\text{As}_2\text{O}_₅} + \log a_o \]  

Where, \(\gamma_{\text{As}_2\text{O}_₅}\) is the Raoultian activity coefficient of As₂O₅ in the slag and \(a_o\) is the volatility of pure As₂O₅ which is a reference for the activity.

Owing to the very rapid dissociative evaporation of Ca₆AsO₄₂ during heating the sample up to the experimental temperature, it was not possible to carry out the transpiration experiment for the slags containing As₂O₅ in the present study.

3・2 Activity coefficient

Based on eqs. (6), (11) and (13), the Raoultian activity coefficients at dilute solution of SbO₁.₅, SbO₂.₅ and AsO₂.₅ in the CaO-SiO₂-FeO₁.₅ slags with \(Q(%\text{CaO}/(%\text{CaO}+%\text{SiO}_₂))\) of 0.37, 0.53 and 1 at 1,573 K can be derived, respectively, if \(a_o\) in each equation is known. Hence, \(\alpha_o\) for Sb₂O₅ and As₂O₅ were measured at 1,573 K in the present transpiration experiments and the obtained values are 0.381 and 0.464, respectively. However, it was not possible in the present experiment to accurately determine \(\alpha_o\) for Sb₂O₅ due to the very remark-

able evaporation and the resultant loss of most of the sample during heating the sample up to the experimental temperature. Hence, its volatility at 1,573 K was calculated by using the vapor pressure data₁³,₁⁴, which were obtained at a low temperature region between 923 and 1,023 K, and extrapolating to 1,573 K. Then, the calculated value of 22.1 was used for \(\alpha_o\) in eq. (6).

The results for the Raoultian activity coefficients of SbO₁.₅, SbO₂.₅ and AsO₂.₅ are listed in Table 1, where the references for these activities are pure liquid Sb₂O₅, solid Sb₂O₅ and solid As₂O₅, respectively. As a general trend, \(\gamma\) for each component decreases with increasing \(Q\) of the slag, in other word, basicity of the slag. \(\gamma_{\text{Sb}_2\text{O}_₅}\) and \(\gamma_{\text{As}_2\text{O}_₅}\) for the slags with \(Q\) of 0.53 and 1 are less than unity, that means, the activities deviate negatively from the Raoultian behavior.

The reported data on the activity coefficient of the antimony and arsenic components in the slag systems are extremely scarce. Takeda et al.₁⁵ reported \(\gamma_{\text{Sb}_2\text{O}_₅}\) of the values ranging between 2 and 4 in the iron-silicate slags, which were derived in an indirect way from the data on the distribution equilibria between the slag and copper phases. Their values are comparable with the present ones for the slags with \(Q\) of 0.37 and 0.53.

4. Conclusion

The volatility, \(\alpha\), of the antimony and arsenic components (SbO₁.₅, SbO₂.₅ and AsO₂.₅) in the CaO-SiO₂-FeO₁.₅ slags with \(Q(%\text{CaO}/(%\text{CaO}+%\text{SiO}_₂))\) of 0.37, 0.53 and 1 were determined at 1,573 K in the mole fraction range of these components in the slags between \(N = 0.005\) and 0.05 by the transpiration method with a vertical volatilization chamber. The log \(\alpha\) versus log \(N\) plots for each component and each slag represented a nearly straight line with a gradient close to that, which was predicted thermodynamically by assuming that SbO₂ and As₂O₅ are the predominant gas species. Hence, the present results strongly suggest that the antimony and arsenic components in the slag phase evaporate as Sb₂O₅(g) and As₂O₅(g), respectively. Once the vapor species could be specified, the vapor pressures of these oxide species were derived from the measured volatilities.

It is clarified that the volatility and vapor pressure decrease with increasing \(Q\) of the slag. This implies that control and adjustment of the slag basicity is of practical importance for eliminating the antimony and arsenic components from the fused oxides by means of volatilization.

The Raoultian activity coefficients, \(\gamma\), which were derived from the measured volatility, decrease with increasing \(Q\), and

<table>
<thead>
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<th>Slag</th>
<th>(Q = 0.37)</th>
<th>(Q = 0.53)</th>
<th>(Q = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SbO₁.₅-added</td>
<td>3.9</td>
<td>2.3</td>
<td>1.8</td>
</tr>
<tr>
<td>SbO₂.₅-added</td>
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<td>0.58</td>
<td>0.26</td>
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<tr>
<td>AsO₂.₅-added</td>
<td>1.5</td>
<td>0.91</td>
<td>0.25</td>
</tr>
</tbody>
</table>
$\gamma_{\text{SbO}_2.5}$ and $\gamma_{\text{AsO}_2.5}$ in the slags with $Q$ of 0.53 and 1 are smaller than unity.

References