The behavior of arsenic trioxide in non-ferrous extractive metallurgical processing

M. Sadegh Safarzadeh¹, J.D. Miller² and H.H. Huang³

¹ Department of Materials and Metallurgical Engineering, South Dakota School of Mines and Technology, 501 East Saint Joseph Street, Rapid City, SD 57701-3995, US
e-mail: sadegh.safarzadeh@sdsmt.edu

² Department of Metallurgical Engineering, College of Mines and Earth Sciences, University of Utah, 135 South 1460 East, Room 412, William C. Browning Building, Salt Lake City, UT 84112-0114, US
e-mail: jan.miller@utah.edu

³ Department of Metallurgical and Materials Engineering, Montana Tech of The University of Montana, 215 ELC Building, 1300 West Park Street, Butte, MT 59701-8997, US
e-mail: hhhuang@mtech.edu

Key words: acid bake; enargite; vapor pressure; arsenolite; claudetite; copper sulfate

Abstract – Study of the acid bake-leach process has shown potential advantages for the treatment of enargite (Cu₃AsS₄) concentrates. Among the most important advantages of the process is the transformation of enargite to water-soluble copper sulfate and highly soluble arsenic trioxide (arsenolite). Because arsenic is retained in the condensed phase during the baking, the vapor pressure of arsenic trioxide should be estimated at typical baking temperatures (e.g. 473 K). To that end, the vapor pressure of As₄O₆ (g) was estimated under the baking conditions based on published thermodynamic values. The vapor pressure of arsenolite at 473 K was found to be approximately 9.03 x 10⁻⁴ atm. Based on the linear regression analysis of the published vapor pressure values for arsenolite in the temperature range 366-579 K, the equation for the best fit line was found to be as follows, with a correlation coefficient of 0.9973:

\[
\log P_{\text{Arsenolite}} (\text{atm}) = \frac{-5780.7}{T} + 9.16
\]

Available information on arsenic trioxide does not allow a definite conclusion regarding the arsenolite/claudetite transformation temperature and their exact melting points. However, the transition temperature has been reported to be in the wide range of 240–506 K in different references. Furthermore, the thermodynamic information concerning arsenolite/claudetite is sparse and at times not consistent. An effort has been made in this paper to compile the most reliable thermodynamic information for arsenic trioxide (arsenolite and claudetite).

Much has been written over the past years on the erratic behavior of arsenic during the various pyro/hydrometallurgical processing of non-ferrous concentrates, in particular, those concentrates containing gold and copper. However, the literature does not offer balanced information regarding the thermodynamic properties of different arsenic trioxide forms. This has left the metallurgical industry in uncertainty as to how to handle the issues related to arsenic management in pyrometallurgical operations. For example, despite the extensive experience of the non-ferrous industry in arsenic removal through roasting and also the high volatility of arsenic oxides/sulfides, the complete removal of arsenic does not occur at roasting temperatures even though it would seem that all of the arsenic should be volatilized.

Several factors appear to affect the volatilization of arsenic upon roasting. The temperature should be high enough to decompose the host sulfide matrix and create a satisfactory vapor pressure of the arsenic species. For example, enargite starts to decompose above 873 K. While the lower temperature in roasting is determined by
the original mineral decomposition, high roasting temperatures may result in sintering and agglomeration of pyrites, which can retard arsenic elimination. The heating rate can also affect arsenic elimination. While rapid heating rates improve arsenic volatilization, the exothermic oxidation reactions may result in local melting of individual particles that can destroy porosity and entrap arsenic-bearing gases. Another important factor in arsenic volatilization is the partial pressure of oxygen. Higher oxygen potentials encourage the formation of arsenates and non-volatile arsenic compounds [1].

Recently, the treatment of enargite concentrates has garnered considerable attention from the copper industry due to a decreasing availability of clean copper concentrates and also due to high gold and silver values associated with enargite mineralogy. These enargite concentrates not only suffer from their refractory nature, which makes them difficult to treat through conventional extraction technologies, but also pose serious environmental issues associated with their high arsenic content. In the context of metallurgical engineering, refractory ores are the primary ores that are difficult to treat through conventional technologies. These ores often need additional pre-oxidation for further treatment. The recent reviews of treatment options for enargite concentrates indicated that both conventional hydrometallurgical and pyrometallurgical options appear to be unable to meet the required techno-economical and environmental criteria for the processing of such concentrates [2, 3]. While the only viable hydrometallurgical technique for the leaching of enargite appears to be pressure leaching (with all its complexities), the roasting of enargite does not drive-off all of the arsenic from the concentrate, contaminating smelting and electrorefining streams. For these reasons, the successful treatment of enargite concentrates remains a significant metallurgical challenge that requires more research.

In keeping with the goal of effective copper recovery and minimum arsenic emission problems, a pyro-hydrometallurgical treatment option has been investigated at the University of Utah, which renders the enargite water-soluble while keeping most of the arsenic in solution. The process includes the baking of enargite concentrates with sulfuric acid at a low temperature (473 K), which transforms the enargite into copper sulfate and arsenic trioxide. Baking is followed by water leaching, which releases copper, arsenic and iron into the solution. This temperature was selected based upon a series of baking experiments considering the fact that the temperature should be high enough to oxidize the enargite, but at the same time it should be low enough to keep the arsenic in the condensed phase. The details of the process can be found elsewhere [4–6].

To understand the behavior of arsenic trioxide and also enargite during the acid baking process at 473 K, a thermodynamic study of these compounds must be performed. Unfortunately there has been confusion in compiling the thermodynamic information, especially for arsenic trioxide, which makes it necessary to review this information and use the most reliable thermodynamic data for stability calculations. The purpose of this paper is thus to evaluate the behavior of arsenic trioxide during the sulfuric acid baking process. The vapor pressure of arsenic trioxide has been approximated based on the published literature.

1 Arsenic trioxide

1.1 Allotropic transformations

Based on the published literature, arsenic trioxide (also known as white arsenic) has three allotropic modifications [7]. Arsenolite (cubic form) has stability below 506 K according to Kelley [8] and is usually formed from the vapor or solution phases. Arsenolite is composed of As₂O₆ dimers [9]. At higher temperatures or in the range 506–586 K claudetite (monoclinic form) is thermodynamically stable, which by itself has two forms (claudetite I and II) [8]. According to Schulman and Schumb [9], claudetite is the stable form of arsenic trioxide in the temperature range 260 K to its melting point. The structure of claudetite is similar to orpiment (As₂S₃). The rate of the transformation of arsenolite to claudetite is very slow, making
it possible to heat up arsenolite to its melting point (545 K) without transformation to claudetite [9–11]. According to Barin [12], however, arsenolite measurements to claudetite at 240 K. Schulman and Schumb [9] have indicated by solubility measurements that claudetite is stable at temperatures as low as 275 K. Also, there is a colorless, amorphous glassy form of As₂O₃, which is obtained by condensing the vapors slowly at temperatures above 523 K and which slowly transforms to claudetite [7, 11, 13–18]. However, based on Mellor [19] if the glassy form is exposed to the air, it gradually transforms to arsenolite. Claudetite may be obtained under specific conditions by either condensing arsenic trioxide vapor at temperatures above 473 K or by prolonged heating of arsenolite or amorphous forms at or above 373 K in the presence of water or dilute sulfuric acid [11, 19]. Water vapor was found to accelerate the transformation of arsenolite to claudetite at 453 K [9]. As₂O₃(s) evaporates as As₂O₅(g) [20].

While all of the researchers agree on the different forms of As₂O₃ being arsenolite, claudetite, and amorphous arsenic trioxide, it is clear from the survey of thermodynamic information regarding different forms of As₂O₃ that the transition temperatures between the allotropic forms are not clearly established, varying in the broad range of 240–506 K. This makes the vapor pressure measurements ambiguous because an allotropic transformation may occur during the heating of the various arsenic trioxides.

### 1.2 Thermodynamic information

Cuypers et al. [7] collected information regarding the melting, boiling and sublimation temperatures for different arsenic trioxide modifications (Table 1). Some additional data from other references has been added to Table 1 by the authors of the present paper. The inconsistent nature of the information can be seen easily from Table 1, although there is less variation in the boiling points.

Cuypers et al. [7] performed thermal gravimetric (TG) analysis of what was reported to be a pro analysis quality arsenolite with an unspecified particle size, which was purchased from Riedel-de Haen. The XRD characterization confirmed the presence of arsenolite (*36-1490*). The TG analysis was performed in a TA instruments’ TGA 951–2000 apparatus in an inert atmosphere provided by nitrogen flow. About 30 mg of arsenolite powder was used in a quartz sample holder. The sample was heated in the nitrogen atmosphere at a rate of 5 °C/min to 723 K, with an isothermal section of 10 min at 383 K. The outlet gases were captured using a train to scrub the gases. At the end of each experiment the train was carefully rinsed with 1 N NaOH solution that was further analyzed for arsenic by the ICP-MS method. The results indicated that in the

<table>
<thead>
<tr>
<th>Phase</th>
<th>Tm (K)</th>
<th>Tb (K)</th>
<th>Ts (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As₂O₃</td>
<td>585.8</td>
<td>730.2</td>
<td>573</td>
</tr>
<tr>
<td>Arsenolite</td>
<td>551</td>
<td>733</td>
<td>551</td>
</tr>
<tr>
<td>Claudetite</td>
<td>466</td>
<td>730.5</td>
<td>588</td>
</tr>
<tr>
<td>Amorphous (glassy) form</td>
<td>473</td>
<td>–</td>
<td>491</td>
</tr>
</tbody>
</table>

*The original authors did not indicate arsenolite, claudetite, or amorphous forms; it was referred to as arsenic trioxide.*
temperature range 443–553 K a mass loss occurred. The derivative thermogravimetric (DTG) profile (derivative of the TG profile) indicated a peak at 544 K (Fig. 1). The authors attributed this peak to the sublimation of arsenolite. A similar TG profile was obtained by Helsen et al. [26], where they heated the arsenolite powder (same as the arsenolite used by Cuypers et al. [7]) at a rate of 5 °C/min up to 773 K containing an isothermal part of 10 min at 473 K. No difference was observed between the TG results performed in the nitrogen atmosphere and in the dry air atmosphere. The DTG peak was observed at a slightly higher temperature (552 K).

The thermodynamic values for arsenolite and claudetite from some credible references are summarized in Table 2. It can be seen that the free energies of formation for these two arsenic oxides are very close at 298 K, but not consistent. While three of references [29–31] indicate that claudetite is slightly more stable than arsenolite, based on the other two references [32, 33] arsenolite is thermodynamically more stable than claudetite at 298 K.

Lynch [34] has given the free energies of formation for arsenolite and claudetite as follows (reactions (1) and (2), respectively):

\[
2\text{As(s)} + 3/2\text{O}_2(\text{g}) = \text{As}_2\text{O}_3(\text{s, arsenolite})
\]

\[
\Delta G^\circ(\text{J/mol}) = -647650 - 36.9T + 123.5T \times \log T - 0.10 \times 10^{-3}T^2 - 125.4 \times 10^{3}T^{-1}
\]

Table 2. Summary of thermodynamic values reported for arsenolite and claudetite.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molar volume (cm³/mol)</th>
<th>S° (J/K mol)</th>
<th>(C_p^\infty(\text{J/K mol}))</th>
<th>(\Delta C_p^\infty) (J/K mol)</th>
<th>Reactivity (\log K)</th>
<th>(a) (0/mol K)</th>
<th>(b\times10^3) (1/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
<tr>
<td><strong>As₂O₃</strong></td>
<td>As₂O₃</td>
<td>107.41</td>
<td>51.12</td>
<td>100.907</td>
<td>-100.907</td>
<td>-144.14 x 10^3</td>
<td>100.18</td>
<td></td>
</tr>
</tbody>
</table>
2As(s) + 3/2O_2(g) = As_2O_3(s, claudetite) \hspace{1cm} (2)

\[ \Delta G^\circ (J/mol) = -630500 - 71.0T + 123.5T \times \log T - 0.10 \times 10^{-3}T^2 - 125.4 \times 10^3T^{-1} \]

(valid over the temperature range 298–585 K).

While according to Becker et al. [35] the transformation temperature of arsenolite to claudetite (which is catalyzed by water) is 453 K, based on the above reactions the transition temperature can be calculated from reaction (3):

\[ 2As_2O_3(s, \text{arsenolite}) = 2As_2O_3(s, \text{claudetite}) \hspace{1cm} (3) \]

\[ \Delta G^\circ (J/mol) = +34300 - 68.2T \]

This gives a transition temperature of 502.93 K, which is very close to the temperature of 506 K, reported by Kelley [8]. A graphical representation of Gibbs free energies of formation for arsenolite and claudetite over the temperature range 298–585 K based on reactions (1) and (2) is shown in Figure 2a, from which it is evident that arsenolite is slightly more stable than claudetite below 502.93 K. This is inconsistent with the values reported in Table 2, where claudetite is slightly more stable than arsenolite at room temperature. Based on information published by Pankratz [33], the calculated transition temperature is 363.79 K (Fig. 2b), which is much less than the value reported by Lynch [34], however, they agree in that arsenolite is the stable phase below the transition temperature.

In contrast, the authors of the present paper observed the formation of arsenolite during sulfuric acid baking of enargite at 473 K [4] and the formation of claudetite upon sulfuric acid baking of enargite at 673 K [5]. These observations are in agreement with a transition temperature of ~503 K.

For liquid arsenic trioxide, the following free energy of formation (reaction (4)) has been reported:

\[ 4As(s) + 3O_2(g) = 2As_2O_3(l) \hspace{1cm} (4) \]

\[ \Delta G^\circ (J/mol) = -1241100 + 388.2T \]

Brooks et al. [36] have given the following equations (Eqs. (5)–(7)) for the free energies of formation of As_2O_3(s), As_2O_3(l), and As_4O_6(g), respectively.

\[ \Delta G^\circ As_2O_3(s) (J/mol) = -668379 + 491.44T \]
\[ - 32.178T \ln T \hspace{1cm} (5) \]

(valid over the temperature range 298–551 K)

\[ \Delta G^\circ As_2O_3(l) (J/mol) = -644770 + 636.27T \]
\[ + 0.0749T^2 + \frac{100004}{T} - 68.408T \ln T \hspace{1cm} (6) \]

(valid over the temperature range 551–730 K)

\[ \Delta G^\circ As_4O_6(g) (J/mol) = -123186 + 1192.9T \]
\[ + 0.1499T^2 + \frac{199765}{T} - 136.82T \ln T \hspace{1cm} (7) \]

(valid over T > 298 K).

Gonzalez et al. [37] reported the standard free energy of reaction (8) for an unspecified
2As$_2$O$_3$ (s) = As$_4$O$_6$ (g) \tag{8}

\Delta G^o (\text{cal/mol}) = +31289.16 - 140.24T + 32.98T \log T.

While this information is useful for estimating the vapor pressure of arsenic trioxide, some authors have experimentally measured the vapor pressure over different temperature ranges.

### 1.3 Vapor pressure estimation

The vapor pressure of arsenolite has been estimated by several researchers over different temperature ranges. This information will be reported and compared in this section. The vapor pressure of claudetite within its range of stability is lower than that of the other states of As$_2$O$_3$. Also, the vapor pressure of the arsenic trioxide present in flue dusts was found to be almost half that of the pure arsenic trioxide \[11\].

The standard Gibbs free energies for reactions (9)-(11) have been estimated by Kelley \[8\], from which the vapor pressures of arsenolite, claudetite and liquid arsenic trioxide can be calculated as follows.

\begin{align*}
2\text{As}_2\text{O}_3 & (s, \ \text{arsenolite}) = \text{As}_4\text{O}_6 (g) \tag{9} \\
\log P \ (\text{atm}) &= \frac{-6670}{T} + 10.81 \\
2\text{As}_2\text{O}_3 & (s, \ \text{claudetite}) = \text{As}_4\text{O}_6 (g) \tag{10} \\
\log P \ (\text{atm}) &= \frac{-4873}{T} + 7.26 \\
2\text{As}_2\text{O}_3(l) &= \text{As}_4\text{O}_6 (g) \tag{11} \\
\log P \ (\text{atm}) &= \frac{-3125}{T} + 4.27
\end{align*}

The transition temperature between arsenolite and claudetite, based upon reactions (9) and (10), is calculated to be 506.13 K, which is in agreement with the transition temperature reported by Kelley \[8\] and Becker et al. \[35\]. The vapor pressure of arsenolite in the temperature range 373–573 K is shown in Figure 3. The data have been collected from four different references \[11, 13, 38, 39\].

Also, the vapor pressure of arsenolite in the temperature range 463–513 K has been measured by Kaiser \[40\] and Li and Hager \[41\]. The results are shown in Figure 4.

Li and Hager \[41\] used high purity arsenic trioxide for vapor pressure measurements. The sample was placed in a boat and the experiments were performed in a tube furnace under a flow of nitrogen. The tube was connected to a condenser assembly which was thoroughly rinsed at the end of the experiment and the strip solution was analyzed for arsenic. The weight change of the boat after the experiment was also recorded to check the mass balance.

Behrens and Rosenblatt \[23\] measured the vapor pressure of arsenolite in the temperature range 367–429 K. They used high purity (>99.99 mol.%) arsenic trioxide, which was further characterized by XRD. The result confirmed that the oxide was arsenolite. They used a standard Knudsen vapor pressure measurement apparatus. There is a considerable difference between their results with those reported by Karutz and Stranski \[42\], whose measurements were
Fig. 5. Vapor pressure of arsenolite in the temperature range 367–429 K.

Fig. 6. Vapor pressure of arsenolite in the temperature range 430–560 K.

Fig. 7. Vapor pressure of arsenolite in the temperature range 615–740 K.

taken over a similar temperature range. These results are compared in Figure 5.

According to Behrens and Rosenblatt [23], the relationship between the vapor pressure of arsenolite and temperature is governed by equation (12).

\[
\ln P (\text{atm}) = \frac{-27.759 \pm 574}{T} + 45.32 \pm 1.46
\]

valid over the temperature range 367–429 K.

The results for the temperature range 430–560 K are compared in Figure 6.

Lisak and Fitzner [43] have estimated the vapor pressure of liquid \( \text{As}_2\text{O}_3 \) in the temperature range 650–740 K and have given the following expression (Eq. (13)) for the calculation of vapor pressure:

\[
\ln P (\text{atm}) = \frac{-5098.3}{T} + 6.869
\]

(valid over the temperature range 650–740 K)

They generated pure arsenic trioxide powder by distillation of high purity arsenic powder in evacuated silica capsules. The formation of arsenolite was confirmed by XRD analysis. They used a glass pressure gauge to measure the vapor pressure. The set up consisted of a two part silica vessel, a vaporization chamber, and a pressure compensation space. Their estimation is very close to the values measured by Rushton and Daniels [10]. Both calculations are compared in Figure 7.

Karutz and Stranski [42] calculated the vapor pressures of arsenolite and claudetite from the following equations (Eqs. (14) and (15)) in the temperature range 567–861 K.

\[
\log P (\text{mm} - \text{Hg}) = \frac{-5451.8}{T} + 11.4679
\]

(arsenolite) (14)

\[
\log P (\text{mm} - \text{Hg}) = \frac{-5282.3}{T} + 10.9083
\]

(claudetite). (15)

The vapor pressure of arsenic trioxide over the temperature range 345–405 K was estimated by Murray and Pottie [44] from equation (16).

\[
\log P (\text{atm}) = \frac{-6077 \pm 18}{T} + (9.944 \pm 0.319).
\]

(16)

They used 99.7% purity arsenic trioxide for the vapor pressure measurement in a Knudsen type apparatus. Whether the arsenic trioxide was arsenolite was not reported. The vapor pressures of arsenolite and claudetite were also measured in the
temperature range 443–573 K by Murray and Pottie [44]. The results are shown in Figure 8, from which data it is observed that arsenolite has a slightly higher vapor pressure.

The vapor pressures measured for arsenolite by the above mentioned authors over different temperature ranges are compared in Figure 9a. Excluding the data of Lisak and Fitzner [43], which may not be compared to other data as they are over a different temperature range, a linear regression analysis of the vapor pressure can be performed over the temperature range 366–579 K. The result is shown in Figure 9b, which indicates that the vapor pressure of arsenolite fits well to the following equation (Eq. (17)), with a correlation coefficient of 0.9973.

\[
\log P \text{ (atm)} = \frac{-5780.7}{T} + 9.16 \quad (17)
\]

Based on the values reported in the literature, the vapor pressure of arsenolite at 473 K was estimated and these results are shown in Table 3, corresponding to an average vapor pressure of \(8.54 \times 10^{-4}\) atm with a standard deviation of \(3.68 \times 10^{-4}\). Furthermore, the vapor pressure at 473 K, calculated from equation (17), gives a very close value of \(8.68 \times 10^{-4}\) atm. While the results are in good agreement with each other, the small difference observed may be due to the inherent errors associated with the measurement techniques or the purity of the arsenic trioxide used by different researchers.

### 1.4 Equilibrium calculations

The vapor pressure of arsenolite in the presence of sulfuric acid can be estimated using a free energy minimization technique [45]. Therefore the equilibrium compounds and their amounts can be calculated based on this analysis. The simplest case is to calculate...
the equilibrium composition for temperatures up to 503 K, the temperature after which the vapor pressure would correspond to claudetite as it is the stable form of arsenic trioxide.

The results are shown in Figure 10a, which indicate $\text{As}_2\text{O}_5$, $\text{As}_2\text{O}_3$ (A), $\text{SO}_2$ (g) $\text{H}_2\text{O}$ (g) as major components and $\text{H}_2\text{SO}_4$ (g), $\text{As}_4\text{O}_6$ (g) and $\text{SO}_3$ (g) as minor reaction products.

In this case, it is observed that the mol.\% of $\text{As}_4\text{O}_6$ (g) at 473 K is $1.38 \times 10^{-2}$, which gives a vapor pressure of $1.18 \times 10^{-4}$ atm corresponding to 0.062\% arsenic loss into the gas phase (equivalent to 0.082\% arsenolite sublimation). A plot of the partial pressure of $\text{As}_4\text{O}_6$ (g) as a function of temperature is shown in Figure 10b. These calculations indicate that the amount of arsenic trioxide sublimated is expected to be negligible, a conclusion that was experimentally validated [4].

In general, the formation of $\text{As}_2\text{O}_5$ is encouraged at higher oxygen potentials.

Therefore, depending on the purpose of roasting, the oxygen potential should be carefully controlled. If the goal of roasting is to remove the arsenic from enargite, the oxygen potential should not exceed the amount required for the formation of $\text{As}_2\text{O}_3$, otherwise the formation of $\text{As}_2\text{O}_5$ will hinder the removal of arsenic from the concentrate. Not only is the formation of $\text{As}_2\text{O}_5$ detrimental in terms of arsenic removal from the concentrate, but it may also form other insoluble compounds with iron, which will complicate the process [2].

While the thermodynamics of arsenic trioxide in the context of thermal stability was reviewed in this paper, it is important to consider the rate of arsenic trioxide evaporation, too. Few researchers have studied the kinetics of arsenic trioxide evaporation [37]. An appropriate understanding of the evaporation rate should be useful for a better evaluation of arsenic removal from different arsenic-bearing feed materials. For example, such analysis is critical for the roasting of high-arsenic copper and gold concentrates, where the arsenic is volatilized and condensed at a later stage in the form of arsenic trioxide. On the other hand, should the arsenic be retained in the condensed phase, for example the acid bake process, such analysis would help researchers predict the behavior of arsenic over extended reaction times.

2 Summary and conclusions

Study of the phase equilibria is critical to understanding the acid bake process for the treatment of enargite concentrates being developed at the University of Utah. An effort was made to calculate the vapor pressure of arsenic trioxide at the baking temperature. While the literature is limited on this topic, there is a fairly good agreement among the authors resulting in an average partial pressure of $8.54 \times 10^{-4}$ atm for arsenolite at 473 K. Compilation of the vapor pressure data from all of the papers and regression analysis over the temperature range 366–579 K results in the following vapor pressure equation, with a correlation coefficient of 0.9973.

$$\log P_{\text{Arsenolite}} \text{ (atm)} = \frac{-5780.7}{T \ (\text{K})} + 9.16.$$
However, some of the thermodynamic values for different forms of arsenic trioxide (arsenolite, claudetite and glassy form) are still confusing and thereby allow no definite conclusion to be reported. For example, a wide range of sublimation points have been reported for arsenic trioxide. The transition temperature from arsenolite to claudetite has been reported to be in the range 240–506 K. Based on the work of Welch and Duschak [11] who compared the vapor pressure of pure arsenic trioxide with the arsenic trioxide present in flue dust, and indicated that the pressure in the latter case was almost half of the former, it may be concluded in the case of acid baking of enargite that the vapor pressure may be significantly lower than the vapor pressure associated with pure arsenolite.

Based on equilibrium calculations, the vapor pressure of arsenolite was calculated to be $1.18 \times 10^{-4}$ atm, corresponding to 0.082% in the presence of sulfuric acid. The results conform well to the experimental results reported earlier in a previous publication [4]. The insights gained from this paper are critical for the acid baking of enargite to be well understood.

Acknowledgements

The authors would like to acknowledge Newmont Mining Corporation for providing the funds for the enargite project at the University of Utah. Ms. Dorrie Spurlock is also highly recognized for proofreading of the manuscript.

References

[13] Committee on Medical and Biological Effects of Environmental Pollutants, National Research Council: Arsenic: Medical and Biological Effects of Environmental Pollutants, Natl. Acad. Sci., Washington D.C., USA, 1977
Appendix I. Thermodynamic information used to calculate Figure 10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature range (K)</th>
<th>( H ) (kcal/mol)</th>
<th>( S ) (cal/mol·K)</th>
<th>( C_p,m(T) = a + 10^b T - 10^c T^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{As}_2\text{O}_3 ) (A)</td>
<td>298–500</td>
<td>-157.19</td>
<td>25.66</td>
<td>( a = 20.96 )  ( b = 10^{-3} )  ( c = 10^{-6} )</td>
</tr>
<tr>
<td>( \text{As}_2\text{O}_3 )</td>
<td>298–1003</td>
<td>-221.31</td>
<td>25.33</td>
<td>( a = 33.05 )  ( b = 11.51 )  ( c = 7.67 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 ) (l)</td>
<td>298–600</td>
<td>-188.41</td>
<td>64.53</td>
<td>( a = 36.77 )  ( b = 9.13 )  ( c = 5.43 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 ) (g)</td>
<td>298–750</td>
<td>-175.70</td>
<td>71.41</td>
<td>( a = 8.85 )  ( b = 45.19 )  ( c = 0.31 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) (l)</td>
<td>273–495</td>
<td>-68.31</td>
<td>16.71</td>
<td>( a = 44.66 )  ( b = -110.95 )  ( c = -4.67 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) (g)</td>
<td>298–1100</td>
<td>-57.79</td>
<td>45.13</td>
<td>( a = 6.79 )  ( b = 2.98 )  ( c = 0.30 )</td>
</tr>
<tr>
<td>( \text{SO}_2 ) (g)</td>
<td>50–500</td>
<td>-70.94</td>
<td>59.32</td>
<td>( a = 6.96 )  ( b = 8.89 )  ( c = 0.01 )</td>
</tr>
<tr>
<td>( \text{SO}_3 ) (g)</td>
<td>50–500</td>
<td>-94.59</td>
<td>61.37</td>
<td>( a = 4.82 )  ( b = 29.87 )  ( c = 0.04 )</td>
</tr>
<tr>
<td>( \text{As}_4\text{O}_6 )</td>
<td>298–582</td>
<td>-314.03</td>
<td>51.34</td>
<td>( a = 16.74 )  ( b = 97.20 )  ( c = 0.00 )</td>
</tr>
<tr>
<td>( \text{As}_4\text{O}_6 ) (g)</td>
<td>298–800</td>
<td>-286.25</td>
<td>97.63</td>
<td>( a = 45.79 )  ( b = 17.72 )  ( c = -8.12 )</td>
</tr>
</tbody>
</table>