

# Thermochemical Nature of Minor Elements in Copper Smelting Mattes

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Equilibrium distribution measurements of As, Sb, and Bi between molten copper and white metal were conducted at 1473 K using a static system. The results of this investigation have been used to evaluate the activity of those elements in white metal, and the results are compared to other data in the literature. An empirical model is presented and used to correlate the activity of As and Sb in matte as a function of the number of vacant electronegative sites in the matte, VS, and a parameter,  $\psi$ , used to represent the strength of the bond between Fe and the minor element in a comparison to that which occurs with Cu. The activity coefficients of As and Sb in matte were found to be represented by the following equations:

$$\log \gamma_{\text{As}} / \gamma_{\text{As}}^{\text{SD}=0} = -0.256 + 93.0\text{VS}$$

$$\log \gamma_{\text{Sb}} / \gamma_{\text{Sb}}^{\text{SD}=0} = -0.192 + 73.0\text{VS}$$

where

$$\text{VS} = X_{\text{S}} + X_{\text{Me}} - X_{\text{Cu}}/2 - \psi X_{\text{Fe}}, \quad \text{Me} = \text{As or Sb}$$

and

$$\log \gamma_{\text{As}}^{\text{SD}=0} = 1.35 - 0.848X_{\text{Cu}_2\text{S}}$$

$$\log \gamma_{\text{Sb}}^{\text{SD}=0} = 2.11 - 0.841X_{\text{Cu}_2\text{S}}$$

$\psi$  approaches unity in white metal to 0.94 and 0.93 for As and Sb, respectively, at a Cu/Fe ratio of 2.5. The above equations can only be applied to copper-rich mattes deficient in sulfur. At Cu/Fe ratios below 2.5, the physicochemical character of the matte changes as the FeS molecules become the predominant species in the matte. In analyzing the data, it was necessary to evaluate the interaction parameters  $\epsilon_{\text{As}}^{\text{S}}$ ,  $\rho_{\text{As}}^{\text{S}}$ , and  $\rho_{\text{As}}^{\text{S,As}}$ , which have been found to have values of 11.7, -27.4, and 11.6, respectively.

## I. INTRODUCTION

COPPER concentrates contain a number of minor elements among which As, Sb, and Bi must be limited in the final product to ensure its commercial viability. Arsenic forms  $\text{Cu}_3\text{As}$  particles in annealed copper and can reduce the electrical conductivity of the metal by 23 pct at an arsenic content of only 0.1 wt pct Bismuth in copper at a concentration of 0.001 wt pct renders the host metal brittle, and both antimony and arsenic raise the recrystallization temperature of copper.<sup>[1,2]</sup>

During smelting, most of the As, Sb, and Bi is usually eliminated by volatilization and slagging during the roasting, smelting, and converting processes. Although considerable work has been conducted in evaluating the behavior of minor elements during smelting, the thermochemical behavior of those elements in matte and slag are not fully understood. Since copper concentrates are becoming increasingly impure, it is essential to elucidate the thermodynamic nature of As, Sb, and Bi in order to

establish effective ways of eliminating those impurities during smelting. Accordingly, in the present investigation, the authors have evaluated the activity of As, Sb, and Bi in both matte and white metal.

Extensive use is made of data already in the literature.<sup>[3-27]</sup> The results obtained in this investigation are compared and reconciled with that data. For the sake of brevity, a review of the earlier studies is presented in the discussion, where the results of those works can be critically evaluated and compared with the results of the present investigation.

## II. EXPERIMENTAL

The equilibrium distribution of As, Sb, and Bi between molten copper and white metal has been investigated using a static distribution technique.

### A. Materials

Reagent grade materials with 4 to 5 nines purity were used throughout this investigation. The phases were prepared from copper metal (shot and powder) and copper sulfide ( $\text{Cu}_{1.8}\text{S}$ ), which were mixed in such proportions to yield 1 g of white metal and 1 g of copper. Arsenic, antimony, and bismuth, in their metallic state, were added to the admixtures such that their content corresponded to either 0.1, 1.0, or 2.5 wt pct.

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## B. Experimental Procedure

The admixture for a specimen was placed in a cylindrical alumina crucible (12-mm ID by 25 mm in height) and sealed in a silica ampoule (14-mm ID by 100 mm in height) under a vacuum of  $(4 \text{ to } 6) \times 10^{-4} \text{ atm}^*$  with a hydrogen-oxygen flame. The sealed ampoules were placed in a ceramic fiber brick which was placed in a DELTECH\*\* furnace, as shown in Figure 1.

\*1 atm =  $1.013 \cdot 10^5 \text{ Pa}$ .

\*\*DELTECH is a trademark of Deltech Engineering, Inc., New Castle, DE.

The specimens were heated slowly to avoid exploding the ampoules. The specimen temperature, which was monitored with a Pt/Pt-13 pct Rh thermocouple, was raised slowly to 723 K over 6 hours and then held at that temperature for approximately 15 hours to allow excess sulfur present in the copper sulfide ( $\text{Cu}_{1.8}\text{S}$ ) and arsenic (when present) to alloy with other metals in the system. By so doing, the vapor pressures of these species never exceeded one atmosphere.

Upon completing the initial heat treatment, the specimen temperature was raised slowly to 1473 K and maintained at that temperature for 24 hours, a time period adequate to attain equilibrium. The temperature of a specimen varied by only  $\pm 2 \text{ K}$  during an experiment. Upon completing an experiment, the ampoules were quickly removed from the furnace (approximately 5 to 10 seconds), quenched in water, and the specimens recovered.

The phases of the quenched specimens were carefully separated and stored for chemical analysis. The metallic and nonmetallic phases, in general, separated easily, leaving only a small residue of white metal on the copper button. That residue was removed by grinding. A thin layer which appeared to be copper was observed on the top surface of some of the white metal specimens. The metallic layer is believed to have precipitated from the specimen upon cooling and thus was not removed. All of the specimens were analyzed for their minor element content using atomic absorption.

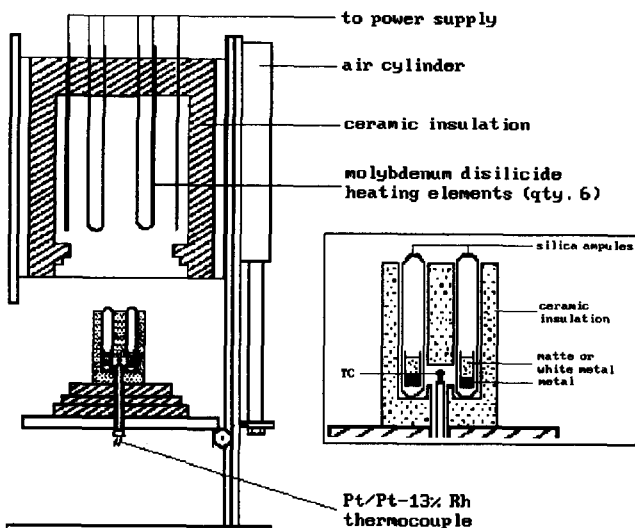


Fig. 1—Experimental apparatus.

A mass balance for the minor element was conducted for each distribution experiment. The calculations revealed that all of the antimony experiments conducted at 2.5 wt pct Sb and one conducted at 1.0 wt pct Sb were faulty. In dissolving the phases associated with those experiments, a precipitate formed. It is believed that the precipitate was an antimony chloride. The loss of antimony in the precipitate would account for the discrepancy in the mass balance. It is possible that precipitation of antimony chlorides may have influenced the results of the other experiments reported for Sb in Table I.

## III. RESULTS

The results of the chemical analyses for the minor elements are reported in Table I. Phase equilibrium studies and the analyzed data for the minor elements can be used to determine the composition of the equilibrated phases. Mole fractions for Cu, S, and the minor elements were determined using the procedures described below.

The miscibility gap for white metal in equilibrium with molten copper has been studied extensively.<sup>[9-16]</sup> The effect of minor elements on that gap has also been examined.<sup>[13,4,16]</sup> From those studies, it has been determined that the mole fraction of sulfur in the metal phase at the miscibility gap remains constant for the concentrations of As, Sb, and Bi utilized in the present work. Similarly, it has been observed that the mole fraction of copper in white metal at the two-phase equilibrium is constant for the concentration of minor elements employed in this investigation. Given these constraints, the following equations were solved simultaneously to obtain values of the mole fractions of Cu, S, and the minor elements in the phases equilibrated:

$$X_{\text{Cu}}^{\text{W}} = 0.676 \quad [1]$$

$$\text{wt pct ME} = \frac{100 X_{\text{ME}}^{\text{W}} MW_{\text{ME}}}{X_{\text{Cu}}^{\text{W}} MW_{\text{Cu}} + X_{\text{S}}^{\text{W}} MW_{\text{S}} + X_{\text{ME}}^{\text{W}} MW_{\text{ME}}} \quad [2]$$

$$X_{\text{S}}^{\text{W}} = 1 - X_{\text{Cu}}^{\text{W}} - X_{\text{ME}}^{\text{W}} \quad [3]$$

and for molten copper,

$$X_{\text{S}}^{\text{C}} = 0.0275 \quad [4]$$

Table I. Experimental Results

Specimen*		Wt Pct As	Wt Pct Sb	Wt Pct Bi
B0.10	W	0.014	0.016	0.031
	C	0.16	0.22	0.20
B1.0	W	0.19	0.092	—
	C	1.85	1.22	—
B2.5	W	0.46	—	0.58
	C	4.64	—	3.70
B2.5**	W	0.46	—	—
	C	4.56	—	—
B2.5†	W	0.44	—	—
	C	4.58	—	—

\*A specimen was prepared for each minor element.

\*\*Equilibration time of 12 h.

†Equilibration time of 36 h.

$$\text{wt pct ME} = \frac{100 X_{\text{ME}}^C MW_{\text{ME}}}{X_{\text{Cu}}^C MW_{\text{Cu}} + X_{\text{S}}^C MW_{\text{S}} + X_{\text{ME}}^C MW_{\text{ME}}} \quad [5]$$

$$X_{\text{Cu}}^C = 1 - X_{\text{S}}^C - X_{\text{ME}}^C \quad [6]$$

In these equations,  $X_i$  is the mole fraction of the  $i$ th species, the superscripts  $W$  and  $C$  represent the phases white metal and molten copper, and ME stands for any one of the minor elements.

The results of those calculations are reported in Table II and have been used along with the data in Table I to calculate the distribution coefficients which are listed in Table II. The coefficients have been calculated in terms of both weight percent ( $L^{C/W}$ ) and mole fraction ( $l^{C/W}$ ) ratios. Again,  $C$  and  $W$  are used to designate molten copper and white metal, respectively.

#### IV. DISCUSSION

##### A. Equilibration Considerations

The static distribution technique was employed in the present work to avoid the volatilization problem that has affected the results obtained in other investigations.<sup>[19,20]</sup> Although volatilization is not a problem with a closed static system, fixing the state of the system is an issue.

The number of variables that must be set to fix the state of the system can be calculated from the Gibbs phase rule

$$F = C - N - P + 2 - R \quad [7]$$

where  $F$  is the degrees of freedom,  $C$  is the number of components,  $N$  is the number of independent chemical reactions which occur between the components,  $P$  is the number of phases, and  $R$  represents any stoichiometric restrictions. White metal equilibrated with molten copper in the presence of a vapor phase involves the species

$\text{Cu}_2\text{S}$ ,  $\text{Cu}$ ,  $\text{S}$ , and  $\text{S}_2$  for which two independent chemical reactions can be written. Applying the phase rule to this system sets  $F$  equal to 1, a condition which can be satisfied by fixing the temperature.

The addition of a minor element to the system offers an additional degree of freedom, in that  $C$  is now 5. The system cannot be controlled by external parameters. This does not, however, pose a serious problem. By using a closed system and using the same starting materials, it is possible to reproduce results.

An example of both the reproducibility that can be achieved with this technique and the time necessary to reach equilibration is presented in Figure 2. Three experiments involving white metal and molten copper doped with 2.5 wt pct As were conducted at equilibration times of 12, 24, and 36 hours. Results in the literature indicate that equilibration should be achieved for the size of systems employed in this investigation in a time under 8 hours.<sup>[19]</sup> The distribution coefficients shown in Figure 2 reveal that equilibration was achieved in less than 12 hours. Twenty-four hours were used in all further experiments to ensure equilibration. The fact that all values for  $L_{\text{As}}^{C/W}$  in the figure are approximately 10 highlights the reproducibility that can be achieved with this technique.

##### B. Activity Calculations

The activities and activity coefficients of the minor elements in the copper alloy,  $\gamma_i^C$ , have been evaluated using the interaction parameters listed in Table III and the solubility data in Table II; again, the superscript  $C$  represents molten copper. The analysis involves the equation

$$\ln \gamma_i^C = \ln \gamma_i^{C,\infty} + \epsilon_i^i X_i + \epsilon_i^S X_S + \epsilon_i^j X_j + \rho_i^i X_i^2 + \rho_i^S X_S^2 + \rho_i^j X_j^2 + \rho_i^{S,i} X_i X_S + \rho_i^{i,j} X_i X_j \quad [8]$$

Table II. Melt Compositions and Distribution Ratios

Specimen		$X_{\text{Cu}}$	$X_{\text{S}}$	$X_{\text{ME}}$	$L_i^{C/W}$	$l_i^{C/W}$	$\gamma_i^W$
Arsenic							
B0.10	W	0.676	0.324	$9.4 \cdot 10^{-5}$	11	14	0.15
	C	0.971	0.0275	$1.3 \cdot 10^{-3}$			
B1.0	W	0.676	0.323	$1.3 \cdot 10^{-3}$	9.7	12	0.15
	C	0.955	0.0275	$1.5 \cdot 10^{-2}$			
B2.5	W	0.676	0.321	$3.1 \cdot 10^{-3}$	10	12	0.20
	C	0.934	0.0275	$3.8 \cdot 10^{-2}$			
B2.5*	W	0.676	0.321	$3.1 \cdot 10^{-3}$	9.9	12	0.20
	C	0.934	0.0275	$3.8 \cdot 10^{-2}$			
B2.5**	W	0.676	0.321	$3.0 \cdot 10^{-3}$	10	13	0.21
	C	0.934	0.0275	$3.9 \cdot 10^{-2}$			
Antimony							
B0.10	W	0.676	0.324	$0.70 \cdot 10^{-4}$	14	16	0.29
	C	0.971	0.0275	$1.1 \cdot 10^{-3}$			
B1.0	W	0.676	0.324	$4.0 \cdot 10^{-4}$	13	16	0.30
	C	0.966	0.0275	$6.3 \cdot 10^{-3}$			
Bismuth							
B0.10	W	0.676	0.324	$8.0 \cdot 10^{-5}$	6.5	7.5	28
	C	0.971	0.0275	$6.0 \cdot 10^{-4}$			
B2.5	W	0.676	0.323	$1.5 \cdot 10^{-3}$	6.4	7.6	28
	C	0.971	0.0275	$1.14 \cdot 10^{-2}$			

\*Equilibration time of 12 h.

\*\*Equilibration time of 36 h.

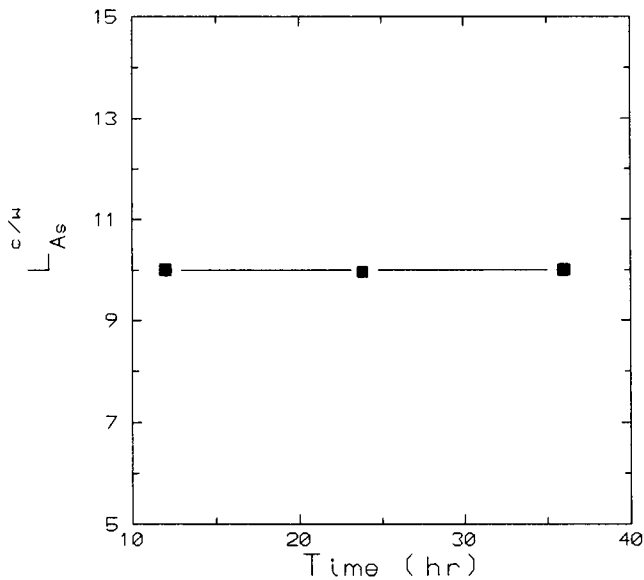


Fig. 2—Equilibrium distribution was reached in less than 10 h.

where  $\gamma_i^{c,\infty}$ ,  $\epsilon_i^i$ , and  $\epsilon_i^j$  are the Henrian activity coefficient, the first-order self-interaction parameter, and the first-order ternary-interaction parameter, respectively. The other terms in the equation are the second-order self-interaction parameter,  $\rho_i^i$ , and the second-order ternary-interaction parameters,  $\rho_i^j$  and  $\rho_i^{ij}$ .

The values for  $\epsilon_{As}^S$ ,  $\rho_{As}^S$ , and  $\rho_{As}^{S,As}$  in Table III for molten copper have been calculated from the work of Hino and Toguri.<sup>[3]</sup> Those authors reported a value of 19.9 for  $\epsilon_{As}^S$ . Use of this value yielded values for the activity coefficient,  $\gamma_{As}^c$ , which when compared to other data, appeared to be too small. This finding was tested against the original data in Reference 3 with the same result (Figure 3). The ternary interaction parameter,  $\epsilon_{As}^{S,As}$ , would normally be obtained by plotting values of  $(\ln \gamma_{As}^c)_{X_{As} \rightarrow 0}$  as a function of  $X_S$ . The value of  $\epsilon_{As}^S$  is obtained by evaluating the slope of the line in the graph as  $X_S$  goes to zero. The data in Reference 3 could not be evaluated in this manner, as values for the activity of As were reported at ever increasing values of  $X_{As}$ .

Values for  $\epsilon_{As}^S$ ,  $\rho_{As}^S$ , and  $\rho_{As}^{S,As}$  were obtained from the data in Reference 3 using a least-squares technique. That technique yielded the following equations:

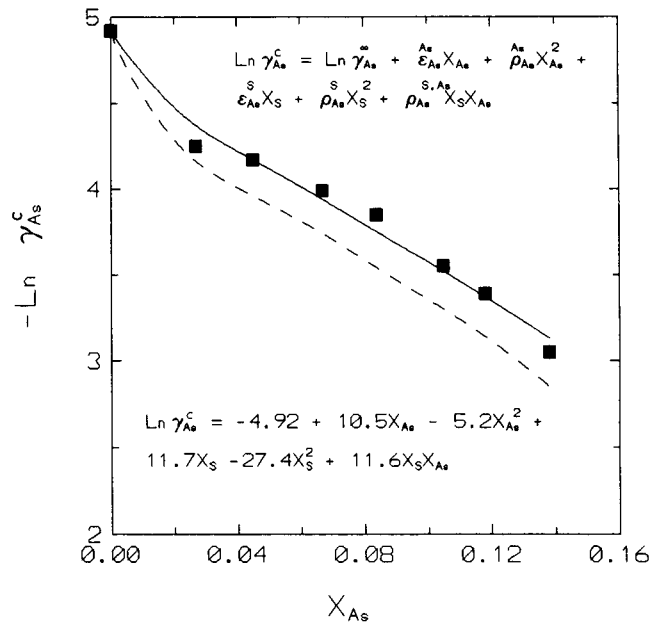


Fig. 3—The experimental points are from Ref. 3. The dotted line has been calculated using the interaction parameter recommended by Hino and Toguri. The solid line has been calculated using interaction parameters obtained from the least-squares routine.

$$\left. \begin{aligned}
 \epsilon_{As}^S \sum_{k=1}^n (X_S^2)_k + \rho_{As}^S \sum_{k=1}^n (X_S^3)_k \\
 + \rho_{As}^{S,As} \sum_{k=1}^n (X_S^2 X_{As})_k &= \sum_{k=1}^n (X_S Z)_k \\
 \epsilon_{As}^S \sum_{k=1}^n (X_S^3)_k + \rho_{As}^S \sum_{k=1}^n (X_S^4)_k \\
 + \rho_{As}^{S,As} \sum_{k=1}^n (X_S^3 X_{As})_k &= \sum_{k=1}^n (X_S^3 Z)_k \\
 \epsilon_{As}^S \sum_{k=1}^n (X_S^3)_k + \rho_{As}^S \sum_{k=1}^n (X_S^4)_k \\
 + \rho_{As}^{S,As} \sum_{k=1}^n (X_S^3 X_{As})_k &= \sum_{k=1}^n (X_S^3 Z)_k
 \end{aligned} \right\} [9]$$

Table III. Henrian Activity Coefficients and Interaction Parameters for As, Sb, and Bi in Molten Copper at 1473 K

Parameter	Minor Element - <i>i</i>			Reference
	As	Sb	Bi	
$\gamma_i^\infty$	$8.6 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$	1.47	3, 4, and 24
$\epsilon_i^S$	11.7	6.1	35	PW,* 4, and 16
$\epsilon_i^{Fe}$	—	—	0	21
$\epsilon_i^{As}$	10.5	—	5.9	3 and 22
$\epsilon_i^{Sb}$	—	10.3	-11	4 and 23
$\epsilon_i^{Bi}$	5.9	-11	-2.3	22, 23, and 24
$\rho_i^j$	-5.2	-5.2	—	3 and 4
$\rho_i^S$	-27.4	—	—	PW and 3
$\rho_i^{S,i}$	11.6	—	—	PW and 3

\*PW = present work.

where

$$Z = \ln \gamma_{As}^C - \ln \gamma_{As}^{C,\infty} - \varepsilon_{As}^{As} X_{As} - \rho_{As}^{As} X_{As}^2 \quad [10]$$

Solving these equations simultaneously yielded the following results:

$$\varepsilon_{As}^S = 11.7 \quad [11]$$

$$\rho_{As}^S = -27.4 \quad [12]$$

$$\rho_{As}^{S,As} = 11.6 \quad [13]$$

These values have been used to calculate the activity of As in molten copper and the results compared to the values calculated with Hino and Toguri's<sup>[3]</sup> value for  $\varepsilon_{As}^S$  and their experimental results. The comparison is presented in Figure 3, wherein it can be observed that the least-squares technique yields greater agreement in calculated activity coefficients than that obtained with the value of  $\varepsilon_{As}^S$  proposed by Hino and Toguri.

A similar least-squares analysis was performed with the data in Reference 4 for antimony. The results were inconclusive, as sulfur does not have as strong an influence on the activity of Sb in copper as it does on As. Additional data with larger variations in both the sulfur and antimony content are needed before the least-squares routine can be successfully utilized.

There is general agreement on the Henrian activity coefficient for Bi in molten copper. The temperature dependence on that coefficient is represented by the following equation:<sup>[24]</sup>

$$\log \gamma_{Bi}^{C,\infty} = \frac{1686}{T} - 0.76 \quad [14]$$

These results have been used to calculate the activity coefficients of the minor element in molten copper and the white metal. Those values for the white metal are presented in Table II and in Figures 4 through 6, where the values obtained in this work are compared to values reported by other investigators. In performing the comparison, the authors have evaluated all distribution data from References 5, 25, and 27 in the manner described above. Activity data obtained from vapor pressure measurement<sup>[3,4,26]</sup> have been used in the comparison without

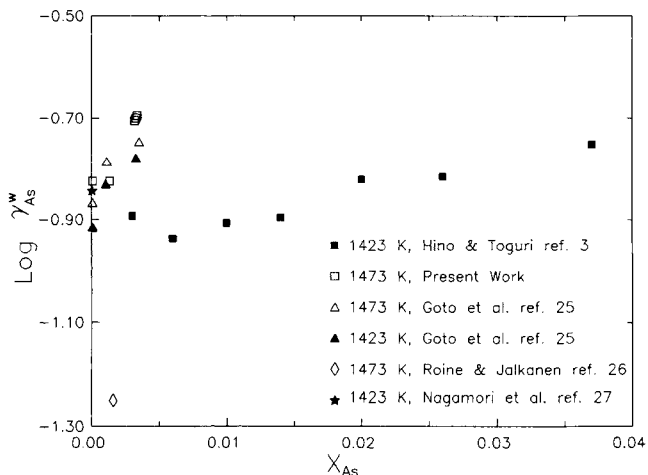


Fig. 4—Comparison of values for the activity coefficient of As in white metal.

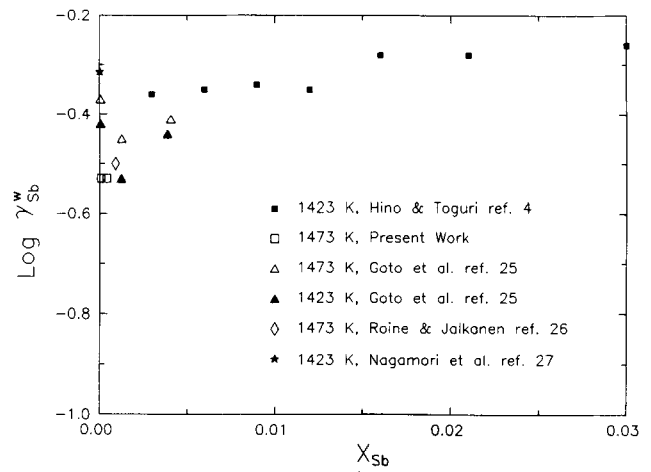


Fig. 5—Values reported for the activity coefficient of Sb in white metal.

reevaluation. The data points attributed to Roine and Jalkanen<sup>[26]</sup> in Figures 4 through 6 were, for the sake of comparison, obtained by extrapolating their results for white metal to the copper-saturated condition.

A quick glance at Figures 4 through 6 may lead one to conclude that there is considerable discrepancy in the data. One should note, however, that the Y-axes in these figures have been expanded and that the data in the literature are in remarkable agreement, with only one exception. The value of  $\gamma_{As}^w$  attributed to Roine and Jalkanen<sup>[26]</sup> in Figure 4 is approximately half the value reported by other investigators and calculated in this study. This difference may be due to the extrapolation or to the experimental technique employed. Roine and Jalkanen used a transportation technique to obtain values for the vapor pressures of the minor elements. That technique is subject to a number of potential errors. In spite of those problems, Roine and Jalkanen obtained values for  $\gamma_{Sb}^w$  and  $\gamma_{Bi}^w$  which are in excellent agreement with other values in the literature, as shown in Figures 5 and 6.

Henrian activity coefficients for As, Sb, and Bi in white metal can be evaluated as they would be for dissolution in any metal solvent. The process involves plotting

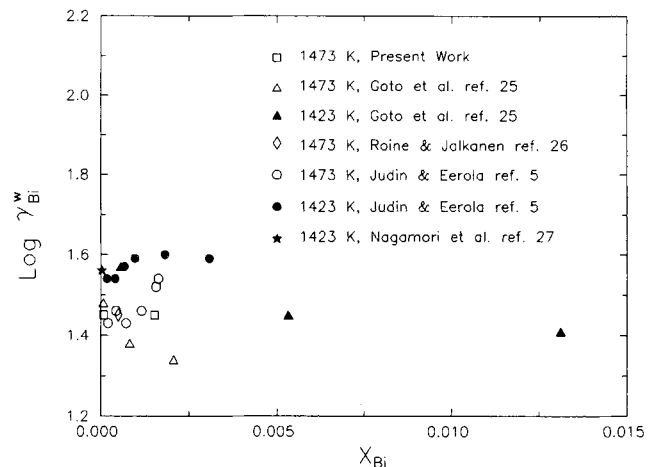


Fig. 6—Comparison of values for  $\gamma_{Bi}^w$ .

In  $\gamma_i^W$  as a function of the mole fraction of  $i$  in white metal and evaluating the intercept. The superscript,  $W$ , is again used to designate white metal. If the analytical technique described above was applied to each study presented in Figures 4 through 6, there would be little discrepancy in the derived values for the Henrian activity coefficients,  $\gamma_{As}^{W,\infty}$ ,  $\gamma_{Sb}^{W,\infty}$ , and  $\gamma_{Bi}^{W,\infty}$ .

While there would be little disagreement in the data regarding values for  $\gamma_{As}^{W,\infty}$ ,  $\gamma_{Sb}^{W,\infty}$ , and  $\gamma_{Si}^{W,\infty}$ , the effect of As concentration on  $\gamma_{As}^W$  is not so clear. The distribution data obtained in this investigation and by Goto *et al.*<sup>[25]</sup> suggest a stronger dependence of  $\gamma_{As}^W$  on  $X_{As}$  than that reported by Hino and Toguri.<sup>[3]</sup> The latter investigators used a Knudsen cell and mass spectrometer to evaluate the vapor pressure of arsenic over copper-saturated white metal. Surface depletion of As may account for the lower values for  $\gamma_{As}^W$ . Additional analysis presented below, however, suggests the results are actually in closer agreement than the results in Figure 4 suggest.

The effect of arsenic content on  $\gamma_{As}^W$  has been evaluated using the data of both the present work and Goto *et al.*<sup>[25]</sup> The results of the analysis are presented in Figure 7, where the agreement in the data is easily seen. A least-squares analysis suggests that the compositional dependence of  $\gamma_{As}^W$  can be represented by

$$\log \gamma_{As}^W = -0.85 + 41X_{As} \quad [15]$$

Analysis of this equation yields values for  $\gamma_{As}^{W,\infty}$  and  $\epsilon_{As}^{As}$  of 0.14 and 94, respectively, at metal saturation.

### C. Representation of Activity Data for Minor Elements in Matte and White Metal

Comparison of activity data for minor elements in matte is more complex, as the data in the literature have been obtained from melts with significant compositional variation. Itagaki and co-workers have proposed a solution to this problem.<sup>[17,18]</sup> They found that the activity coefficients for As and Sb in matte equilibrated with speiss can be represented by a single line (for each element) when the logarithm of the activity coefficient is plotted against the logarithm of the sum of the activities of Cu

and Fe. Furthermore, they *proposed* that "a similar effect of the iron and copper activities on the activity of arsenic can also be expected" for matte systems not saturated with metal or speiss.<sup>[17]</sup>

One of the authors (DCL) has, for some time, felt that a single line resulting from a plot of  $\log \gamma_{As}^M$  (or  $\log \gamma_{Sb}^M$ ) vs  $\log (a_{Cu} + a_{Fe})$  would depend on the range of compositions employed. It is unlikely that the interaction between As or Sb in matte with copper and iron will be identical over all values for the sum of  $a_{Cu}$  and  $a_{Fe}$ .

Roine and Jalkanen's data<sup>[26]</sup> have been used to test the concept that the activity coefficient of As and Sb in matte can be represented as a function of the sum of the activities of Cu and Fe in the melt. Roine and Jalkanen conducted their experiments at both low values and constant mole fractions for the minor elements. Thus, the values for the activity coefficients calculated from their data approach the Henrian value and are not subject to the influence of variable concentration. The results of that analysis are presented in Figure 8. The data in these figures reveal that the Cu/Fe molar ratio has an impact on  $\gamma_{As}$  and  $\gamma_{Sb}$ . In general, a decrease in the Cu/Fe ratio leads to an increase in the activity coefficient of the minor elements. This result can be interpreted as representing the nature of bonds between the minor elements and both Cu and Fe. From these results, one can conclude that there is greater attraction between both As and Sb with Cu than exists with Fe.

The suggestion that the activity coefficients of As and Sb might be represented, for each element, as a single function of the logarithm of the sum of the activities of Cu and Fe does not appear to hold for nonmetal-saturated mattes. In addition, the use of  $\log (a_{Cu} + a_{Fe})$  as the independent variable is less than ideal. Values for  $\log (a_{Cu} + a_{Fe})$  are difficult to determine and subject to considerable error.

The phase diagram for the Ni-S-As system reveals that As tends to substitute for sulfur.<sup>[28]</sup> Thus, Roine and Jalkanen's data<sup>[26]</sup> have been plotted as a function of the sulfur deficiency for matte, which has been approximated as follows:

$$SD = X_S - \frac{X_{Cu}}{2} - X_{Fe} \quad [16]$$

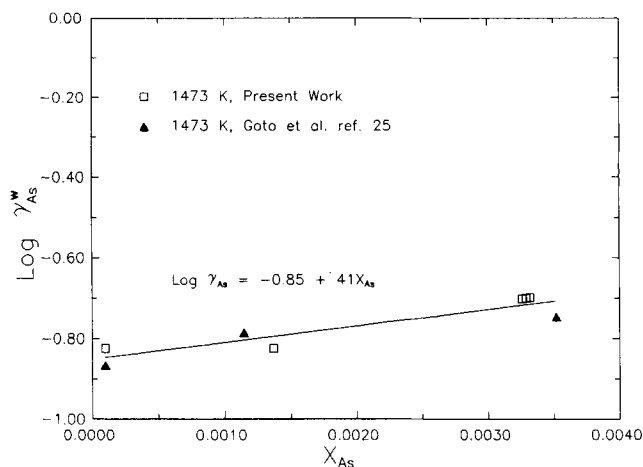


Fig. 7—The values of  $\gamma_{As}^W$  obtained by Goto *et al.*<sup>[25]</sup> and the values obtained in the present work compare favorably. Both research groups used the distribution technique.

The sulfur deficiency is zero for compositions on the  $Cu_2S$ -FeS pseudo binary line, negative when the matte composition is on the metal-rich side of the binary line, and positive when the composition is located on the sulfur-rich side of the binary line. The results of those figures are presented in Figure 9. Examination of those figures reveals that the new plots suffer from some of the same disadvantages associated with similar plots using  $\log (a_{Cu} + a_{Fe})$ . Variations in the Cu/Fe ratio shift the lines for the activity coefficients, as was observed in Figure 8. Small errors in measurements of either the sulfur deficiency or  $\log (a_{Cu} + a_{Fe})$  can lead to substantial errors in the evaluation of the activity coefficients given the steep slope of the curves in Figures 8 and 9.

The use of the sulfur deficiency, even though it is similar to the sum of the activities of Cu and Fe, has a significant advantage. The sulfur deficiency can be

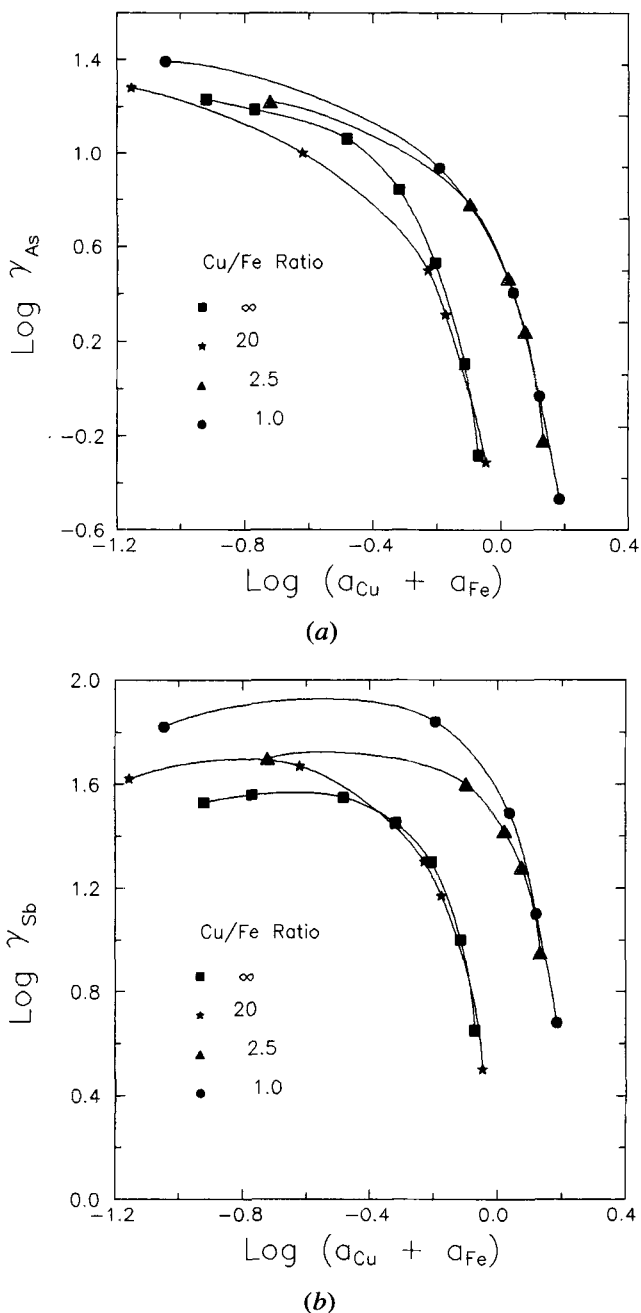


Fig. 8—The activity coefficient data for (a) As and (b) Sb in matte and white metal plotted as a function of the combined activities of Cu and Fe in the melt.<sup>1261</sup>

determined easily and accurately from compositional measurements.

While there is an advantage to be gained in using the sulfur deficiency over  $\log (a_{\text{Cu}} + a_{\text{Fe}})$ , a comparison of Figure 8 with Figure 9 reveals that the advantage does not extend to the correlation of activity data. The discrepancy in the activity data can be reconciled through a fundamental analysis of the system. An examination of binary phase diagrams for the minor elements in solution with Cu and Fe reveals that As and Sb form intermetallic compounds with both metals. The Bi-Cu and the Bi-Fe phase diagrams indicate that these systems behave differently. There is little mutual solubility of Bi in either Cu or Fe, and no intermetallics are formed. All

three minor elements form multiple sulfides. Unfortunately, the thermochemical nature of the sulfides is not well defined.

When the sulfur deficiency is negative, there are sulfur sites for minor elements to occupy and to coordinate with Cu and Fe. The binary phase diagrams for As and Sb indicate an energetic attraction between these elements and Cu and Fe. Since Roine and Jalkanen<sup>1261</sup> ran experiments at a fixed concentration of the minor elements, a decrease in the sulfur deficiency leaves more unfilled sulfur sites. The Cu and Fe atoms that surround those sites will seek to lower their energy by associating with As or Sb. The resultant effect should be a decrease in the activity for As and Sb, as has been observed with the activity coefficients in Figure 9. Furthermore, it is expected that the capacity of matte to adsorb As and Sb should increase with an increase in the number of vacant sulfur sites.

For sulfur deficiency greater than 0, however, no sites are available, and therefore, minor elements most likely enter the matte as sulfides. From the experimental data in Figure 9, it appears that arsenic sulfides are not readily dissolved in matte, whereas a decrease in the activity coefficient for Bi as the sulfur deficiency increases from 0 suggests that bismuth sulfides are dissolved in high sulfur content mattes. Antimony appears to dissolve in high sulfur content mattes, particularly at low Cu/Fe ratios.

The analysis suggests that there are two processes involved in the dissolution of minor elements in matte and white metal. With sulfur depletion, the minor elements can be dissolved in the matte through interaction with metallic Cu and Fe. In high sulfur content mattes, no free metallic species are available, and thus, the minor elements enter the matte as sulfides. In the analysis that follows, the authors focus on the sulfur-depleted melts and As and Sb, minor elements that form intermetallic compounds with both Cu and Fe.

#### D. Sulfur-Deficient Melts

For the dissolution of As and Sb in matte, the melt can be viewed as consisting of molecules of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ . The bonding in those molecules is not purely covalent. Both  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  exist as polarized molecules. The sulfur is electronegative, while copper and iron are electropositive. As such, there will be a tendency for the molecules of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  to align themselves such that the sulfur atom in a sulfide molecule will be surrounded by copper and iron atoms in other sulfide molecules. In sulfur-deficient melts, the excess metal species associate with bonded sulfur atoms and attempt to form a covalent bond with the sulfur. The unbound metal atoms have a higher chemical potential and would share an electron with a more electronegative atom if present. The very presence of unbound metal atoms effectively creates nonmetallic sites that, in the case of sulfur-deficient melts, can be viewed as electronegative in character. Arsenic and antimony dissolve in matte on electronegative sites. The experimental results in Figure 9 reveal that for a fixed sulfur deficiency, the activity coefficients for both As and Sb increase with increasing iron content in the matte. Iron does not effectively bond with As and Sb in

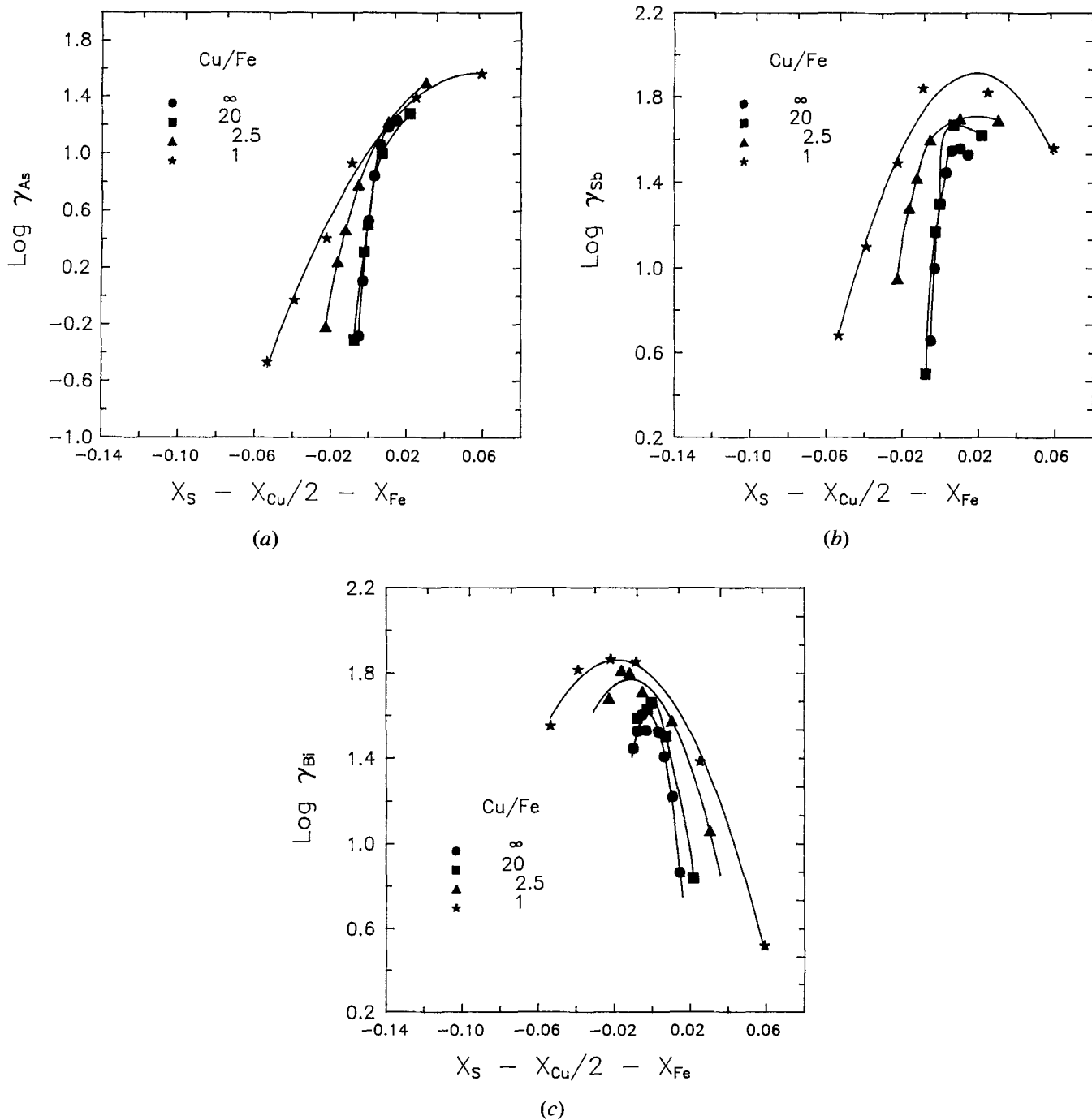


Fig. 9—The activity coefficient data for As, Sb, and Bi in matte and white metal plotted as a function of the sulfur deficiency of the matte.<sup>[26]</sup>

matte as does Cu. Accordingly, the sulfur deficiency can be recast as follows:

$$SD' = X_S - \frac{X_{Cu}}{2} - \psi X_{Fe} \quad [17]$$

where  $\psi$  accounts for the difference in the bonding characteristics between Cu and Fe.

Psi has been used to quantify the difference in bonding between the minor elements and the free Cu and Fe in the matte. Values for  $\psi$  have been determined by fitting the activity coefficient data for matte (with a specific Cu/Fe ratio) to the activity coefficient data for white

metal. In the fitting process, psi was varied, and a least-squares technique was used to test the fit with each value of  $\psi$ . The value of  $\psi$  that yielded the highest Pearson correlation coefficient was selected for use at the specified Cu/Fe ratio. Values for  $\psi$  can be approximated by the following equations:

$$\psi = \frac{-0.11}{Cu/Fe} + 0.99 \quad (\text{As, } Cu/Fe \geq 2.5) \quad [18]$$

$$\psi = \frac{-0.086}{Cu/Fe} + 0.96 \quad (\text{Sb, } Cu/Fe \geq 2.5)$$



Psi is an empirical function that varies with the Cu/Fe ratio. In a sulfur-deficient white metal, minor elements are surrounded by unbound Cu in proportion to the number of covalent bonds. The Cu-ME molecules are surrounded by molecules of  $\text{Cu}_2\text{S}$ . This situation changes as the Cu/Fe ratio decreases. At a sulfur deficiency equal to 0 and a Cu/Fe molar ratio of 2, the minor element (probably present as a sulfide) is surrounded by an equal number of  $\text{Cu}_2\text{S}$  and FeS molecules. A decrease in sulfur deficiency will alter this condition and will leave the minor element surrounded by unbound metal which will most likely be Fe, as  $\text{Cu}_2\text{S}$  is more thermodynamically stable than FeS. The minor element will form an intermetallic with the iron, which itself will be surrounded by  $\text{Cu}_2\text{S}$  and FeS in near equal amounts.

The experimental data of Roine and Jalkanen<sup>[26]</sup> have been fitted to  $X_S - X_{\text{Cu}}/2 - \psi X_{\text{Fe}}$ , as shown in Figure 10 for arsenic. The data utilized have been limited to those with a value of sulfur deficiency less than 0. The results indicate that for Cu/Fe molar ratios equal to and greater than 2.5, the activity coefficient data can be correlated to the data for white metal.

At a Cu/Fe ratio of 1, no such correlation is possible. The composition of the matte at this value of the ratio is  $2/3\text{FeS}$  and only  $1/3\text{Cu}_2\text{S}$ . The physicochemical behavior of the matte is dominated by FeS at Cu/Fe equals 1. Because a single correlation can be achieved with white metal and mattes with Cu/Fe ratios equal to and greater than 2.5 (Figure 10), it is apparent that  $\text{Cu}_2\text{S}$  dominates the physicochemical behavior of the matte at the stated compositions.

In order to further include the physicochemical character of the matte in analyzing the behavior of minor elements in matte, all results are presented as a ratio of the activity coefficient to that which exist (for the specific minor element) for a specified Cu/Fe ratio at a sulfur deficiency of 0. Values of  $\log \gamma_i^{\text{SD}=0}$  have been taken from Roine and Jalkanen<sup>[26]</sup> and are plotted in Figure 11.

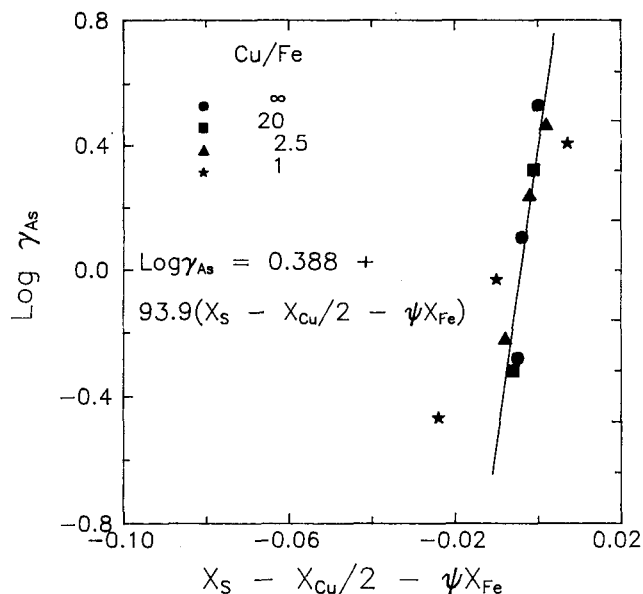
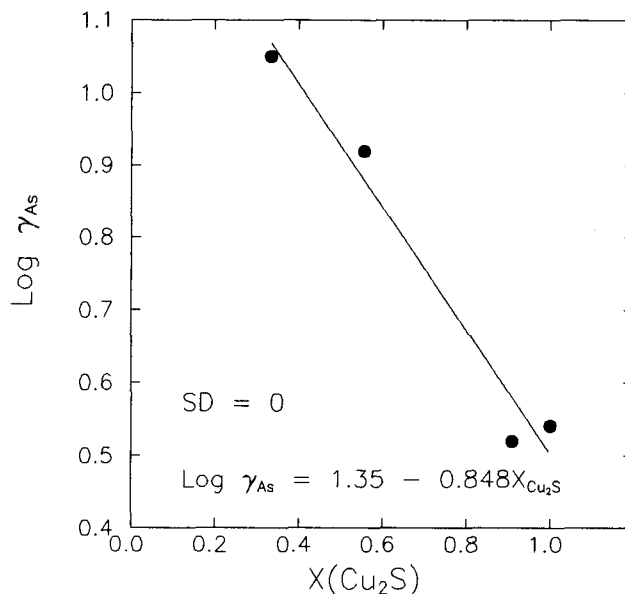
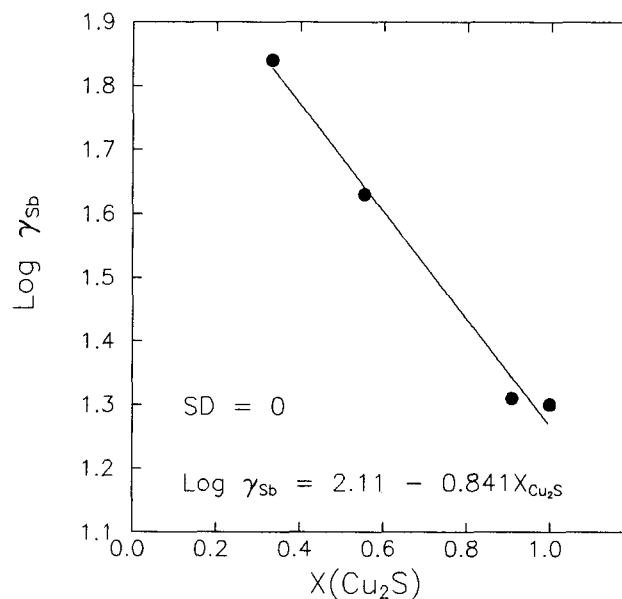


Fig. 10—The activity data for As in sulfur-deficient and copper-rich mattes represented as a single line using the modified sulfur deficiency,  $\text{SD}'$ .<sup>[26]</sup>



(a)



(b)

Fig. 11—Values for the activity coefficient for (a) As and (b) Sb in matte at  $\text{SD} = 0$ .<sup>[26]</sup>

The results of the present investigation compare favorably with Roine and Jalkanen's data for As,<sup>[26]</sup> as shown in Figure 12. The comparison for antimony, as shown in Figure 13, is not as good. This difference may be due to the problems reported earlier in analysis for Sb. Hino and Toguri's results<sup>[3,4]</sup> for  $\gamma_{\text{As}}^w$  and  $\gamma_{\text{Sb}}^w$  appear to increase only slightly as the sulfur deficiency decreases. An opposite trend exists with Roine and Jalkanen's data. The results from those workers reveals a rapid decrease in the activity coefficients for both As and Sb with decreasing values of  $\text{SD}'$ . The difference in results is due to the variation of concentration of minor elements employed.

Roine and Jalkanen<sup>[26]</sup> conducted their experiments at

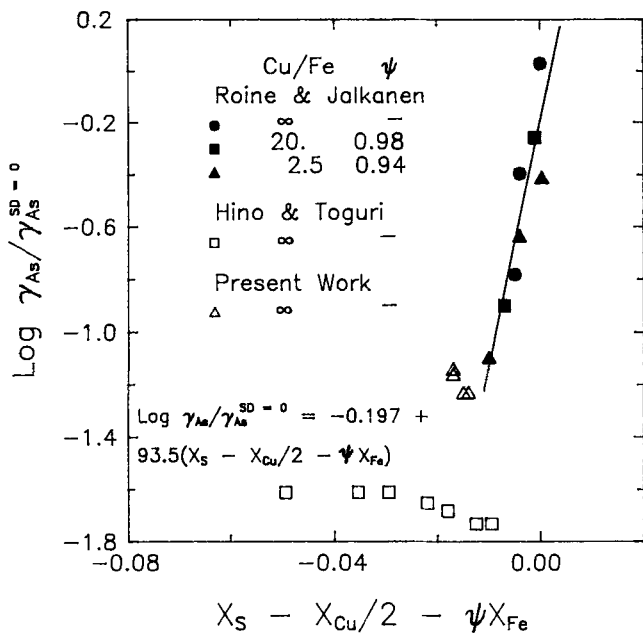


Fig. 12—Comparison of values for the activity coefficient of As in matte and white metal plotted against the modified sulfur deficiency. Data from Refs. 3, 26, and the present work.

nearly constant and very dilute concentrations of minor elements. Thus, the sulfur deficiency for their work reflects the number of vacant sites in a sulfur-deficiency matte. The concentration of As and Sb varied only slightly in the present work and significantly in the investigation conducted by Hino and Toguri.<sup>[3,4]</sup> That variation can impact the number of vacant sites and thereby the ease with which minor elements can be incorporated in the matte.

The number of vacant sites is approximated by the equation

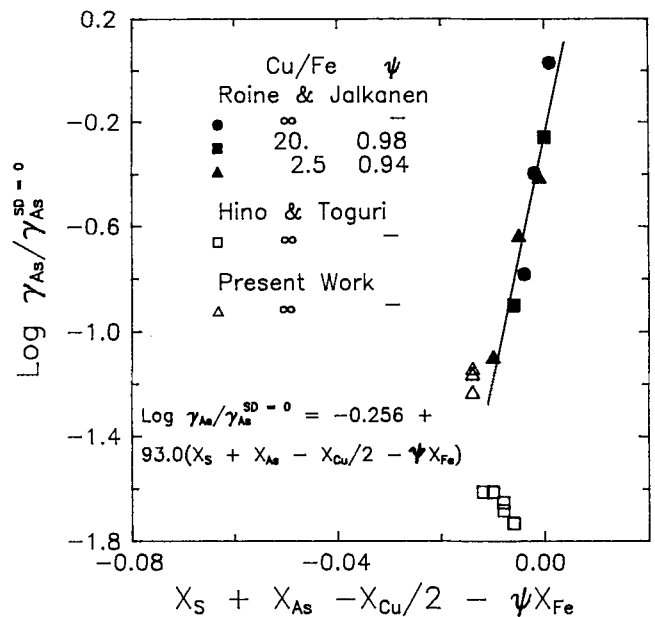


Fig. 14—The comparison presented in Fig. 12 is significantly enhanced when the data are plotted against the number of vacant sites  $VS$  the modified sulfur deficiency. Data from Refs. 3, 26, and the present work.

$$VS = X_S + X_{Me} - \frac{X_{Cu}}{2} - \psi X_{Fe} \quad [19]$$

A negative value for  $VS$  reflects the presence of unpaired Cu and Fe and therefore vacant sites. The activity coefficient data for As and Sb have been plotted as a function of  $VS$  in Figures 14 and 15. A comparison of these figures with Figures 12 and 13 reveals that the change in the abscissa has little effect on the present work and that conducted by Roine and Jalkanen.<sup>[26]</sup> This is not an unexpected result, given the small concentrations of minor

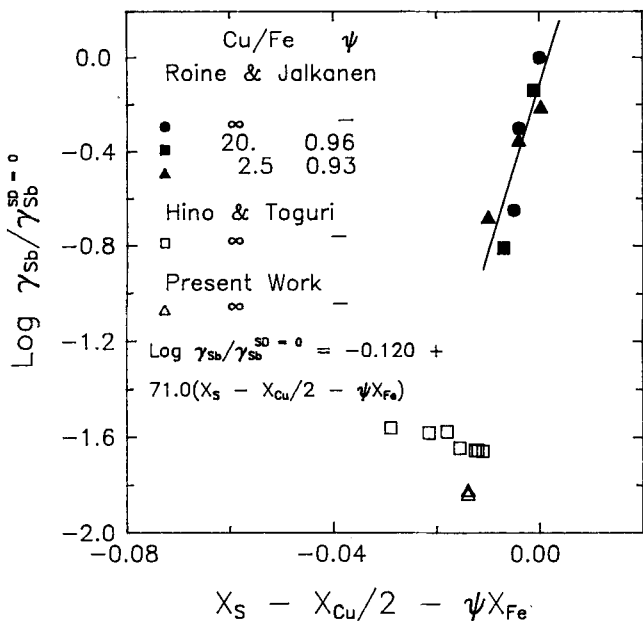


Fig. 13—Comparison of values for the activity coefficient of Sb in matte and white metal plotted against the modified sulfur deficiency. Data from Refs. 4, 26, and the present work.

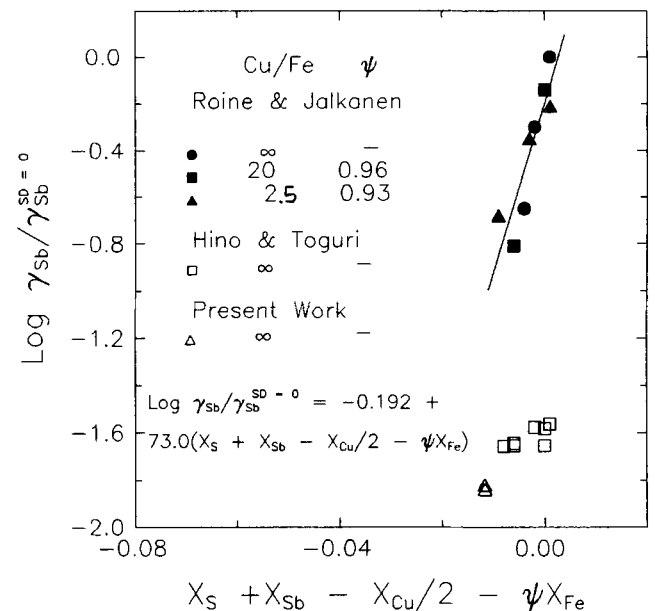


Fig. 15—Plotting the data against the number of vacant sites minimizes the discrepancy in the data observed in Fig. 13. Data from Refs. 4, 26, and the present work.

elements employed in those studies. The change in the abscissa has a striking effect on the results of Hino and Toguri.<sup>[3,4]</sup> Their results now appear to be in general conformity with those of both the present study and Roine and Jalkanen. This is particularly true of the arsenic data. Any variation in Hino and Toguri's data from that of the other studies represented in Figures 14 and 15 can, at least in part, be attributed to the fact that the temperature of their experiments was 50 K lower than the others. Another potential source of difference involves the effect of minor element concentration. It would appear that the concentration effect is small in comparison to the influence vacant sites have on the activity coefficient of As and Sb in matte.

## V. SUMMARY AND CONCLUSIONS

Empirical models serve a purpose in helping identify controlling parameters which can be examined and incorporated in quantitative models. In this article, the physicochemical behavior of As, Sb, and Bi in matte has been examined and an empirical model presented for their dissolution. The following observations have been made.

1. There is relative agreement in activity data for As, Sb, and Bi at infinitely dilute concentrations in copper-saturated white metal. This agreement can be observed in Figures 4 through 6. An analysis of the data of Hino and Toguri<sup>[3]</sup> in Figure 4 suggests that the activity of As in copper-saturated white metal increases only gradually with As concentration. The data obtained in the present study and analysis of the distribution data of Goto *et al.*,<sup>[25]</sup> results obtained at lower As concentrations than that employed by Hino and Toguri, reveal a much stronger dependence of the activity on the arsenic concentration. This discrepancy may be related to the different concentrations of As employed or error in the self and ternary interaction parameters for As in molten copper. The latter could significantly affect the results obtained through distribution measurements. Surface depletion of the white metal in Hino and Toguri's results may also account for the difference. The concentration effect does not appear to be a problem for  $\gamma_{Sb}^W$  and  $\gamma_{Bi}^W$ .
2. Itagaki *et al.*<sup>[17,18]</sup> have proposed that the activity coefficient of As and Sb in matte can be represented as a function of the log ( $a_{Cu} + a_{Fe}$ ). This relationship should only work for sulfur-deficient mattes in which free metal atoms exist. Mattes containing an excess of sulfur should dissolve minor elements as sulfides. The concept that the activity coefficients for As and Sb in matte of variable composition can be represented by a single line when plotted against log ( $a_{Cu} + a_{Fe}$ ) has been tested with Roine and Jalkanen's data.<sup>[26]</sup> No correlation was observed, as shown in Figure 8.
3. Correlation of the activity coefficient data with the sulfur deficiency yields a similar correlation, as experienced with log ( $a_{Cu} + a_{Fe}$ ). Both variables, the sulfur deficiency and log ( $a_{Cu} + a_{Fe}$ ), reflect the concentration of free metal in sulfur-deficient mattes. The sulfur deficiency does have a distinct advantage in

that it can be calculated from knowledge of the composition of the matte. The composition data for Cu, S, and Fe, however, must be expressed to three significant figures.

The lack of correlation of the activity coefficient data with the sulfur deficiency has been attributed to variation in the strength of bonding between minor elements and both Cu and Fe. The sulfur deficiency has been redefined as

$$SD' = X_S - \frac{X_{Cu}}{2} - \psi X_{Fe}$$

where  $\psi$  is used to reflect the difference in the bonding strength for Cu and Fe.

4. The analysis for values of  $\psi$  has revealed that the chemical character of the matte changes at Cu/Fe ratios between 1 and 2. The activity coefficient data for As and Sb at the Cu/Fe ratio of 1 could not be correlated with the white metal data, as was accomplished with data at Cu/Fe ratios of 20 and 2.5. The change in the chemical character of the matte is attributed to the fraction of FeS in the melt.
5. The correlation of the activity coefficients with the sulfur deficiency has been improved by the inclusion of the concentration of the minor element itself. The resulting factor more accurately reflects the actual number of vacant sites and thereby the concentration of free metal. With the use of vacant sites to represent the activity coefficient data, higher concentrations of minor elements can be effectively represented.

The experimental results of Hino and Toguri<sup>[3,4]</sup> for As and Sb do not agree with the other experimental result plotted in Figures 12 and 13. Hino and Toguri used larger concentrations of As and Sb than other investigators. When their data are plotted as a function of the number of vacant sites, as has been done in Figures 14 and 15, there is greater agreement in the data. It is to be noted, however, that the effect of concentration of minor elements is not represented with the use of vacant sites. It appears that the concentration effect is not as strong as the effect associated with the concentration of free metal.

## NOMENCLATURE

$a_i$	Raoultian activity for the <i>i</i> th species
$l_i^{O/P}$ , $L_i^{O/P}$	distribution coefficient of the <i>i</i> th species as partitioned between phases O and P on a molar basis and weight basis, respectively
ME	minor element
$MW_i$	molecular weight of the <i>i</i> th species
SD, SD'	sulfur deficiency for matte as defined by Eqs. [16] and [17].
VS	vacant sites as defined by Eq. [19]
$X_i$	mole fraction of <i>i</i> th species
$\epsilon_i$ , $\epsilon_i^j$	first-order interaction parameters
$\gamma_i$	Raoultian activity coefficient of the <i>i</i> th species
$\rho_i^i$ , $\rho_i^j$ , $\rho_i^{i,j}$	second-order interaction parameters
$\psi$	an empirical function that relates the effectiveness of Fe in the interaction with minor elements As and Sb to that of Cu

## Superscripts

C	molten copper
M	matte
W	white metal
$\infty$	infinite dilution

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## REFERENCES

1. W.H. Dennis: *Metallurgy of the Non-Ferrous Metals*, 2nd ed., Sir Isaac Pitman and Sons, London, 1961, pp. 169-72.
2. *Metals Handbook*, 8th ed., T. Lyman, ed., ASM, Metals Park, OH, 1961, vol. 1, p. 1008.
3. M. Hino and J.M. Toguri: *Metall. Trans. B*, 1986, vol. 17B, pp. 755-61.
4. M. Hino and J.M. Toguri: *Metall. Trans. B*, 1987, vol. 18B, pp. 189-94.
5. V. Judin and M. Eerola: *Scand. J. Metall.*, 1979, vol. 8, pp. 128-32.
6. K. Friedrich and M. Wachlert: *Metall. Erz.*, 1912-1913, vol. 10, pp. 976-79.
7. C.S. Smith: *Trans. AIME*, 1938, vol. 128, pp. 325-36.
8. D. Smith: Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1952.
9. F. Johannsen and H. Vollmer: *Erzmetall*, 1960, vol. 13, pp. 313-22.
10. K. Sudo: *Sci. Rep. Res. Tohoku Univ.*, 1958, vol. 10, pp. 435-52.
11. C.W. Bale and J.M. Toguri: *Can. Metall. Q.*, 1976, vol. 15, pp. 3-18.
12. J. Schmiedl, V. Repcak, and S. Cempa: *IMM Trans.*, 1977, vol. 86, pp. C88-C91.
13. W.A. Krivsky: Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1954.
14. R. Schuhmann and O.W. Moles: *Trans. AIME*, 1951, vol. 191, pp. 235-41.
15. K. Bornemann and K. Wagenmann: *Ferrum*, 1913-1914, vol. 11, pp. 276-82, 293-94, 303, 306, 310-13, and 331-32.
16. V. Judin and M. Eerola: *Scand. J. Metall.*, 1981, vol. 10, pp. 201-04.
17. K. Itagaki, M. Hino, and A. Yazawa: *Erzmetall*, 1983, vol. 36, pp. 59-64.
18. K. Itagaki, Y.H. Lee, and A. Yazawa: *Erzmetall*, 1984, vol. 37, pp. 179-81.
19. M. Nagamori, P.J. Mackey, and P. Tarasoff: *Metall. Trans. B*, 1975, vol. 6B, pp. 295-301.
20. J.B. See and W.J. Rankin: National Institute for Metallurgy, Report 2099, South Africa, 1981.
21. X.H. Jiang, D.C. Lynch, and W.G. Davenport: *Metall. Trans. B*, 1988, vol. 19B, pp. 427-32.
22. X.H. Jiang, D.C. Lynch, and W.G. Davenport: *Can. Metall. Q.*, 1988, vol. 27, pp. 23-26.
23. X.H. Jiang, D.C. Lynch, and W.G. Davenport: *IMM Trans. C*, 1989, vol. 98, pp. C144-C146.
24. X.H. Jiang, D.C. Lynch, and W.G. Davenport: *IMM Trans. C*, 1988, vol. 97, pp. C102-C104.
25. S. Goto, O. Ogawa, and I. Jimbo: *Australia-Japan Extractive Metallurgy Symp. Proc.*, Australian Institute of Metallurgy, Sydney, Australia, 1980, pp. 127-32.
26. A. Roine and H. Jalkanen: *Metall. Trans. B*, 1985, vol. 16B, pp. 129-41.
27. M. Nagamori, P.J. Mackey, and P. Tarasoff: *Metall. Trans. B*, 1975, vol. 6B, pp. 197-98.
28. R.A. Yund: *Am. J. Sci.*, 1962, vol. 260, pp. 761-82.