Vapor Pressure Determination of Arsenic Activity in a Molten Cu-Fe-S Matte

K. H. LAU, R. H. LAMOREAUX, and D. L. HILDENBRAND

The activity of As in a molten copper smelting matte of composition 35.0 mass pct Cu, 35.8 mass pct Fe, and 29.9 mass pct S has been derived from vapor pressure measurements at 1336 K. The initial As doping level was 1.6 mass pct. Mass spectrometry showed the principal vapor phase species to be As_2; smaller amounts of AsS and S_2 were also present. The activity coefficient of As in the matte, γ (As), was found to have the value 0.7 ±0.2 (mole fraction)$^{-1}$ in the composition range studied. Activity values found in the present study were an order of magnitude smaller than those determined by an isopiestic method, and were about two orders of magnitude greater than those derived from measurements of As distribution between copper and white metal. The vapor pressure method is believed to be more direct and reliable; sources of error in the various methods are discussed.

I. INTRODUCTION

THE distribution of trace elements (As, Sb, Bi, Pb) among white metal, slag, matte, and vapor phases in copper smelting processes is of interest for reasons of product quality and emission control. However, the behavior of the trace elements under process conditions is not well understood, and much of the existing thermodynamic data used in analyzing these systems are of uncertain accuracy. This state of affairs is due in large part to the inherently difficult nature of the laboratory experiments required in studying the high temperature chemistry and solution behavior of the complex phases involved.

One part of the overall problem concerns the thermodynamic activities of trace elements dissolved in the molten matte (Cu-Fe-S) phase and the use of activity data in evaluating the transfer of these elements between the various pyrometallurgical phases and the vapor phase. Itagaki et al[1] reported activity data on arsenic in Cu-Fe-S mattes, obtained by equilibrating matte samples at one temperature with the vapor phase over condensed arsenic at lower temperature. This appears to be the only information available on arsenic in low grade mattes. As described later, some data on arsenic in high grade mattes containing <4 mass pct Fe can be derived by combining the distribution measurements of Nagamori et al[2] and Asano and Wada[3] with the data of Lynch[4] on activity of As in Cu. Derived arsenic activities in the low and high grade mattes differ by two orders of magnitude, much more than one would expect for such a change in matte composition. In view of such differences, the general scarcity of trace element activity data, and the susceptibility of such measurements to serious systematic errors, we undertook a new investigation using a different experimental method based on vapor pressure.

We present here a description of the method and some initial measurements on arsenic activities in a low grade molten Cu-Fe-S matte. Sources of error are evaluated, the results are compared with those described above, and the prospects for extending and improving the measurements are discussed.

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II. EXPERIMENTAL

A. Apparatus and Procedure

The torsion-effusion technique was used to determine the total pressure of gases in equilibrium with a specimen of matte doped with arsenic. In this technique, which has been described in previous publications,[5,6] the substance under investigation is contained in an effusion cell suspended from a torsion fiber. Vapor effusing from orifices offset from the suspension axis induces a rotation of the cell which is directly related to the pressure within. Under molecular flow conditions, the pressure, P, can be calculated from the relation

$$P = \frac{2k\Theta}{\Sigma afq} \qquad [1]$$

where k is the torsion constant of the suspension fiber, Θ is the angle through which the cell is rotated, and a, f, and q are the area, force factor,[7] and moment arm of each effusion orifice. In the studies described here, the torsion fiber and effusion cell suspension system were attached to the arm of a Cahn electrobalance so that sample mass and cell deflection could be monitored continuously; the results yield vapor molecular weights and changes in sample composition due to loss of volatile components. The technique permits direct measurement of the equilibrium pressure over a previously characterized specimen.

Matte specimens were prepared by heating the elements to 1453 K in a closed graphite crucible in an argon atmosphere, and holding in the molten state for two hours. According to the phase diagram of Chang, et al,[8] the resulting 35.0 mass pct Cu-35.8 mass pct Fe-29.2 S mass pct matte melts at approximately 1220 K. The arsenic-doped matte was prepared from a mixture of powdered As and matte placed in a graphite crucible which was then sealed in a quartz tube under vacuum. The tube was slowly heated to 923 K in a temperature gradient so that excess pressure due to unreacted As vapors could be relieved by condensation in the cooler end of the tube. The entire tube was gradually inserted into the hot zone of the furnace and heated to 1173 K, about 50 K below the melting point. After annealing for four hours at this temperature, the tube was cooled in the furnace and removed for inspection. The inside

wall of the tube was clean, indicating that the As had reacted completely with the solid matte. The tube was then heated to 1373 K, above the melting point of the matte, for one-half hour and quenched to room temperature. After removal from the tube, the material was crushed for the vapor pressure measurements. The As content was determined by atomic absorption analysis by the Commercial Testing and Engineering Company of Golden, Colorado.

For the torsion-effusion measurements, a crushed specimen was loaded into a graphite effusion cell, the effusion cell was loaded into the apparatus, and the system was evacuated. The temperature was then raised rapidly to the temperature of interest. The mass of the cell and sample was monitored continuously with the microbalance to record any mass loss. When the desired temperature was reached, the angular deflection of the effusion cell from its equilibrium position was noted. The cell deflection and mass loss were then observed over a period of time. The apparatus null point was checked at intervals by lowering the temperature to the point where the vapor pressure was negligible.

Although vapor composition does not enter into the torsion-effusion equation, the composition of the vapor had to be known before the measured pressures could be related to As activities. The Nuclide magnetic sector mass spectrometer and experimental technique used in the present study have been described previously.[9,10] Vapor species effusing from a loaded graphite Knudsen cell containing a ground specimen were ionized by electron impact. The resulting ions were mass analyzed, and then detected by an electron multiplier. A movable beam-defining slit located between the cell and ion source was used to differentiate between effusion beam species and residual gases in the ion source. The neutral vapor species were identified by the masses, isotopic distributions, and threshold appearance potentials of the ions. Threshold appearance potentials were evaluated by the vanishing current method from ionization efficiency curves recorded by an x-y recorder. All ion intensity measurements were made at 3 eV above threshold appearance potentials to avoid contributions from fragmentation processes.

B. Results

Both doped and undoped matte specimens were studied by high-temperature mass spectrometry. The only species observed over molten undoped matte between 1300 and 1380 K was S_2. The mass spectrometric results on two specimens of matte doped with 1.6 mass pct As are shown in Table I; intensities shown are those of the parent ions measured a few volts above ionization threshold, where they indicate the neutral relative abundances. These studies were done at a somewhat lower temperature, where the doped matte was solid rather than liquid since the As_2 pressure over the liquid was greater than practical for mass spectrometry. As seen in the table, the predominant species evolved from As-doped matte was As_2, with minor amounts of S_2 and AsS. The relative importance of these species should be approximately the same over the liquid matte since the activities of As and S must be the same in solid and liquid matte at the melting temperature, and no drastic change is expected as the temperature of the liquid matte is raised. The vapor mass spectra show clearly that the sulfur potential of the matte is relatively unaffected by arsenic doping, and that

the observed vapor pressure increase on doping is associated with As_2 vaporization.

Vapor pressures measured for doped and undoped matte specimens by the torsion-effusion method are shown in Table II. Visual examination of effusion cell residues confirmed that all specimens heated above 1220 K had melted, in agreement with the phase diagram data.[8] The measurements on doped matte were made sequentially on a single specimen; the As content was calculated for points after the first by assuming the mass loss of the matte was primarily As.

The total pressure of the undoped matte specimen is represented by the equation

$$\log P(\text{atm}) = 6.658 - 14883/T(K) \qquad [2]$$

based on our measurements over the range 1300 to 1380 K. This equation predicts a pressure of 3.6×10^{-4} atm at 1473 K, in essentially exact agreement with the S_2 pressure of Chang, et al[8] for mattes of this Cu-Fe-S composition. The agreement of the extrapolated pressure with the critically reviewed value provides strong support for

Table I. Vapor Mass Spectra of Matte Containing 1.6 Mass Pct As[a]

Temperature (K)	Species As_2^+	AsS^+	S_2^+
	Specimen 1		
1145.4	56.1	2.91	2.07
1129.4	37.5	1.89	1.40
1130.9	36	1.88	1.41
1100.2	30.5	1.14	0.65
1108.2	30.8	1.16	0.70
	Specimen 2		
1119.8	12.9	1.00	1.16
1090.7	9.0	0.46	0.40
1096.0	10.0	0.60	0.63
1164.6	215	8.25	4.11
1164.6	178	7.95	4.35

[a]Ion intensity in arbitrary units

Table II. Equilibrium Pressures of Doped and Undoped Matte*

T (K)	Mass Pct As in Matte	$10^3 \times$ (As) in Matte	$10^4 P$ (Total) (atm)
1285	1.60	10.22	3.23
1338	1.50	9.57	4.68
1338	1.20	7.65	2.07
1334	1.08	6.88	1.71
1334	1.04	6.63	1.34
1334	0.89	5.67	0.79
1334	0.75	4.77	0.61
1334	0.68	4.33	0.49
1334	0.59	3.75	0.38
1334	0.52	3.31	0.30
1334	0.48	3.05	0.29

Undoped matte: $\log P$ (atm) $= 6.658 - 14,883/T$ (K) (1300 to 1380 K)

*Composition of undoped matte: 35.0 mass pct Cu, 35.8 mass pct Fe, 29.2 mass pct S. (1 atm = 1.01325×10^5 Pa)

use of the torsion-effusion technique in measurement of matte pressures.

The presence of S_2 and AsS in the vapor complicates the calculation of As activities from the total pressure values of doped matte shown in Table II. Since As_2 is the predominant species over the matte at ~1.5 mass pct doping level, the As activity can be calculated with reasonable accuracy for the points in Table II by the method outlined in the Appendix. Under these conditions, the S_2 pressure is close to that observed over undoped matte at the same temperatures. A summary of the derived activity data is given in Table III. Below about 1 mass pct, the derived activities are increasingly less accurate, since for these points As_2 and S_2 pressures are roughly comparable, and the results are sensitive to the assumed S_2 pressure. Also, in this region vaporization losses of As and S from the matte are of comparable magnitude, so that the residual As content of the sample becomes less certain. The activities of As in the matte are consistent with the defining relationship

$$a(As) = \gamma(As \text{ in matte})x(As \text{ in matte}) \quad [3]$$

where x is the mole fraction As in matte, and γ is the activity coefficient with the value 0.7 ± 0.2 (mole fraction)$^{-1}$ in the composition range from 1.04 to 1.6 mass pct As, as seen in Table III. For the composition range below 1 mass pct As, an estimate of the activity can be made by assuming Henry's law is followed, at least approximately, and that this activity coefficient is applicable in the dilute solution region.

The activity values of the present work are an order of magnitude smaller than those found by Itagaki, *et al*[1] and almost two orders of magnitude greater than those calculated from the results of Nagamori, *et al*.[2] Some of the possible reasons for these differences are discussed in the following section.

III. DISCUSSION

The behavior of the As in copper smelting mattes has been studied previously by the two methods discussed below. The As activities found by these techniques differ from each other and from the present results. Some of the possible sources of error are identified for each technique, and the reliability of experimental results is assessed.

A. *Isopiestic Measurements*

Itagaki, Seino, and Yazawa[1] made the most extensive study of As activity in mattes. The isopiestic method was used, in which As pressure over condensed As at one temperature was used to fix the As activity at the higher temperature of the matte specimen. Measurements were carried out for five compositions in the Cu_2S-FeS pseudobinary system (A-type mattes), and for two compositions deficient in sulfur (B-type mattes). They found values of the activity coefficient of As in A-type mattes ranging from 7.7 to 22.8 (mole fraction)$^{-1}$ at 1373 K, depending on matte composition. The activity of As was linearly proportional to its mole fraction in these mattes over the concentration range of dissolved As studied, up to $x_{As} = 0.01$. Their A-2 matte, which was 32 mass pct Cu, 38.1 mass pct Fe, and 29.9 mass pct S, had the composition closest to the

Table III. Derived As Activities*

T (K)	Mass Pct As	$10^5 p$ (S_2) (atm)	$10^4 p$ (As_2) (atm)	$10^7 p$ (As) (atm)	$10^3 a$ (As)	γ
1285	1.60	1.19	2.7	2.1	8.9	0.87
1338	1.50	3.43	3.6	5.0	7.5	0.78
1338	1.20	3.43	1.3	3.1	4.6	0.60
1334	1.08	3.17	1.1	2.8	4.4	0.64
1334	1.04	3.17	0.8	2.3	3.7	0.56

*The pressure of S_2 in the vapor was assumed equal to that over pure matte at the same temperature. The pressure of As (g) over pure condensed As was 2.4×10^{-5} atm at 1285 K, 6.2×10^{-5} atm at 1334 K, and 6.7×10^{-5} atm and 1338 K (1 atm = 1.01325×10^5 Pa).
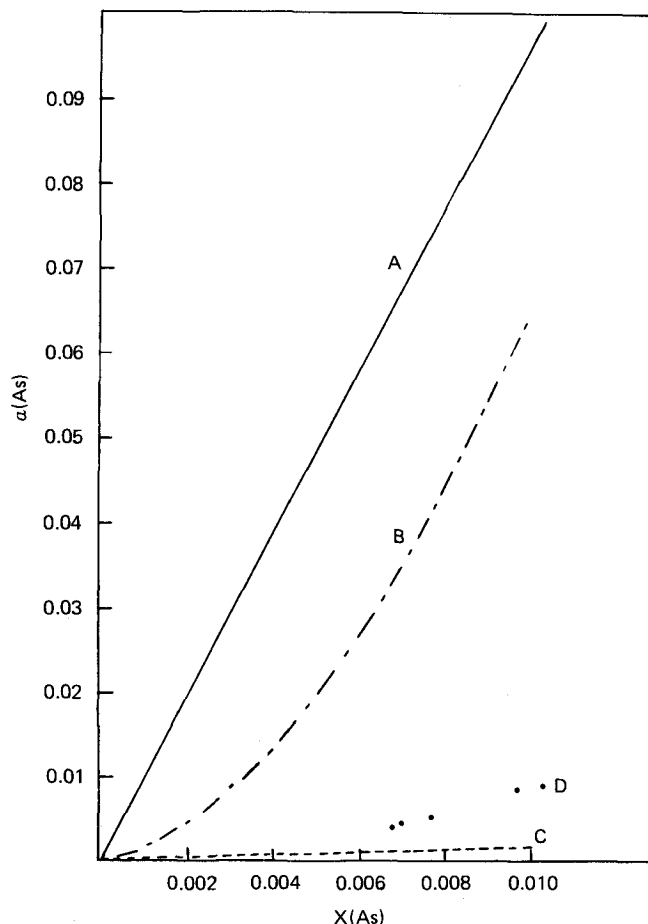

Fig. 1 — Activity of As in copper smelting mattes at 1334 K. A — Ref. 1 (A-2 matte), $\times$ 0.1; B — Ref. 1, recalculated, $\times$ 0.1; C — Ref. 3, $\times$ 10; D — this work. Reference state for As — pure condensed As.

matte used in the present work, and was studied from 1273 to 1373 K. The activity coefficient interpolated for the A-2 matte at 1334 K was 9.6 (mole fraction)$^{-1}$. The result, which is an order of magnitude greater than that of the present study at the same temperature, is shown in Figure 1 along with the results of the remaining investigators.

In the analysis of their results, Itagaki, *et al*[1] used the data in Hultgren, *et al*[11] to derive p° (As) values in evaluating As activities in the matte phase. Better enthalpy of formation data are now available for the As vapor species,[12,13,14] as pointed out in the Appendix; the magnitude of the bias

introduced into the results of Itagaki, et al^1 by the use of the older data was calculated as follows. The As activity at 1334 K was calculated for matte compositions up to 0.01 mole fraction assuming that the activity coefficient γ was constant and equal to 9.6 (mole fraction)$^{-1}$. Using the data of Hultgren, et al,[11] the pressure $p°$ (As) that would be present over pure condensed As at this temperature was calculated. The sum of the As species pressures corresponding to this pressure of As (g) at 1334 K was determined, as was the temperature at which the vaporization of pure As gave this total pressure. This procedure, so far, was the reverse of the calculational method used by Itagaki, et al^1 to calculate activities. The temperature found by this method was then used along with the thermodynamic data presented in Tables IV and V to recalculate the activities of As in the matte. The recalculated activities are shown in Figure 1.

B. Distribution Measurements

Asano and Wada[3] measured the distribution ratio of As between copper and pure Cu_2S,

$$L_{As} = \text{mass pct As in Cu/mass pct As in } Cu_2S \quad [4]$$

An equivalent definition applies if Cu_2S is replaced by matte. At 1473 K, L_{As} was 9 at infinite dilution and decreased at higher concentrations. Nagamori, Mackey, and Tarassoff[2] measured the distribution of As between liquid Cu and a high grade matte at 1423 and 1523 K, and derived the relationship

$$L_{As} = 17 + 0.10[T(K) - 1473] \quad [5]$$

No dependence on matte composition was found below 4 mass pct Fe. The As concentrations found in their equilibrated specimens were less than 0.009 mass pct.

The data of Nagamori, et al^2 were used to calculate the activity of As under the same conditions as in the present experiments, neglecting the difference between the matte composition of their study and that of the present work. For As concentrations up to 1 mass pct, the relationships

$$x(\text{As in Cu}) = (8.5 \times 10^{-3})\text{mass pct(As in Cu)} \quad [6]$$

and

$$x(\text{As in matte}) = (6.4 \times 10^{-3})\text{mass pct(As in matte)} \quad [7]$$

hold to within 1 pct. From Eq. [4], L_{As} = 3.1 at 1334 K. This temperature is below the melting point of copper; thus, the value of L calculated for this temperature is for the equilibrium of matte with supercooled liquid copper. Substituting relations [6] and [7] into Eq. [4] and solving

$$x(\text{As in Cu})/x(\text{As in matte}) = 4.1 \quad [8]$$

for equilibrium between the phases. For the dilute solution limit, the equality of As activities in the two phases leads to the expression

$$x(\text{As in Cu})\gamma°(\text{As in Cu}) = x(\text{As in matte})\gamma°(\text{As in matte}) \quad [9]$$

where $\gamma°$ represents the activity coefficient applicable in the dilute solution Henry's law region. Solving

$$\gamma°(\text{As in matte}) = 4.1 \, \gamma°(\text{As in Cu}) \quad [10]$$

Table IV. Enthalpies of Formation at 298.15 K for Arsenic Vapor Species[a] and AsS(g)[b]

Species	$(\Delta Hf°_{298})/R$ (kK)
As(g)	34.5 ±0.3
As$_2$(g)	22.9 ±0.3
As$_3$(g)	26.0 ±3.9
As$_4$(g)	18.8 ±0.1
AsS(g)	22.4 ±0.5

[a]The data from Reference 11 for As$_2$ and As$_4$ were combined with the data of Reference 14 for As and As$_3$.
[b]Reference 12

Table V. Gibbs Energy Functions for As Species[a] and AsS(g)[b]

$$-(G°_T - H°_{298})/RT = A + B \log T + CT + D/T$$
$$(\pm 0.01, 298 \text{ to } 1600 \text{ K})$$

Species	A	B	C	D
As(g)	4.17	5.765	-1.764×10^{-6}	747.
As$_2$(g)	−0.07	9.956	6.648×10^{-5}	1303.
As$_3$(g)	−11.37	16.701	9.706×10^{-5}	2181.
As$_4$(g)	−25.26	22.162	1.358×10^{-4}	2905.
As(cond)	−14.73	6.475	3.142×10^{-4}	867.
AsS(g)	0.94	9.818	2.947×10^{-4}	1316.

[a]Calculated as described in text, and presented in dimensionless units.
[b]Reference 15

The dilute solution activity coefficient for As in Cu, interpolated from the data given by Lynch,[4] is 4×10^{-3} (mole fraction)$^{-1}$. Lynch[4] analyzed literature data on the activity of As in Cu using Hultgren's data,[11] and analysis of the data using the thermodynamic values given in the present work would change this value somewhat, although not by more than the considerable uncertainty in the literature data. For the above value of the activity coefficient of As in Cu, the activity coefficient of As in matte is calculated to be 1.6×10^{-2} (mole fraction)$^{-1}$, compared with the value 9.6 (mole fraction)$^{-1}$ derived from the work of Itagaki, et al,[1] and the value 0.7 ±0.2 (mole fraction)$^{-1}$ of the present work. The matte investigated by Nagamori, et al^2 contained a maximum of 4 mass pct Fe compared to the 35.8 mass pct Fe matte of the present study; this composition difference is expected to account for only a minor part of the discrepancy. The activities calculated from the data of Asano and Wada[3] would be approximately half of those of Nagamori, et $al.^2$

C. Sources of Error

The most obvious error sources in the distribution coefficient and isopiestic techniques are inclusion of copper in the matte in the former and failure to saturate the matte with As in the latter. These would lead to low values of the As activity for the distribution experiments and high values for the isopiestic experiments. The small amounts of As present in specimens would lower the accuracy that could be obtained by chemical analysis. Another source of error in these experiments is the loss of As to container walls during cooling. Potential errors in the pressure measurement of the present study are comparatively small (<5 pct); the main

uncertainties in the work are in the As activities of the lower doping levels, where corrections for background S_2 and AsS pressures became increasingly inaccurate. For As levels above 1 mass pct, the uncertainties are relatively small and the activity data are believed to be reliable.

D. *Further Studies*

The results obtained to date demonstrate the capabilities of the torsion-effusion vapor pressure method combined with mass spectrometric identification of vapor species, in determining trace element activities in copper pyrometallurgical phases. Based on the experience gained in obtaining these results, further experiments are being planned with improved experimental techniques to decrease uncertainties and extend the range of substances investigated. Some of the planned efforts include measurements on mattes of different compositions using several initial doping levels to decrease composition uncertainties and modifications of mass spectrometric technique to permit sampling of the vapor over liquid doped mattes. The effects of temperature and oxygen potentials on the activity of dissolved As, Sb, and Bi will also be investigated. Although the present results are less complete than desirable, we are presenting them at this time because of their potential usefulness in copper metallurgy, and because further experiments will take some time to complete.

ACKNOWLEDGMENT

APPENDIX

A. *As Activity Relationships*

At the low pressures observed, ideal gas behavior was assumed. The As activity was therefore obtained from the relationship

$$a(As) = p(As)/p^\circ(As) \qquad [11]$$

where p is the calculated pressure of monatomic As, and p° is the pressure of monatomic As over pure condensed As, calculated by using the data of Tables IV and V for the reaction

$$As(cond) = As(g) \qquad [12]$$
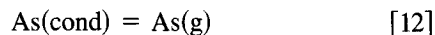
The pressure of As(g) in equilibrium with condensed As, $p^\circ(As)$, is given by the equilibrium constant for this reaction,

$$K = p^\circ(As) \qquad [13]$$

The pressure of monatomic As is calculated from the total pressure of As species by consideration of gas phase equilibria among these species.

Elemental As in the vapor in equilibrium with the doped matte exists principally as As_2, but also as As_4, As_3, and As. The vapor phase As equilibria are related through the reactions

$$\frac{1}{4} As_4(g) = As(g) \qquad [14]$$

$$\frac{1}{2} As_4(g) = As_2(g) \qquad [15]$$

$$\frac{3}{4} As_4(g) = As_3(g) \qquad [16]$$
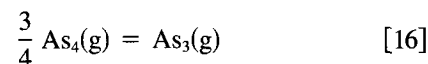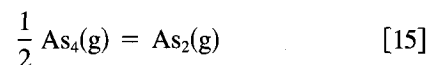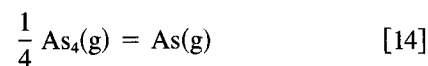
with the equilibrium constants

$$K_1 = \exp(-\Delta G_1/RT) = p(As)/p(As_4)^{1/4} \qquad [17]$$
$$K_2 = \exp(-\Delta G_2/RT) = p(As_2)/p(As_4)^{1/2} \qquad [18]$$
$$K_3 = \exp(-\Delta G_3/RT) = p(As_3)/p(As_4)^{3/4} \qquad [19]$$

The partial pressures of the individual As species can be found from the total pressure of As species by using the relationship

$$P(\text{total As}) = p(As) + p(As_2) + p(As_3) + p(As_4) \qquad [20]$$

Substituting Eqs. [17–19] into Eq. [20],

$$P(\text{total As}) = K_1 p(As_4)^{1/4} + K_2 p(As_4)^{1/2} + K_3 p(As_4)^{3/4} + p(As_4) \qquad [21]$$

The value of $p(As_4)$ found by solving this equation can then be used in Eqs. [17–19] to calculate the partial pressures of the remaining As species.

The activity coefficient of As in matte was calculated using the relationship

$$\gamma(As) = a(As)/x(As) \qquad [22]$$

where $a(As)$ is the As activity and $x(As)$ is the mole fraction of As in the matte.

B. *Calculation of AsS Partial Pressure*

The partial pressures of AsS, S_2, and As_2 are related through the reaction

$$As_2(g) + S_2(g) = 2AsS(g) \qquad [23]$$

for which the equilibrium constant is

$$K = p(AsS)^2/[p(As_2)p(S_2)] \qquad [24]$$

Since As_2 is the principal As vapor species under the conditions of the present study, the relationship between the total pressure and the partial pressures is given by

$$P(\text{total}) = p(As_2) + p(S_2) + p(AsS) \qquad [25]$$

If $p(S_2)$ is known, Eqs. [24] and [25] can be combined to yield the relationship

$$p(AsS)^2 + Kp(S_2)p(AsS) + K(S_2)[p(S_2) - P(\text{total})] = 0 \qquad [26]$$

The value of $p(AsS)$ for given values of $P(\text{total})$ and $p(S_2)$ is the positive root of this quadratic equation. The value of $p(As_2)$ can then be found by using Eq. [25].

C. *Thermodynamic Data*

Since the compilation of Hultgren, *et al*[11] was published, new determinations of the enthalpies of formation of the As vapor species have been made.[12,13,14] The older mass

spectrometric data were biased by the low condensation coefficient of As_4, which led to erroneously high values for its equilibrium pressures. The tables of thermodynamic functions for As species in Reference 11 cover the temperature by range up to 1200 K. The values of the Gibbs energy function for condensed As were estimated up to 1600 K by extrapolating Hultgren's heat capacity data and integrating by standard methods; the Gibbs energy functions for the vapor species were calculated to the same temperature by statistical methods using molecular constants from the sources cited by Hultgren.[11] The Gibbs energy functions used in the present work are shown in Table V. Data for $S_2(g)$ were taken from the JANAF tables.[15] The enthalpy of formation and Gibbs energy function data used in the present work are presented in Tables IV and V as the rationalized quantities $\Delta Hf^{\circ}_{298}/R$ and $-(G^{\circ}_T - H^{\circ}_{298})/RT$, where R is the gas constant, taken as 8.3144 J/mol K or 1.9872 cal/mol K. The units are thus kK for $\Delta Hf^{\circ}_{298}/R$, where $1kK = 10^3$ K, and dimensionless for the Gibbs energy function.

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