Phase Relations and Activity of Antimony in Cu–Fe–S–Sb System at 1473 K

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To analyze the behavior of antimony in the copper smelting process, the phase relations and the activity of antimony in the miscibility gap of Cu–Fe–S–Sb system with antimony as a minor element have been determined at 1473 K by the quenching method and the double Knudsen cell-mass spectrometric method, respectively. The experiments have been conducted for the charges in the miscibility gap with mass%Fe/mass%Cu ratios of 0, 0.023, 0.072 and 0.113 with varying antimony content. The activity measurements indicate that the antimony activities in both the metal and matte phases show extremely negative deviation from the ideal behavior. The Raoultian activity coefficients at infinite dilution in the metal and matte phases are found to be almost constant against the charges in the miscibility gap and they are $1.1 \times 10^{-2}$ and $2.5 \times 10^{-1}$ for the metal and matte phases, respectively. The vapor pressures of predominant species of Sb, Sb$_2$ and SbS in the gas phase equilibrated with the immiscible solutions have been calculated on the basis of the determined activity coefficients and they are very small at less than 1 Pa even when the antimony content in the metal phase is increased up to 10 mass%.

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1. Introduction

Raw materials for copper production usually contain substantial amounts of the group VA elements in the periodic table, which are deleterious to the properties of the produced copper. These minor elements such as arsenic, antimony and bismuth are distributed to the matte and metal phases, which make removal problems during the copper smelting process. Outright elimination of these impurities is essential and has to be undertaken prior to or during the converting stage by means of slagging and volatilization.

An understanding of their behavior in the copper smelting process requires knowledge of their thermodynamic properties in the related metallurgical substances, of which the matte is of practical importance. It is mainly composed of copper, iron and sulfur, having compositions in an area surrounded by the Cu$_2$S–FeS tie line and the line bc in Fig. 1. By further removing iron and sulfur in the matte, the compositions shift into a range of the miscibility gap surrounded by abcd in Fig. 1 and then molten copper is finally produced.

As for antimony, the phase relations in the miscibility gap of the Cu–S–Sb ternary system have been reported by Asano and Wada. However, no data are available for the phase relations when antimony is added in the miscibility gap of the Cu–Fe–S system. The antimony activities in molten copper have been reported by Azakami and Yazawa, Bode et al., and Itoh and Azakami. Those in the Cu$_2$S–FeS mattes have been reported by Itagaki et al., and Roine and Jalkanen, while those in the Cu$_2$S matte equilibrated with copper at 1423 K by Hino and Toguri. Nagamori has analyzed the antimony activity in the Cu–S melts on the basis of statistical thermodynamics. However, the antimony activities in the Cu–Fe–S mattes existing in the miscibility gap, which contain antimony as a minor element, are not available.

Thus, following a study of the Cu–Fe–S–As system, the phase relations and antimony activities in the miscibility gap of the Cu–Fe–S–Sb system were determined at 1473 K by the quenching method and the double Knudsen cell-mass spectrometric method, respectively, in the present study.

2. Experimental

2.1 Determination of phase relations

The compositions of copper, iron and sulfur in the starting samples were fixed at the points of A, B, C and D in Fig. 1 and the equilibrium relations between the molten metal (copper alloy) and matte phases were determined at 1473 K when the amount of antimony added to the Cu–S and Cu–Fe–S systems varied. The samples of about $6 \times 10^{-3}$ kg were prepared by proportionally mixing the copper and iron sulfides, which were pyrometallurgically synthesized, as well as the copper and iron chips. High purity elemental antimony was also put in the sample to control the composition. The sample was vacuum-sealed in a quartz ampoule with an inner diameter of $8 \times 10^{-3}$ m and then it was kept in a vertical tube furnace at 1473 K for 72 ks to attain equilibrium. It was then rapidly cooled in water to obtain the metal and matte portions. After
separation, they were analyzed by inductively coupled plasma spectrometry (ICP) for the determination of antimony content. Iron content was determined by the volumetric titration with K₂Cr₂O₇ while sulfur content gravimetrically as BaSO₄.

### 2.2 Measurement of antimony activity

The principle, apparatus and experimental procedures have been described in detail in a previous paper,⁹ thus only a brief description is to be presented as follows.

The antimony activities were determined basing on the ratio of intensities of the antimony vapor between the samples in which the antimony activities are known and unknown. The intensity of the monatomic Sb species was determined in the present study because it was mostly prevailing of all the antimony species in the equilibrium vapor. Hence, the antimony activity, \( a_{\text{Sb}} \), is given by eq. (1).

\[
a_{\text{Sb}(u)} = \frac{p_{\text{Sb}(u)}}{p_{\text{Sb}}} \tag{1}
\]

Rearranging eq. (1) leads to eq. (2) which redefines the antimony activity in terms of the known (r) and unknown (u) antimony activities. The fundamental relationship between the measured ion intensity, \( I_{\text{Sb}^+(r)} \), and the partial pressure of Sb, \( p_{\text{Sb}} \), in the equilibrium vapor in the Knudsen cell is given by eq. (3).

\[
p_{\text{Sb}} = K I_{\text{Sb}^+} T
\]

Where \( K \) is a constant which includes a relative ionization cross section and multiplier efficiency, and \( T \) is temperature of the sample. Substituting eq. (3) into eq. (2) leads to eq. (4).

\[
a_{\text{Sb}(u)} = C [I_{\text{Sb}^+(u)}/I_{\text{Sb}^+(r)}] a_{\text{Sb}(r)} \tag{4}
\]

The constant \( C \), that compensates for the geometrical discrepancies between the two cells, can be determined for each particular pair of cells by performing a complimentary run using the same pure materials in both cells and copper was used in the present study.

In each experimental run, the reference and unknown samples of about 10⁻³ kg were put in a pair of the Knudsen cells made of alumina with an inner diameter of 8.8 × 10⁻³ m and a height of 14 × 10⁻³ m. An orifice with a diameter of 5 × 10⁻⁴ m was made at the side wall. The ratios of compositions between copper, iron and sulfur were fixed at the points of \( A, B, C \) and \( D \) in Fig. 1 and the antimony content was varied in the sample. The ionizing energy, which was employed to avoid fragmentation of the Sb species, was 2.08 × 10⁻¹⁸ J (13 eV). The background intensity was recorded by turning the cell holder by about 90°. The net ion intensity was obtained as the difference between them. The same procedure was repeated at least three times and the average intensity ratios were determined.

The compositions of the unknown sample were fixed in a miscibility gap with the metal (copper alloy) and matte phases. To determine the compositions of these phases equilibrated at 1473 K, rapidly cooled specimens are required for the chemical analysis. However, the rapid cooling was structurally not possible for the present mass spectrometer assembly. Hence, the compositions were evaluated from the data on the equilibrium phase relations determined in the separate experiments of the present study.

### 2.3 Reference samples for activity measurements

Two Cu–Sb binary alloys with the compositions of \( N_{\text{Sb}} = 0.054 \) and 0.100 were used for the reference samples in the present experiments to determine the activity of antimony in the Cu–Fe–S–Sb system. No data are available for the antimony activity in this system at the temperature of present experiments, 1473 K, though Itoh and Azakami⁴ determined the activity in a temperature range between 1173 and 1373 K using a Knudsen-effusion method. Hence, in the supplemental experiments of the present study, the activity values were derived at 1473 K by a non-isothermal isopiestic method.

About 1.5 × 10⁻³ kg of a starting Cu–Sb alloy sample was put at the bottom portion in a quartz ampoule with an inner diameter of 1.3 × 10⁻² m and a length of 1.2 × 10⁻¹ m. The ampoule had a small silica cup attaching to its top portion and about 5 × 10⁻⁴ kg of another Cu–Sb alloy sample was put in the cup. Then, the ampoule was sealed under vacuum of about 10⁻² Pa and kept in a heating furnace. It had a given temperature profile in the longitudinal direction so that the temperatures of the bottom and top portions in the ampoule might be fixed at 1473 and 1373 K, respectively, with a temperature uniformity of about 2 × 10⁻² m within ±2 K. It was confirmed in the preliminary experiments that the equilibrium between the alloy systems in both portions was made in 604.8 ks. Hence, the ampoule was heated for 604.8 ks, then, rapidly cooled in a water bath. The compositions of copper and antimony in the cooled alloy samples were determined by titration with EDTA and the ICP method, respectively.

Since Sb, Sb₂ and Sb₄ are prevailing in the gas species of antimonyⁱ⁰ and the vapour pressure of copper is considered to be negligible for the Cu–Sb alloy with the copper content less than \( N_{\text{Cu}} = 0.95 \)⁴ the following relationship is established between the samples at both portions in the closed ampoule, based on a principle of the isopiestic method that the total pressure is equal anywhere in a closed system once the equilibration is made in the system.

\[
(p_{\text{Sb}} + p_{\text{Sb}_2} + p_{\text{Sb}_4})_{1473 \text{K}} = (p_{\text{Sb}} + p_{\text{Sb}_2} + p_{\text{Sb}_4})_{1473 \text{K}} \tag{5}
\]

with

\[
n_{\text{Sb}(l)} = n_{\text{Sb}(g)} \tag{6}
\]

and

\[
p_{\text{Sb}} = K_a a_{\text{Sb}}^g \tag{7}
\]

The equilibrium constants, \( K_a \), for the reaction (6) can be known from the thermodynamic data table¹⁰ and the values of antimony activity at 1373 K are reported by Itoh and Azakami.¹³ By using these data and solving eq. (5), the activity of antimony in the Cu–Sb binary alloys at 1473 K can be derived. The obtained logarithmic Raoultian activity coefficients of antimony at 1473 K are plotted in Fig. 2 against (1 − \( N_{\text{Sb}} \))². It is known from Fig. 2 that the reference samples of \( N_{\text{Sb}} = 0.054 \) and 0.100 present the antimony activities of 1.67 × 10⁻³ and 3.39 × 10⁻³, respectively.
Table 1 Composition of samples, measured ion intensity ratios and activity of Sb in Cu–Fe–S–Sb system at 1473 K.

<table>
<thead>
<tr>
<th>Charge composition (mass%)</th>
<th>Matte phase</th>
<th>Metal phase</th>
<th>Reference (Cu–Sb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Fe/%Cu %Cu %S %Sb</td>
<td>$N_{Cu}$</td>
<td>$N_{Fe}$</td>
<td>$N_{S}$</td>
</tr>
<tr>
<td>0</td>
<td>0.904</td>
<td>0.046</td>
<td>0.021</td>
</tr>
<tr>
<td>0</td>
<td>0.509</td>
<td>0.126</td>
<td>0.364</td>
</tr>
<tr>
<td>0.023</td>
<td>0.666</td>
<td>0.334</td>
<td>—</td>
</tr>
<tr>
<td>0.023</td>
<td>0.668</td>
<td>0.327</td>
<td>0.005</td>
</tr>
<tr>
<td>0.062</td>
<td>0.342</td>
<td>0.006</td>
<td>0.893</td>
</tr>
<tr>
<td>0.054</td>
<td>0.347</td>
<td>0.002</td>
<td>0.876</td>
</tr>
<tr>
<td>0.023</td>
<td>0.351</td>
<td>0.005</td>
<td>0.866</td>
</tr>
<tr>
<td>0.023</td>
<td>0.346</td>
<td>0.002</td>
<td>0.851</td>
</tr>
<tr>
<td>0.023</td>
<td>0.310</td>
<td>0.010</td>
<td>0.834</td>
</tr>
</tbody>
</table>

0.072 | 0.624 | 0.034 | 0.342 | — | 0.966 | 0.010 | 0.024 | — | — | — |
| 0.072 | 0.619 | 0.039 | 0.340 | 0.002 | 0.947 | 0.008 | 0.020 | 0.025 | — | — |
| 0.072 | 0.612 | 0.040 | 0.346 | 0.002 | 0.932 | 0.007 | 0.021 | 0.040 | 0.054 | 0.400 | 6.00 × 10⁻⁴ |
| 0.072 | 0.622 | 0.037 | 0.338 | 0.003 | 0.927 | 0.008 | 0.020 | 0.045 | 0.054 | 0.625 | 8.00 × 10⁻⁴ |
| 0.072 | 0.628 | 0.032 | 0.336 | 0.004 | 0.906 | 0.007 | 0.024 | 0.063 | 0.054 | 0.960 | 1.41 × 10⁻³ |
| 0.072 | 0.659 | 0.030 | 0.305 | 0.006 | 0.893 | 0.007 | 0.025 | 0.075 | 0.10 | 0.481 | 2.49 × 10⁻³ |
| 0.072 | 0.680 | 0.031 | 0.319 | 0.008 | 0.867 | 0.008 | 0.026 | 0.099 | 0.10 | 0.936 | 4.63 × 10⁻³ |

0.113 | 0.547 | 0.108 | 0.345 | — | 0.950 | 0.030 | 0.020 | — | — | — |
| 0.113 | 0.541 | 0.109 | 0.348 | 0.002 | 0.926 | 0.026 | 0.021 | 0.027 | — | — |
| 0.113 | 0.554 | 0.103 | 0.341 | 0.002 | 0.926 | 0.025 | 0.018 | 0.031 | 0.054 | 0.380 | 5.51 × 10⁻⁴ |
| 0.113 | 0.553 | 0.101 | 0.343 | 0.003 | 0.915 | 0.025 | 0.021 | 0.039 | 0.054 | 0.465 | 7.86 × 10⁻⁴ |
| 0.113 | 0.569 | 0.097 | 0.331 | 0.003 | 0.905 | 0.022 | 0.019 | 0.054 | 0.054 | 0.776 | 1.26 × 10⁻³ |
| 0.113 | 0.552 | 0.095 | 0.350 | 0.003 | 0.881 | 0.024 | 0.020 | 0.075 | 0.10 | 0.401 | 2.48 × 10⁻³ |
| 0.113 | 0.541 | 0.102 | 0.351 | 0.006 | 0.865 | 0.024 | 0.018 | 0.093 | 0.10 | 0.597 | 4.09 × 10⁻³ |

3. Results

The composition of the charges, the mole fraction of the components in the coexisting metal and matte phases, the mole fraction of the reference Cu–Sb binary alloy, the intensity ratio of Sb and the calculated antimony activity taking the liquid standard state are summarized in Table 1 for given ratios of mass%Fe/mass%Cu in the charge.

3.1 Phase relations

The equilibrium compositions of the immiscible metal and matte phases in the Cu–Fe–S system at 1473 K are shown in Fig. 1. As far as the composition of the matte phase is concerned, the present result is in a good agreement with the literature data reported by Nagamori et al.11) and Chang et al.12) though the conjugate lines reported by Chang et al.12) considerably shift to the iron side of the metal phase. The sulfur content in the metal phase is in a good agreement with that reported by Nagamori et al.11) while smaller than the value reported by Nagamori et al.11)

The phase relations in the Cu–S–Sb ternary system at 1473 K are shown in Fig. 3. It is found that the slope of the conjugate lines increases with increasing antimony content in the charge. The sulfur content in the matte phase decreases with increasing antimony content in the charge, while that in the metal phase is almost constant at $N_s = 0.029–0.036$. The miscibility gap reported by Asano and Wada1 is shown with the broken lines in Fig. 3, which is very close to the present result.
Phase Relations and Activity of Antimony in Cu–Fe–S–Sb System at 1473 K

Fig. 3 Phase relations between the matte and metal phases within the miscibility gap of Cu–S–Sb ternary system with the charge composition of %S/%Cu = 0.118 at 1473 K.

Fig. 4 Phase relations between the matte and metal phases within the miscibility gap of Cu–Fe–S–Sb quarternary system with the charge composition of %Fe/%Cu = 0.072 at 1473 K.

The phase relations in the Cu–Fe–S–Sb system with mass%Fe/mass%Cu of 0.072 in the charge are shown in Fig. 4. The composition plots for the metal and matte phases are located on the approximately smooth lines, respectively. This suggests that all the conjugate lines in Fig. 4 are on a given cross section in the compositional Cu–Fe–S–Sb tetrahedron, which makes a contact to the bottom Cu–Fe–S plane. As in the Cu–S–Sb system, the slope of the conjugate line increases with increasing antimony content in the charge, while the sulfur content in the metal phase is almost constant. The similar phase relations were found for other Cu–Fe–S–Sb systems with different charge compositions.

The distribution ratios of antimony between the matte and metal phases, defined as \( L_{\text{m/c}} = \frac{\text{mass}\%\text{Sb in matte}}{\text{mass}\%\text{Sb in metal}} \), were calculated from the data in Table 1 and are shown in Fig. 5, in relation to the mole fraction of antimony in the metal phase. It is found that \( L_{\text{m/c}} \) is likely to be independent of the charges with \( A \sim D \) within scattering of the data, as illustrated with the broken line, and tends to slightly increase with increasing antimony content.

3.2 Activity and activity coefficient of antimony

The activity of antimony in the Cu–S–Sb system at 1473 K is shown in Fig. 6, in relation to the atomic fraction of antimony in the matte or metal phase. For comparison, the data at 1423 K reported by Hino and Toguri\(^7\) are illustrated with the broken lines in Fig. 6. The antimony activity in the metal phase shows an extremely large negative deviation from ideality, while that in the matte phase is much larger than in the metal phase for the same antimony concentration in each phase even though it still shows a considerably large negative deviation from the Raoult’s law. The present results are found to be in an excellent agreement with those by Hino and Toguri\(^7\) when the temperature difference between both experiments is not taken into account. The activity of antimony in the Cu–Fe–S–Sb system with mass%Fe/mass%Cu of 0.113 in the charge at 1473 K is shown in Fig. 7. It is found that the antimony activities in both phases are very similar to those in the Cu–S–Sb ternary system, showing large negative deviations from the Raoult’s law. The relationship between the antimony activity and the mole fraction of antimony in the matte or metal phase for other Cu–Fe–S–Sb systems with different mass%Fe/mass%Cu in the charge resembles to that shown in Fig. 7.

The Raoultian activity coefficients of antimony, \( \gamma_{\text{Sb}} \), in the matte phase at the miscibility gap of the Cu–S–Sb and Cu–Fe–S–Sb systems with different charge compositions at 1473 K are shown in Fig. 8, in relation to the mole fraction of antimony in the matte phase. It is found that \( \gamma_{\text{Sb}} \) is likely to be independent of the charges with \( A \sim D \) and log \( \gamma_{\text{Sb}} \) almost proportionally increases with \( N_{\text{Sb}} \) in the matte phase.
within scattering of the data. By the least square mean treatment, log $\{\gamma_{SB}\}$ can be expressed as

$$\log \{\gamma_{SB}\} = -0.596 + 43.0[N_{SB}] \quad (8)$$

with $[\gamma_{SB}^0]$ at infinite dilution of $2.5 \times 10^{-1}$.

The Raoultian activity coefficients of antimony, $[\gamma_{SB}]$, in the metal phase at the miscibility gap of the Cu–S–Sb and Cu–Fe–S–Sb systems with different charge compositions at 1473 K are shown in Fig. 9, in relation to the mole fraction of antimony in the metal phase. $[\gamma_{SB}]$ is also likely to be independent of the charges with $A \sim D$ and $\log [\gamma_{SB}]$ almost proportionally increases with $[N_{SB}]$, which can be expressed as

$$\log [\gamma_{SB}] = -1.95 + 5.84[N_{SB}] \quad (9)$$

with $[\gamma_{SB}^0]$ at infinite dilution of $1.1 \times 10^{-2}$.

4. Discussions

4.1 Distribution ratio of antimony

The distribution ratio of antimony between the matte and metal phases, as shown in Fig. 5, is almost independent of the mass%Fe/mass%Cu in the charge and this result will be thermodynamically analyzed on the basis of eq. (10), that is established for the phase equilibrium between the matte and metal phases.

$$[\gamma_{SB}][N_{SB}] = [\gamma_{SB}][N_{SB}] \quad (10)$$

By rearranging eq. (10) and converting the mole fraction to the mass% basis, the following equation is obtained.

$$L_{SB}^{m/c} = \frac{[\text{mass}\%\text{Sb}]/[\text{mass}\%\text{Sb}]}{[\text{mass}\%\text{Cu}]/[\text{mass}\%\text{Cu}]} = (\{n_T\}/[n_T])(/[\gamma_{SB}])/([\gamma_{SB}]) \quad (11)$$

where $[n_T]$ and $[n_T]$ are the mole amount of 0.1 kg in the matte and metal phases, respectively. $[\gamma_{SB}]$ and $[\gamma_{SB}]$ in eq. (11), as respectively shown in Figs. 8 and 9, are almost independent of the mass%Fe/mass%Cu in the charge. Hence, for $L_{SB}^{m/c}$ to be independent of the charge, $[n_T]/[n_T]$ in eq. (11) is also to be independent. $[n_T]/[n_T]$, which were calculated from the compositions in the equilibrium matte and metal phases in Table 1, are found to be between 1.21 and 1.27, that almost satisfies the condition required for the nondependency of $L_{SB}^{m/c}$ on the charge composition. This observed coordination among the $L_{SB}^{m/c}$, $\gamma_{SB}$ and compositions between/in the equilibrium matte and metal phases, in terms of their nondependency on the mass%Fe/mass%Cu in the charge, may suggest a validity of the present experimental results.

4.2 Influence of iron on antimony activity

One of the authors5) clarified that the copper and iron activities have a serious effect on the antimony activity in the matte with compositions close to those on a tie line connecting Cu$_2$S and FeS in the Cu–Fe–S system, due to a strong chemical affinity of antimony with copper and iron, and that the activity coefficient of antimony in the matte remarkably decreases with increasing copper or iron activity. According to Nagamori et al.,1) the copper activity in the miscibility gap of the Cu–Fe–S system at 1473 K shows a very large value of about 0.96, while the iron activity increases almost proportionally from 0 at mass%Fe/mass%Cu of 0 in the charge to about 0.5 at the mass%Fe/mass%Cu of 0.113. Hence, it is of interest to know how the iron activity, under the condition of very large copper activity, has an effect on the antimony activity in the miscibility gap of the Cu–Fe–S–Sb system.

The present experimental results, as shown in Fig. 8, strongly indicate that the influence of iron on the antimony activity is very small. This means that the effect to the antimony activity is
not intensified by iron when the copper activity significantly prevails to that of iron.

The activity coefficient of antimony in the metal phase with antimony, sulfur and iron as minor elements is given by eq. (12) as a function of interaction parameters when the second and higher order terms are neglected.

\[
\ln[\gamma_{\text{CuFeS}}] = \ln[\gamma_{\text{Cu}}^0] + \varepsilon_{\text{Cu}}^0 S_{\text{Cu}}^0 + \varepsilon_{\text{S}}^0 S_{\text{S}}^0 + \varepsilon_{\text{Fe}}^0 S_{\text{Fe}}^0
\] (12)

Because \([N_{\text{S}}]\) at the miscibility gap in the Cu–Fe–S system is almost constant against mass\%Fe/mass\%Cu in the charge, as shown in Fig. 1 and Table 1, the limiting activity coefficient of antimony, \(\gamma_{\text{CuFeS}}^0\), can be given by eq. (13)

\[
\ln[\gamma_{\text{CuFeS}}^0]_{\text{CuFe-S}} = \ln[\gamma_{\text{Cu}}^0] + \varepsilon_{\text{Cu}}^0 S_{\text{Cu}}^0 + \varepsilon_{\text{Fe}}^0 S_{\text{Fe}}^0
\] (13)

The present study, as shown in Fig. 9, clarified that \(\gamma_{\text{CuFeS}}^0\) in the matte phase is largest of these metalloid elements. This suggests that the interaction parameter of \(\varepsilon_{\text{Fe}}^0\) in eq. (13) is very small.

### 4.3 Comparison of limiting activity coefficients between metalloid elements

The limiting activity coefficients of some metalloid elements in the Cu–S–X ternary system with X=Se, Te, As or Sb at 1473 K are listed in Table 2. The value of \(\gamma_{\text{CuFeS}}^0\) in the metal phase is between those of \(\gamma_{\text{Cu}}^0\) and \(\gamma_{\text{S}}^0\), while the value of \(\gamma_{\text{Sb}}^0\) in the matte phase is largest of these metalloid elements. This suggests that antimony is least stable in matte (sulfide) phase.

According to the quasi-chemical model,\(^{14}\) the limiting activity coefficient of X, \(\gamma_{\text{X(Cu-S)}}\), in the Cu–S melt with the copper and sulfur mole fractions of \(N_{\text{Cu}}\) and \(N_{\text{S}}\) is given by eq. (14)

\[
N_{\text{Cu}}[\gamma_{\text{Cu(Cu-S)}}]/\gamma_{\text{X(Cu)}}]^{1/Z} + N_{\text{S}}[\gamma_{\text{S(Cu-S)}}]/\gamma_{\text{X(S)}}]^{1/Z}
= [1/\gamma_{\text{X(Cu)}}]^{1/Z}
\] (14)

Where Z is the coordination number, \(\gamma_{\text{Cu(Cu-S)}}\) and \(\gamma_{\text{S(Cu-S)}}\) are the Raoultian activity coefficients of copper and sulfur in the Cu–S melts, and \(\gamma_{\text{X(Cu)}}\) and \(\gamma_{\text{X(S)}}\) are the limiting activity coefficients of X in the Cu–X and S–X binary melts, respectively. The reported values of \(\gamma_{\text{X(Cu)}}\) in the Cu–X binary melts at 1473 K for X=Se,\(^{13}\) Te\(^{13}\) and As\(^{15}\) are 1.4 \times 10^{-2}, 1.2 \times 10^{-1} and 8.6 \times 10^{-3}, respectively and that for Sb can be evaluated to be 3.2 \times 10^{-2} from Fig. 2. The value of \(\gamma_{\text{X(Cu-S)}}\) is reported by Bale and Toguri,\(^{16}\) and \(\gamma_{\text{X(Cu)}}\) can be known from the partial pressure of S2 in the Cu–S melt, determined by Bale and Toguri,\(^{16}\) and the equilibrium partial pressure of pure liquid sulfur evaluated from the thermodynamic data.\(^{17}\) By putting these values in eq. (14) along with \(\gamma_{\text{X(S)}}\), which are listed in Table 2, \(\gamma_{\text{X(S)}}\) can be derived.

<table>
<thead>
<tr>
<th>X</th>
<th>(\gamma_{\text{X(Cu)}})</th>
<th>(\gamma_{\text{X(S)}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>6.5 \times 10^{-3}</td>
<td>5.8 \times 10^{-4}</td>
</tr>
<tr>
<td>Te</td>
<td>7.3 \times 10^{-2}</td>
<td>9.3 \times 10^{-3}</td>
</tr>
<tr>
<td>As</td>
<td>4.3 \times 10^{-3}</td>
<td>5.5 \times 10^{-2}</td>
</tr>
<tr>
<td>Sb</td>
<td>1.1 \times 10^{-2}</td>
<td>2.5 \times 10^{-1}</td>
</tr>
</tbody>
</table>

\(\gamma_{\text{Cu}}\): copper-rich phase

\(\gamma_{\text{Cu}}\): copper matte phase

### 4.4 Partial pressure of antimony component

It has been experienced in the practical operations of copper smelting that elimination of antimony by means of volatilization is very hardly attained in the copper-making stage of the converting process or in the reducing smelting to make the speiss phase which is mainly composed of copper, iron, arsenic and antimony. Hence, partial pressures of the antimony components in the metal and matte phases of the miscibility gap are of practical concern in the copper smelting.

Based on the activity coefficient of antimony in the metal and matte phases derived in the present study and the equilibrium constants for the related reactions as listed in Table 3, partial pressures of the predominant antimony gas species of Sb, Sb2 and SbS were calculated and is shown in Fig. 10. The partial pressure of SbO is shown with broken lines, which was evaluated for a condition that a slag phase with the FeO activity of 0.35, which corresponds to the iron silicate slag with saturated silica is to be equilibrated with the matte and metal phases. The partial pressures calculated for the miscibility gap with the charge of mass\%Fe/mass\%Cu with 0.113, as shown in Fig. 10, remarkably increase with increasing antimony content in the metal phase. It is found that Sb is prevailing in the range of higher antimony content and even

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(g)</td>
<td>-3.06</td>
<td>18)</td>
</tr>
<tr>
<td>2Sb(g) = Sb2(g)</td>
<td>-0.63</td>
<td>18)</td>
</tr>
<tr>
<td>Sb(g) + 1/2S2(g) = SbS(g)</td>
<td>3.6</td>
<td>19)</td>
</tr>
<tr>
<td>Sb(g) + 1/2O2(g) = SbO(g)</td>
<td>3.44</td>
<td>20)</td>
</tr>
</tbody>
</table>

![Fig. 10](image-url)
prevails over $S_2$. Nevertheless, the partial pressure of Sb at 10 mass% Sb in the metal still presents a small value of about 0.1 Pa. This suggests a difficulty in eliminating antimony from the miscibility gap system by means of volatilization.

5. Conclusions

The phase relations in the miscibility gap of the Cu–Fe–S–Sb system with antimony as a minor element were investigated at 1473 K by the quenching method. The double Knudsen cell-mass spectrometric method was successfully applied to determine the antimony activity coefficients in the metal and matte phases of the miscibility gap at 1473 K. The phase relations and antimony activities were determined for the charge compositions in the miscibility gap. The main results of the present study are summarized in the following.

1. The distribution ratio of antimony defined as $[\text{mass}\% \text{Sb in matte}] / [\text{mass}\% \text{Sb in metal}]$ is found to be less than unity and slightly increases with increasing antimony content in the metal phase but to be almost independent of the charge compositions in the miscibility gap.

2. The antimony activities show large negative deviations from the ideal behavior in both molten metal and matte phases.

3. The activity coefficients of antimony in both molten metal and matte phases are almost constant at a given antimony content against the charge composition in the miscibility gap.

4. The activity coefficients of antimony in the metal and matte phases in its dilute concentration change almost linearly with the antimony mole fractions and the following relationships are obtained, respectively.

$$
\log[\gamma_{\text{Sb}}]_{\text{metal}} = -1.95 + 5.84[N_{\text{Sb}}]
$$

$$
\log[\gamma_{\text{Sb}}]_{\text{matte}} = -0.596 + 43.0[N_{\text{Sb}}]
$$

with $\gamma_{\text{Sb}}^{\infty}$ at infinite dilution of $[\gamma_{\text{Sb}}^{\infty}]_{\text{metal}} = 1.1 \times 10^{-2}$ and $[\gamma_{\text{Sb}}^{\infty}]_{\text{matte}} = 2.5 \times 10^{-1}$.

5. The limiting activity coefficients of some metalloid elements in the Cu–S–X ternary system with X=Se, Te, As or Sb at 1473 K show that the value of $\gamma_{\text{Sb}}^{\infty}$ in the metal phase is between those of $\gamma_{\text{Te}}^{\infty}$ and $\gamma_{\text{Se}}^{\infty}$, while the value of $\gamma_{\text{Sb}}^{\infty}$ in the matte phase is largest of these metalloid elements. This suggests that antimony is least stable in the matte (sulfide) phase.

6. The vapor pressures of predominant Sb, Sb$_2$, and SbS$_2$ species in the gas phase equilibrated with the immiscible solutions in the Cu–Fe–S–Sb system, which were calculated on the basis of the obtained antimony activity coefficients, are very small at less than 1 Pa even when the antimony content in the metal phase is increased up to 10 mass%. This suggests that elimination of antimony by means of volatilization is very hardly attained once the metal phase appears in the copper smelting process.

REFERENCES