

Chapter 1

Arsenic thermodynamic data and environmental geochemistry

An evaluation of thermodynamic data for modeling the aqueous environmental geochemistry of arsenic

D. Kirk Nordstrom¹ and Donald G. Archer²

¹*U.S. Geological Survey, Boulder, CO, USA*

²*National Institute of Standards and Technology, Gaithersburg, MD, USA*

Thermodynamic data are critical as input to models that attempt to interpret the geochemistry of environmentally important elements such as arsenic. Unfortunately, the thermodynamic data for mineral phases of arsenic and their solubilities have been highly discrepant and inadequately evaluated. This paper presents the results of a simultaneous weighted least-squares multiple regression on more than 75 thermochemical measurements of elemental arsenic, arsenic oxides, arsenic sulfides, their aqueous hydrolysis, and a few related reactions. The best-fitted thermodynamic database is related to mineral stability relationships for native arsenic, claudetite, arsenolite, orpiment, and realgar with pe-pH diagrams and with known occurrences and mineral transformations in the environment to test the compatibility of thermodynamic measurements and calculations with observations in nature. The results provide a much more consistent framework for geochemical modeling and the interpretation of geochemical processes involving arsenic in the environment.

1. INTRODUCTION

Aqueous geochemical models have become routine tools in the investigation of water-rock interactions (Alpers and Nordstrom, 1999; Drever, 1997; Langmuir, 1997; Nordstrom and Munoz, 1994; Parkhurst and Plummer, 1993), in the study of bioavailability and toxicity of contaminants to organisms (Morrison, 1989; Parker et al., 1995), in the prediction of arsenic behaviour in mining pit lakes in Nevada (Tempel et al., 1999), in the

prediction of arsenic mobility from mine wastes (Doyle et al., 1994), in the prediction of ore deposit formation (Heinrich and Eadington, 1986), and in any quantitative interpretation of reactions in aqueous solution and natural water (Morel and Hering, 1993; Stumm and Morgan, 1996). As with all computerized models, the quality of the output depends on the quality of the input and thermodynamic data is one of the primary sets of data input to most geochemical codes. Unfortunately, the consistency and quality of thermodynamic data is not adequate for the wide variety of aqueous geochemical calculations needed for water quality investigations. Data for environmentally relevant arsenic species is a good example. Grenthe et al. (1992 p. 390), in their major critique of uranium thermodynamic data, stated that a complete re-analysis of thermodynamic data for arsenic species is necessary and data on uranium-arsenic complexes and compounds would necessarily be compromised. Nordstrom (2000) agreed with this conclusion and considered the consequences of estimating stability constants for some divalent and trivalent arsenate complexes on speciation of arsenate for some ground waters from Bangladesh. Those results demonstrated that speciation can change considerably but saturation indices are not significantly affected for these dilute waters. Presumably, waters of higher concentration would be affected more strongly.

Numerous compilations of thermodynamic data are available and many of these contain thermodynamic data for arsenic species. However, mere numbers of compilations do not provide any idea of the quality of the data nor the number or quality of the original measurements upon which the data are based. The presence of nearly identical property values in apparently different sources may give the erroneous impression that the properties for a particular substance are well determined when in fact they may be based on the same original source that, like a cousin, may be twice removed from the reference given. Most compilations of data for arsenic species cannot be considered reliable. The database of Sadiq and Lindsay (1981) has been used to speciate arsenic for waters and soils by Sadiq et al. (1983), and Sadiq (1990, 1997). Unfortunately, this database was not developed using critical evaluation procedures (e.g. see Ball and Nordstrom, 1998; Nordstrom, 2000) and several errors can be found there, including lack of consistency with thermodynamic relationships, inappropriate use of values from the literature, no evaluation of original sources, no evaluation of networks, and no consideration of temperature dependence. This database is not unique; there are many other similarly unevaluated compilations in the published literature. Many dangerous assumptions such as those outlined above can befall the unaware investigator.

Another factor that exacerbates this sort of problem is that some databases were republished at later dates without incorporation of changes in the literature that had occurred since the original publication date. The more

recent publication dates might lead one to believe that these databases are based on more up-to-date information than might actually be the case. Examples involve publication series such as Wagman et al. (1968, 1982) or the series of Robie and Waldbaum (1968), Robie et al. (1978), and Robie and Hemingway (1995).

We illustrate these problems with a specific case. Young and Robins (2000) listed 13 values of the Gibbs energy of formation, $\Delta_f G$, of orpiment, $\text{As}_2\text{S}_3(\text{cr})$, each from a different literature source. These values ranged from $-168.8 \text{ kJ}\cdot\text{mol}^{-1}$ to $-82.4 \text{ kJ}\cdot\text{mol}^{-1}$ and, if examined closely, fell into groups of values. The first group contained two values, -168 and $-169 \text{ kJ}\cdot\text{mol}^{-1}$, and were cited as Wagman et al. (1982) and Robie et al. (1978). However, the Wagman et al. (1982) citation was a republication of values from an earlier publication (Wagman et al., 1968) whose properties for arsenic compounds were generated about 1964 and were not documented. Robie et al. (1978) took the 1964 value from Wagman et al. (1968), changed it slightly and republished it. Another group of values falls around -95 to $-99 \text{ kJ}\cdot\text{mol}^{-1}$. One of those values, $-96.23 \text{ kJ}\cdot\text{mol}^{-1}$, was obtained by Barton (1969) from examination of multi-phase equilibrium temperatures for liquid (arsenic + sulfur), realgar, and orpiment, assumptions about the fugacity of sulfur in mixed arsenic + sulfur melts, and extrapolations from the melting temperature to 298 K. Naumov et al. (1974) made a small change in this value and included it in their data compilation. Also in this group are two solubility studies in which the Gibbs energies of formation were calculated from the measured solubilities and, among other things, the Gibbs energy of formation of $\text{H}_3\text{AsO}_3^{\text{aq}}$, where the latter value was taken from Naumov et al. (1974). Naumov et al. based their value of $\Delta_f G$ for $\text{H}_3\text{AsO}_3^{\text{aq}}$, in part, on a value of $\Delta_f G$ for arsenolite calculated from an erroneous value reported by Beezer et al. (1965). Because the values calculated from the two solubility studies were based on erroneous auxiliary data, their agreement with Barton's (1969) equilibrium study is happenstance. Another group of values ranged from -90.7 to $-91.5 \text{ kJ}\cdot\text{mol}^{-1}$ and was based on a fluorine combustion study from Johnson et al. (1980) combined with various auxiliary data. Finally, two additional, but smaller values (-86 and $-82.4 \text{ kJ}\cdot\text{mol}^{-1}$), were listed. One of these values was from Pokrovski (1996) who reanalyzed earlier solubility data using yet another set of auxiliary thermodynamic data, and the other was from Bryndzia and Kleppa (1988) who used direct synthesis calorimetry to determine the enthalpy of formation. Bryndzia and Kleppa (1988) reported $-83.0 \text{ kJ}\cdot\text{mol}^{-1}$ for the enthalpy of formation of orpiment. To make matters worse, the more recent compilation of Robie and Hemingway (1995) lists the enthalpy as $-91.6 \text{ kJ}\cdot\text{mol}^{-1}$ with Bryndzia and Kleppa (1988) as the source. Thus, we see examples of most of the problems mentioned above.

In this paper we present the results of an evaluation of selected thermodynamic data of arsenic species. The results are of two types with one that consists of data that have been fitted with a weighted least-squares regression, and a second that is derived from the first least-squares determined group by standard thermodynamic relationships. The results (in Tables 1a, 1b, and 2) and their implications for geochemistry and geochemical modelling are then discussed with known occurrences, observed mineral transformations in the environment and calculated pe-pH relationships. The objective is to provide a consistent and coherent framework of thermodynamic calculations and field relationships for mineral stabilities among arsenic species.

2. GENERAL APPROACH AND THE EVALUATION OF ELEMENTAL ARSENIC

From hundreds of papers that were found from the literature containing measurements on arsenic reactions from which thermodynamic data might have been extracted, measurements on 77 substances or reactions contained in 40 studies were selected for simultaneous least-squares regression. These substances or reactions were limited to elemental arsenic and simple compounds, the oxides and sulfides, their solubilities and hydrolysis products. Elemental arsenic was regressed separately because a different fitting procedure was used. This procedure is explained below. Details of the original papers that formed the basis for the least-squares regression of all the data and corrections that were made to the original measurements will be found in Archer and Nordstrom (2000). These details are beyond the scope of this paper.

Treatment of the measured reactions for arsenic species required adoption of thermodynamic properties of some other substances, e.g. $H_{2(g)}$, $Cl^-_{(aq)}$, etc. Most previous thermodynamic property compilations suffer from some type of networking problem. Consequently, such a choice cannot be made lightly. The most obvious choices could be either Wagman et al. (1968) or the CODATA values from Cox et al. (1989). The Wagman et al. (1968) values were generated quite some time ago and there are apparent problems with sulfate and carbonate species. These species are, of course, important in geochemical modeling of ground waters. On the other hand, there are problems with thermodynamic properties of at least some of the alkali halides given in the CODATA recommendations (Archer, 1992; Rard and Archer, 1995), species that are also important in geochemical modeling. We also have reactions that involve species not considered by Cox et al.

(1989) as being "key", e.g. $I_3^-(aq)$. There are undisclosed optimized properties inherent in the CODATA recommendations, a fact that makes thermodynamic consistency based on the CODATA properties not possible (Archer, 2000). Hence, we chose to use the Wagman et al. (1968) properties, recognizing that its problems potentially affect the present work less than would the problems associated with the CODATA values. Properties given below are based on the common conventional standard pressure of 1 atm (101.325 kPa).

Thermodynamic properties for $As_{(α,cr)}$ were calculated from a least-squares representation using a cubic-spline method described previously (Archer, 1992; Archer et al., 1996). Briefly, a function $f(T)$ was used, where:

$$f(T) = [T \cdot \{ (C_{p,m}^\circ - \gamma_{el}T) / C_p^\circ \}^{-1/3} - bT] / T^\circ \quad (1)$$

and where T is temperature, T° was 1 K, $C_{p,m}^\circ$ was the molar heat capacity, C_p° was $1.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, γ_{el} was the coefficient for the contribution to the heat capacity of the conduction electrons, and b was arbitrarily chosen to be 0.32 for the present case. The function $f(T)$ of equation (1) was fitted with a cubic spline using polynomials of the form:

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i \quad (2)$$

where the subscript i refers to the polynomial that contains the specified value of T and spans the temperature range T_i to T_{i+1} . A particular (T_i, d_i) pair is referred to as a "knot." A "natural spline" end condition (*i.e.* second derivative equal to 0) was imposed at the highest temperature end knot. The end condition imposed at the lowest temperature knot was a value of $-b$ (-0.2) for the first derivative. This approach was equivalent to assuming that the Debye temperature was independent of temperature near 0 K. (For the purpose of calculation: $T_{i+1} > T > T_i$). The calculated heat capacity was:

$$C_{p,m}^\circ / C_p^\circ = \left(\frac{T}{T^\circ f(T) + bT} \right)^3 + \gamma_{el}T / C_p^\circ \quad (3)$$

Equation (3) was integrated numerically to obtain the enthalpy. The model was determined by fitting to the selected values with a nonlinear least-squares program. The vector of residuals was calculated using the numerical integration of equation (3) to obtain the enthalpy increments. Included in the representation were the enthalpy increment measurements from Klemm et al. (1963) and the heat capacity values given by Culvert

(1967), Paukov et al. (1969), and Anderson (1930). The heat capacity measurements from Culvert ranged from 0.7 K to 4 K. We have included only the measurements from 1 K to 4 K, as the lower temperature measurements are affected significantly by nuclear spin contributions. The heat capacity measurements from Paukov et al. and Anderson spanned the temperature ranges of 13.8 K to 289 K and of 57 K to 291 K, respectively. The enthalpy increment measurements reported by Klemm et al. (1967) were performed with a Bunsen ice calorimeter. Klemm et al. found eccentricities in several different properties of arsenic near 500 K, including the enthalpy, unit cell measurements, and electrical and magnetic properties. Taylor et al. (1965) measured the unit cell dimensions, and electrical and magnetic properties, as functions of temperature for arsenic crystals. They did not observe the effects reported by Klemm et al. Because the second-order transition reported by Klemm et al. was not reproducible, we did not include it in our representation of the thermal properties of arsenic. The results gave the standard state entropy at 298 K of $35.78 \pm 0.18 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ which compares very favourably to the value obtained by Ball et al. (1988) of $35.735 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ by refitting the heat capacity data of Hultgren et al. (1973). The value given by Hultgren et al. (1973) is $35.69 \pm 0.84 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and appears in Robie et al. (1978) and Robie and Hemingway (1995). The entropy value of $35.63 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ that appears in Table 1a was obtained by taking the fitted elemental arsenic data and fitting it with all the other arsenic data. Even though this entropy value has decreased slightly in the overall fitting, the residual ($0.145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) indicates that the entropy has a lower uncertainty than indicated by Hultgren et al. (1973) and the difference in the entropy from refitting is not significant.

3. RESULTS AND DISCUSSION

The results of simultaneous weighted least-squares regression of the data and some of the unfitted but derived quantities are shown in Tables 1a, 1b, and 2. Table 1a displays elemental arsenic, its simple oxides, and the reactions for arsenic oxidizing to arsenic trioxides. Table 1b introduces the hydrolysis species for As(III) and As(V) in solution, the hydrolysis reactions, and the solubility reactions for the simple oxides. Single species are shown at the top of each table with the reactions underneath. The following discussion describes some of the mineral occurrences for these substances, describes their relative stabilities from field observations, and considers the implications of the evaluated thermodynamic data in terms of these occurrences.

Table 1a. Arsenic Oxides

Species or reaction data for standard state conditions, 298.15 K and 1 atm	$(\Delta_f G^\circ; \Delta_r G^\circ)$ / $\text{kJ}\cdot\text{mol}^{-1}$	$(\Delta_f H^\circ; \Delta_r H^\circ)$ / $\text{kJ}\cdot\text{mol}^{-1}$	$(\Delta_r S^\circ; S^\circ)$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$(C_P^\circ; \Delta_r C_F^\circ)$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
As(α ,cr)	0.0	0.0	35.63	24.43
O ₂ (g)	0.0	0.0	205.029	29.355
H ₂ (g)	0.0	0.0	130.574	28.824
H ₂ O(l)	-237.178	-285.830	69.91	75.29
As ₂ O ₃ (cubic, Arsenolite)	-576.34	-657.27	107.38	96.88
As ₂ O ₃ (monoclinic, Claudetite)	-576.53	-655.67	113.37	96.98
As ₂ O ₅ (cr)	-774.96	-917.59	105.44	115.9
As ₂ O ₃ (cubic) + O ₂ (g) = As ₂ O ₅ (cr)	-198.62	-260.32	-206.97	-10.3
2As(α ,cr) + 3H ₂ O(l) = As ₂ O ₃ (cubic) + 3H ₂ (g)	135.19	200.22	218.11	-91.38
2As(α ,cr) + 3H ₂ O(l) = As ₂ O ₃ (monoclinic) + 3H ₂ (g)	135.00	201.82	224.10	-91.28

3.1 Minerals in the As-S-O system

There is no known mineral with the formula of As₂O₅ but polymorphic minerals have been identified for As₂S₃ and As₂O₃. These minerals are compiled in Table 3 along with their formulae, crystal class and space group, and references for their crystallography and occurrence. Additional arsenic sulfide minerals of different stoichiometries than As₂S₃ have been included in this list because they commonly occur with the other phases, although no thermodynamic data is known for them.

Arsenolite and claudetite have nearly identical free energies of formation, making it difficult to determine the most stable phase under standard state conditions. Wagman et al. (1982) give claudetite as the most stable

Table 1b. Solubility and Hydrolysis of Arsenic Oxides

Species or reaction data for standard state conditions, 298.15 K and 1 atm	$(\Delta_f G^\circ; \Delta_r G^\circ)$ / $\text{kJ}\cdot\text{mol}^{-1}$	$(\Delta_f H^\circ; \Delta_r H^\circ)$ / $\text{kJ}\cdot\text{mol}^{-1}$	$(\Delta_r S^\circ; S^\circ)$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Log K
$\text{H}_3\text{AsO}_3(\text{aq})$	-640.03	-742.36	195.83	
$\text{H}_2\text{AsO}_3^-(\text{aq})$	-587.66	-714.74	112.79	
$\text{HAsO}_3^{2-}(\text{aq})$	(-507.4)			
$\text{AsO}_3^{3-}(\text{aq})$	(-421.8)			
$\text{H}_3\text{AsO}_4(\text{aq})$	-766.75	-903.45	183.07	
$\text{H}_2\text{AsO}_4^-(\text{aq})$	-753.65	-911.42	112.38	
$\text{HAsO}_4^{2-}(\text{aq})$	-713.73	-908.41	-11.42	
$\text{AsO}_4^{3-}(\text{aq})$	-646.36	-890.21	-176.31	
$\text{H}_3\text{AsO}_3(\text{aq}) = \text{H}_2\text{AsO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$	52.37	27.62	-83.04	-9.17
$\text{H}_2\text{AsO}_3^-(\text{aq}) = \text{HAsO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq})$	(80.3 $\pm$ 1.0)			(-14.1)
$\text{HAsO}_3^{2-}(\text{aq}) = \text{AsO}_3^{3-}(\text{aq}) + \text{H}^+(\text{aq})$	(85.6 $\pm$ 1.5)			(-15.0)
$\text{As}_2\text{O}_3(\text{cubic}) + 3\text{H}_2\text{O}(\text{l}) = 2\text{H}_3\text{AsO}_3(\text{aq})$	7.814	30.041	74.55	-1.38
$\text{As}_2\text{O}_3(\text{monoclinic}) + 3\text{H}_2\text{O}(\text{l}) = 2\text{H}_3\text{AsO}_3(\text{aq})$	8.003	28.443	68.56	-1.34
$\text{H}_3\text{AsO}_4(\text{aq}) = \text{H}_2\text{AsO}_4^-(\text{aq}) + \text{H}^+(\text{aq})$	13.10	-7.97	-70.69	-2.30
$\text{H}_2\text{AsO}_4^-(\text{aq}) = \text{HAsO}_4^{2-}(\text{aq}) + \text{H}^+(\text{aq})$	39.93	3.02	-123.76	-6.99
$\text{HAsO}_4^{2-}(\text{aq}) = \text{AsO}_4^{3-}(\text{aq}) + \text{H}^+(\text{aq})$	67.36	18.20	-164.88	-11.80
$\text{H}_3\text{AsO}_4(\text{aq}) + \text{H}_2(\text{g}) = \text{H}_3\text{AsO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	-110.46	-124.74	-47.90	19.35

Table 2. Arsenic Sulfides

Species or reaction, data for standard state conditions, 298.15 K and 1 atm	$(\Delta_f G^\circ; \Delta_r G^\circ)$ / kJ·mol ⁻¹	$(\Delta_f H^\circ; \Delta_r H^\circ)$ / kJ·mol ⁻¹	$(\Delta_r S^\circ; S^\circ)$ / J·K ⁻¹ ·mol ⁻¹	$(C_p^\circ; \Delta_r C_p^\circ)$ / J·K ⁻¹ ·mol ⁻¹	Log K
S(cr, rhombic)	0	0	31.8	22.6	
S ₂ (g)	79.33	128.37	228.07	32.47	
H ₂ S(aq)	-27.87	-40.21	121	167	
HS ⁻ (aq)	12.05	-17.64	62.8	-92	
AsS(α, Realgar)	-31.3	-31.8	62.9	47	
AsS(β, Realgar)	-30.9	-31.0	63.5	47	
As ₂ S ₃ (α, Orpiment)	-84.9	-85.8	163.8	163	
As ₂ S ₃ (amorphous orpiment)	-76.8	-66.9	200		
As ₃ S ₄ (SH) ₂ ⁻ (aq)	(-125.6)				
AsS(OH)(SH) ⁻ (aq)	(-244.4)				
4AsS(α, cr) + S ₂ (g) = 2As ₂ S ₃ (α, cr)	-123.9	-168.4	-148.1	106	21.7
As ₂ S ₃ (α, cr) + 6H ₂ O(l) = 2H ₃ AsO ₃ (aq) + 3HS ⁻ (aq) + 3H ⁺ (aq)	264.1	263.1	-3.2		-46.3
As ₂ S ₃ (α, cr) + 6H ₂ O(l) = 2H ₃ AsO ₃ (aq) + 3H ₂ S(aq)	144.3	195.4	171		-25.3
As ₂ S ₃ (am) + 6H ₂ O(l) = 2H ₃ AsO ₃ (aq) +	136.2	176.5	136		-23.9
1.5As ₂ S ₃ (am) + 1.5H ₂ S(aq) = As ₃ S ₄ (SH) ₂ ⁻ (aq) + H ⁺ (aq)	31.4				-5.5
0.5As ₂ S ₃ (am) + 0.5H ₂ S(aq) + H ₂ O = AsS(OH)(SH) ⁻ (aq) + H ⁺ (aq)	45.1				-7.9

Table 3. Arsenic oxide and sulfide minerals

Mineral Name	Chemical Formula	Space Group	References
(Native) Arsenic	As, trigonal	R $\bar{3}$ m	Anthony et al. (1990)
Arsenolamprite	As, orthorhombic	Bmab	Anthony et al. (1997)
Arsenolite	As ₂ O ₃ , cubic	Fd3m	Anthony et al. (1997)
Claudetite	As ₂ O ₃ , monoclinic	P2 ₁ /n	Anthony et al. (1990)
Orpiment	α -As ₂ S ₃ , monoclinic	P2 ₁ /n	Anthony et al. (1990), Stojanovic (1982)
Realgar	α -AsS, monoclinic	P2 ₁ /n	Anthony et al. (1990), Stojanovic (1982)
Realgar	β -AsS, monoclinic	C2/c	Anthony et al. (1990), Yu and Zoltai (1972)
Pararealgar	AsS, monoclinic	P2 ₁ /c	Roberts et al. (1980), Bonazzi et al. (1995)
Alacrinite	AsS, monoclinic	C2/c	Popova et al. (1986), Burns and Percival (2001)
Uzonite	As ₄ S ₅ , monoclinic	P2 ₁ /m	Popova and Polyakov (1985)
Dimorphite	As ₄ S ₃ , orthorhombic	Pnma	Anthony et al. (1990)
Duranusite	As ₄ S, monoclinic	P2 ₁ /m	Blackburn and Dennen (1997)

polymorph. Robie and Hemingway (1995), however, list arsenolite as the most stable phase, giving Wagman et al. (1982) as the only source for the free energy data yet reporting rather different numbers. Careful consideration of solubility, electrochemical, vapor pressure, heat capacity, entropy, and reaction enthalpy data along with the least squares weighted regression of the data leads to claudetite having the greater stability by $-0.19 \text{ kJ}\cdot\text{mol}^{-1}$ (Archer and Nordstrom, in press). One of the more definitive studies was by Kirschning and Plieth (1955) who determined the temperature of transition to be -33°C , above which claudetite was the more stable phase. Palache et al. (1944) report an observation that suggests claudetite forms at higher temperatures than arsenolite ($>100^\circ\text{C}$), as well as paramorphism of arsenolite after claudetite but with such a small difference in free energy, small changes in temperature, pressure, grain size, humidity, and the salinity of solutions in contact could easily change the relative stability. It is clear that arsenolite and claudetite have formed as a secondary product of weathering. These dimorphs are typically white powdery coatings that have formed from the oxidation of arsenopyrite (Palache et al., 1944; Roberts and Rapp, 1965), from the oxidation of realgar (Beyer, 1989; Kelley, 1936;

Palache et al., 1944). from the oxidation of native arsenic (Clark, 1970; Palache et al., 1944), and from the weathering of scorodite (Eckel, 1997). They are often intimately associated with each other (Dana and Ford, 1949).

Orpiment appears to have a wide range of stability, being found as a hypogene mineral in epithermal ore deposits (i.e. formed from ascending hydrothermal solutions at temperatures of roughly 50-200°C, Lindgren, 1928; Park and MacDiarmid, 1975), as a precipitate in hot springs of warm to boiling temperatures (see Chapter 4, this volume), in fumarolic encrustations (Vergasova, 1983; White and Waring, 1963), as a sublimate from mine fires and burning coal seams (Lapham et al., 1980; Palache et al., 1944; Zacek and Ondrus, 1997), and, commonly, as a supergene mineral (formed under surface or near-surface weathering conditions) from the weathering of realgar and sometimes arsenopyrite (Dana and Ford, 1949; Palache et al., 1944). Realgar, however, seems to be more typical of hypogene mineralization. Beran et al. (1994), for example, found fluid inclusions in realgar from the Allchar deposit, Macedonia, that gave homogenization temperatures of 144-170°C. At the Mercur gold deposit in Utah, USA, Jewell and Parry (1988) found a calcite-realgar vein assemblage in which the fluid inclusion in the calcite gave formation temperatures of 150-190°C. Orpiment also occurs at Mercur in a separate vein assemblage with pyrite. Although realgar is found in fumarolic encrustations, mine fire sublimates, and hot spring environments (Clarke, 1924; Palache et al., 1944; Zacek and Ondrus, 1997), it is not commonly found as a direct precipitate from solution at temperatures less than 100°C like orpiment. As long ago as 1851, de Senarmont (1851) found that when either pulverized realgar or orpiment were heated in a sealed tube with Na_2CO_3 at 150°C they would recrystallize to realgar. Mixtures of realgar and orpiment were observed by the senior author to coat rocks from a hydrothermal steam vent of about 180°C at Solfatara, Italy (also see Sinno, 1951). Migdasov and Bychkov (1998) note that a zonation between orpiment and realgar seems to occur in the Uzon Caldera, Kamchatka, with realgar occurring between 70 and 95°C. This temperature range seems to be the lowest observed for the formation of realgar that we are aware of. It is also noteworthy that the occurrence of an amorphous (to X-ray diffractometry) orpiment phase is well known (Eary, 1992) but no one has reported an amorphous realgar phase. Amorphous phases commonly result when insoluble precipitates are formed at low temperatures (0-50°C). These observations suggest that realgar may be more stable at higher temperatures and orpiment is more stable at low temperatures. To test the consistency of this observation with thermodynamic data, we calculated the equilibrium boundaries between orpiment and α -realgar and between α -realgar and arsenic as a function of the partial pressure of $\text{S}_{2(g)}$, P_{S_2} , and temperature. It was assumed that the fugacity of $\text{S}_{2(g)}$ was equal to the partial pressure. The results shown in

Figure 1 indicate that although the stability field of orpiment decreases with increasing temperature, so does the stability field of realgar because of encroachment from the expanding field of native arsenic. Both orpiment and realgar require higher fugacities of sulfur to maintain equilibrium stability at higher temperatures. Although there are uncertainties in the thermodynamic properties for realgar and orpiment that need further refinement, the general features of this stability diagram are probably correct. Hence, both orpiment and realgar are stable over a wide range of temperature but realgar is stable over a narrow range of sulfur fugacity. Although this stability diagram does not show any increasing stability of realgar with temperature, it does point out an important aspect. Orpiment and realgar are often found together and sometimes one or the other is found alone. These observations can help to constrain the sulfur fugacity of the hydrothermal system. The coexisting orpiment/realgar assemblage provides a convenient buffer for the sulfur fugacity and may provide a fugacity estimate if the temperature is known or a geothermometer if the fugacity is known.

The formation of sulfide minerals such as realgar and orpiment is usually thought of as a simple inorganic precipitation phenomenon. Recent investigations by Huber et al. (2000), however, have found an anaerobic, hyperthermophilic, facultatively organotrophic archaeon that respire arsenate and precipitates realgar. *Pyrobaculum arsenaticum*, is the first microorganism to be reported that can precipitate realgar biologically over its temperature range of growth, 68 to 100°C. It grows chemolithoautotrophically with carbon dioxide as a carbon source, hydrogen as electron donor, and arsenate, thiosulfate, or sulfur as electron acceptors. It also respire selenate when grown organotrophically and forms elemental selenium. It was isolated from the Pisciarelli Solfatara, Italy. Newman et al. (1997) also found a bacterium, *Desulfotomaculum auripigmentum*, that precipitates orpiment both intracellularly and extracellularly.

Realgar, when exposed to solar radiation, transforms to a powdery material identified as pararealgar, a polymorph of realgar (Roberts et al., 1980). Pararealgar differs from realgar only in the manner in which the As_4S_4 molecules stack in the unit cell (Bonazzi et al., 1995). When different wavelengths of light were tested, Douglass et al. (1992) found that less than 670 nm was needed to detect the transformation and the lower the wavelength, the faster the reaction. Raman spectroscopy has been used to characterize pararealgar and it has become an important tool in the understanding of art history and art preservation (Trentelman et al., 1996). Earlier literature (Palache et al., 1944; Wells, 1962) describes realgar as breaking down to orpiment and arsenolite when exposed to light for long periods of time. This observation is interesting in that it suggests that the assemblage orpiment plus arsenolite may be more stable than realgar under standard state conditions.

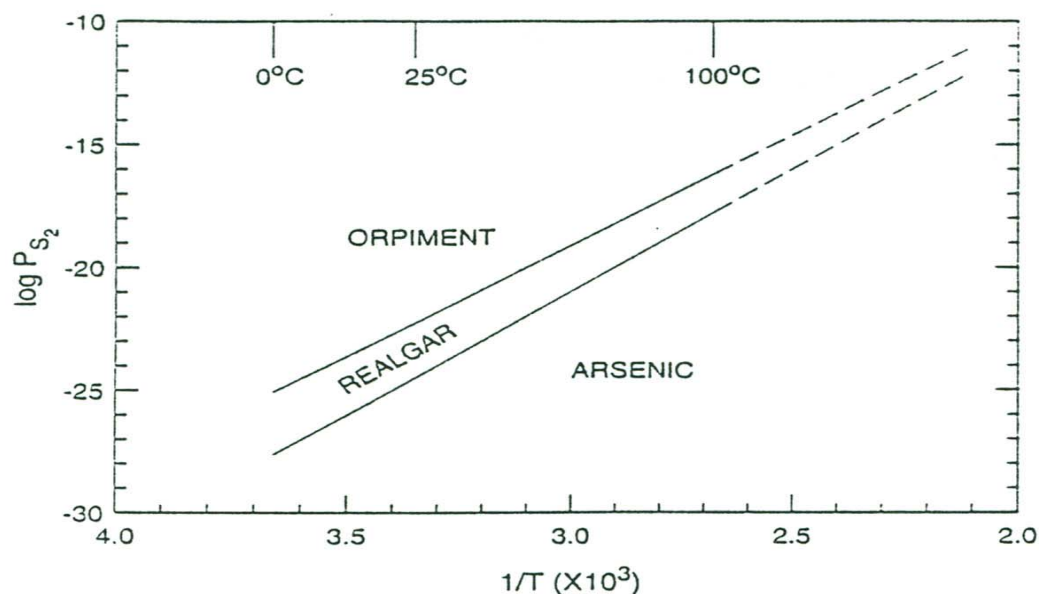


Figure 1. Univariant stable equilibria between orpiment, realgar, and arsenic as a function of P_{S_2} and $1/T$ where T is in degrees Kelvin.

Apparently alacrinite is also a low-temperature polymorph that simply stacks differently as well (Burns and Percival, 2001). We are not aware of any thermodynamic data on either pararealgar or alacrinite but since the crystal structures are identical except for molecular stacking, the free energies should be very similar to within the accuracy of calorimetric or solubility measurements. Duranusite and dimorphite (and possibly uzonite) are secondary alteration products of realgar (Clark, 1972; Marquez-Zavalia et al., 1999).

Native arsenic has been reported from numerous arsenic-rich mineral deposits (Clarke, 1924; Dana and Ford, 1949; Eckel, 1997; God and Zemann, 2000) but the descriptions of small aggregates, crystalline, massive, and botryoidal arsenic are consistent with a hypogene origin (e.g. Clark, 1970; Paronikyan and Matevosyan, 1965). It is commonly found when there is an abundance of arsenic sulfide minerals in a hydrothermal deposit. Hence, native arsenic is a product of low-temperature epithermal mineralization (50-200°C) under sulfur-deficient and strongly reducing conditions rather than a weathering product. Where native arsenic is found exposed to weathering, under dry conditions, it has usually developed a coating of arsenolite or claudetite or both (Clark, 1970; Palache et al., 1944). In low-temperature sedimentary conditions (0-50°C) there is frequently much more sulfur and iron available than arsenic so that the arsenic is incorporated into arsenian pyrite or orpiment rather than occurring in the native form. Arsenolamprite is a dimorph of arsenic that is very rare and is

known to occur in carbonate-hosted mineralized zones. It may be stabilized by high concentrations of trace elements because the original type material contained up to 3% Bi.

Many other arsenic-containing minerals are known and have some thermochemical measurements but they are beyond the scope of this paper.

3.2 $p\epsilon$ -pH diagrams for arsenic

The tabulated thermodynamic data can be used to develop the $p\epsilon$ -pH diagrams for arsenic, shown in Figures 2 and 3, that summarize the predominance fields for aqueous species and the mineral stability fields, respectively. These diagrams also help to focus the discussion on environmentally relevant geochemical processes.

The predominance area diagram of Figure 2 shows that, under oxidizing conditions, arsenate hydrolyzes to four possible species for the range of pH encountered in surface and ground waters, although the fully dissociated arsenate ion would be rare because very few waters reach a pH greater than 11.5. Under reducing conditions, the fully protonated arsenite species is predominant over a wide range of pH and because it is not ionized and adsorbs less strongly than arsenate species, dissolved arsenite tends to be much more soluble than arsenate. Hence, reducing conditions usually lead to increased concentrations of arsenic in ground waters provided that arsenic is available in the aquifer or the sediments. Arsine, AsH_3 , was estimated to be at the same $p\epsilon$ and pH conditions as the formation of hydrogen, i.e. the lower limits for water. Hence, it does not show on this diagram.

Figure 3 shows the sequence of stable minerals from fully oxidized arsenic pentoxide to fully reduced native arsenic in the presence of 10^{-4}m total dissolved sulfide. Native arsenic has a narrow stability field only under the strongest reducing conditions, consistent with field observations except that in the field it seems to form at higher temperatures than 25°C . No mineral corresponds with As(V) oxide because it is extremely soluble (about 40 grams per 100 grams of solution, Menzies and Potter, 1912) and the addition of the type of divalent cations commonly found in surface and ground waters would promote the precipitation of metal arsenates that are less soluble than the pentoxide (e.g. calcium arsenate precipitation, Nishimura and Robins, Dunning, 1988; Nishimura and Robins, 1998).

The stability field for orpiment occurs between realgar and claudetite and the stability field for realgar is barely visible at all in contrast to other diagrams such as that found in Brookins (1986). The relative stability field for realgar can change significantly with small changes in free energy for either (or both) orpiment and realgar and further refinement of the data

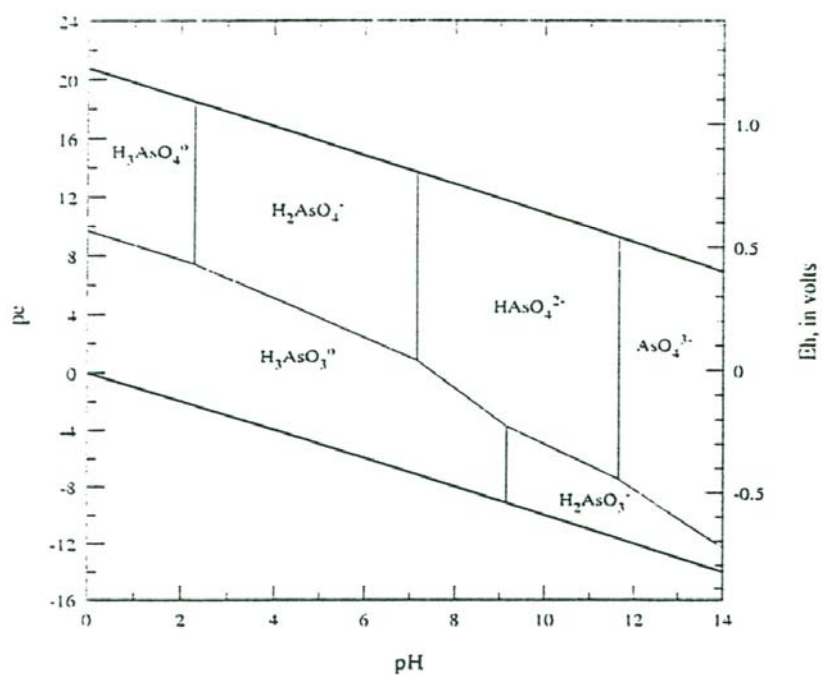


Figure 2. pe - pH diagram for predominant aqueous species of arsenic at equilibrium and 298.15 K and 1 atmosphere pressure.

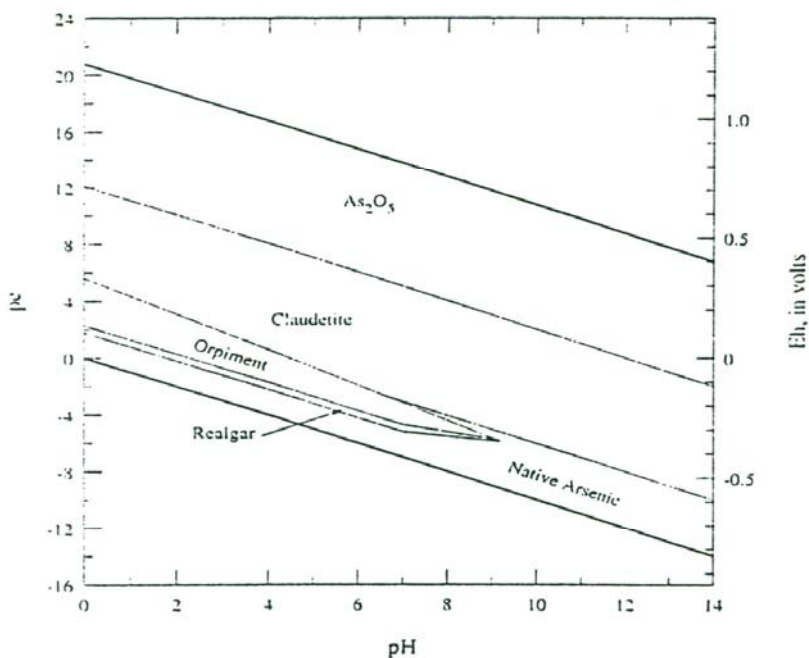


Figure 3. pe - pH diagram for equilibrium mineral stabilities in the $As-O-S-H_2O$ system at 298.15 K and 1 atmosphere pressure. Total dissolved sulfur = 10^{-4} m.

would help eliminate these ambiguities. An earlier attempt to fit the thermodynamic data resulted in an impossible chemography in which realgar was never stable over any temperature range relative to native arsenic and orpiment. Errors in enthalpy, entropy, and free energy are too large at the moment to get a better estimate for these stability fields than what we have tabulated.

3.3 Matters of stoichiometry

The first problem has to do with the appropriate stoichiometry of a compound. For example, arsenic (III) oxide appears in the literature as As_2O_3 or As_4O_6 . Similarly, the formula for realgar appears variously as As_4S_4 , As_2S_2 , or AsS . The higher order stoichiometries reflect the unit structure of bonding in dominantly covalent compounds. They are useful from a bonding and crystal structure viewpoint but serve no purpose in chemical thermodynamics and only the simplest unit stoichiometry is used in this paper: As_2O_3 for arsenolite and claudetite, AsS for realgar, and As_2S_3 for orpiment.

Several different formulae were given in the earlier literature to describe the species formed when As_2O_3 was dissolved in water under neutral or mildly acidic conditions. In fact, one finds several of these listed in Wagman et al. (1968; 1982) which gave properties for both $\text{H}_3\text{AsO}_3(\text{aq})$ and $\text{HAsO}_2(\text{aq})$. Those species were redundant to each other in Wagman et al. (1982), as were the species $\text{AsO}_2^-(\text{aq})$ and $\text{H}_2\text{AsO}_3^-(\text{aq})$. Redundant species cannot be included in model calculations, if one expects to obtain correct results from the simulation. These two redundancies were not identified as such in the original tables but were noted by Wagman et al. (1982) in an introduction to the 1982 publication. Raman spectra (Loehr and Plane, 1968) were consistent with H_3AsO_3 being the predominant form of dissolved As(III) in dilute neutral solution. We adopted this formulation here and did not consider the other earlier formulae.

3.4 Polymerization in aqueous solution

At higher concentrations of dissolved As(III), polymeric species may form in solution and the implications from their formation must be understood. A particular equilibrium constant for an aqueous reaction will depend on what species, or what other reactions, are presumed to exist in the solution. It sometimes happens that tables of thermodynamic properties may have been generated by averaging equilibrium constants for a particular reaction or by averaging other thermodynamic properties derived therefrom. In some instances, appropriate attention had not been given to the fact that

the equilibrium constants that were being averaged had been obtained originally from different assumptions regarding the species present in the solution. Such averaged equilibrium constants will introduce errors in the overall model assumed for the system. An example of indiscriminate averaging of equilibrium constants for the generation of tabulated thermodynamic properties was given previously by one of the authors (Archer, 1998).

Such a problem arises with respect to the first dissociation constant of arsenious acid, $\text{H}_3\text{AsO}_{3(\text{aq})}$. Table 4 gives some of the equilibrium constant values found in the literature for the first deprotonation step. The values in the table are for 298.15 K and all are standard-state values; this means that adjustments were made to some of the values given in the literature. The values in the table fall, more or less, into two groups of values. The first four values were determined from potentiometric titration followed with a glass electrode. The value from Garrett et al. (1940) was obtained from a study of the pH and the solubility of As_2O_3 in solutions containing different amounts of sodium hydroxide or hydrogen chloride. The two values from Ivakin et al. (1976) were determined from 1) a study of the absorptivity of arsenic-containing solutions and 2) potentiometric titrations of arsenious acid with an alkaline solution of arsenious acid.

Two distinctly different model assumptions characterize the two groups of values. The first group was obtained with an assumption that the only reaction that occurred in the solution was the deprotonation reaction as in equation 4.



The second group of values came from studies where it was assumed that polymerization reactions occurred, such as the formation of $\text{H}_5\text{As}_2\text{O}_6^-$, in addition to the deprotonation reaction. For chemical and mathematical reasons, the dissociation constant calculated from a set of measurements becomes smaller as one introduces polymeric anions into the model. The differences of the models chosen, at first appearance, could serve to explain the differences of the equilibrium constants given in the previous table. Unfortunately, the situation, from the perspective of data evaluation, is more complex. In principle, there should be a sufficient dilution of arsenious acid for which one would not expect the formation of a significant proportion of species like $\text{H}_5\text{As}_2\text{O}_6^-$ upon addition of base. For such a condition, the equilibrium constant determined assuming that only the monomer exists, should approach that determined for the multi-species model. Britton and Jackson (1934) performed potentiometric titration at two concentrations of arsenious acid (0.0170 and 0.0914 molar) and obtained essentially the same

value. Therefore, all of the variation of the equilibrium constants is not yet explained by the assumptions of different models.

Table 4. Equilibrium constants for the first deprotonation step of arsenious acid

K	Source
7.4×10^{-10}	Britton and Jackson (1934)
7.04×10^{-10}	Antikainen and Tevanen (1961)
7.08×10^{-10}	Vesala and Saloma (1977)
5.25×10^{-10}	Salomaa et al. (1969)
2.4×10^{-10}	Garrett et al. (1940)
6.8×10^{-10}	Ivakin et al. (1976)
5.4×10^{-10}	Ivakin et al. (1976)

Raman spectroscopic studies of aqueous solutions of arsenious acids have been conducted for water solutions saturated with arsenic oxide and for ratios of $[\text{OH}^-]/[\text{As(III)}]$ ranging from 3.5 to 15 (Loehr and Plane, 1968). The spectra obtained in those studies were interpreted as being consistent with the formation of mono-arsenic species only. No peak was observed that was attributed to either an As-As bond or to an As-O-H-O-As species, where a delocalization occurs about the hydrogen atom. Ivakin et al. (1976) assumed that one of the species that existed in aqueous solution was $\text{H}_6\text{As}_2\text{O}_6(\text{aq})$. However, colligative property determinations, e.g. the freezing-point depression measurements from Roth and Schwartz (1926), were not consistent with significant dimerization of the arsenious acid. Thus, one is left with a quandary. One can accept the conclusion from the Raman spectroscopy and the larger value of K for eq 4. But then one has no way of explaining the greatly increased solubility of As(III) in basic solutions over that predicted by assumption of the monomeric-only model. Conversely, if one accepts the formation of poly-As(III) species in solution, then how does one interpret the Raman spectroscopy results? (There is a recent theoretical study that suggests the existence of circular trinuclear arsenic species in neutral solution (Tossell, 1997). Additionally, a recent study by Pokrovski et al. (1996) may also support the existence of polynuclear arsenic species in solution.). The problem of which value or which model to accept for the first deprotonation step, is not merely academic. This is because the Gibbs energy of formation of H_2AsO_3^- is a primary contribution to the Gibbs energies of formation of the aqueous arsenite ion and crystalline arsenite compounds.

Our interest here is the generation of a set of properties that are useful for modeling the geochemistry of clean and contaminated waters, industrial

process and waste fluids, and related problems. These fluids are generally dilute in arsenic and do not contain the high levels of hydroxide considered by Garrett et al. (1940). Therefore, we have not included in our tables, or method, the polymeric forms suggested by Garrett et al. (1940), Ivakin et al. (1976), and Pokrovski et al. (1996).

3.5 Complications in chloride media

Wagman et al. (1968, 1982) gave a value for the Gibbs energy of formation of undissociated arsenic acid. That value was obtained from values reported by Foerster and Pressprich (1927) and auxiliary values. Foerster and Pressprich (1927) measured the electromotive force (emf) of cells in which the electrochemical reaction was presumed to be:



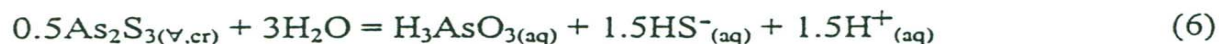
To suppress dissociation of the arsenic acid, the measurements were conducted in solutions acidified with hydrochloric acid of (1 to 6) M. The presence of large amounts of chloride in the acidified arsenic solutions is problematic. The formation of $\text{As}(\text{OH})_x\text{Cl}_{(3-x)\text{aq}}$ for x from 0 to 2, has been proposed to explain the observed increases of solubility of As(III) in hydrochloric acid (Garrett et al., 1940).

Arcand (1957) determined distribution coefficients of As(III) between a hydrochloric acid phase and a dichlorodiethyl ether phase. He used his measurements, determined at different concentrations of $\text{HCl}_{(\text{aq})}$, to argue that complexes of the type $\text{As}(\text{OH})_x\text{Cl}_{(3-x)}$ existed in those solutions for x from 0 to 3. He used solubility data of arsenic trioxide in $\text{HCl}_{(\text{aq})}$ and $\text{HClO}_{4(\text{aq})}$ to argue the existence of $\text{As}(\text{OH})_2^+_{(\text{aq})}$ in acid solutions also. He calculated approximate equilibrium constants for formation of $\text{As}(\text{OH})_2^+_{(\text{aq})}$, $\text{As}(\text{OH})_2\text{Cl}_{(\text{aq})}$, $\text{AsOHCl}_2_{(\text{aq})}$, and $\text{AsCl}_3_{(\text{aq})}$. Finally, he showed that the assumptions of species and values of the equilibrium constants nearly quantitatively represented the dependence of Foerster and Pressprich's (1927) emf measurements on the concentration of hydrochloric acid in the solution. Consequently, there were unaccounted species with different activities in Foerster and Pressprich's (1927) measurement cells and the lack of accounting of these species may have compromised the determination of $\Delta_r G$ determined for eq 5 in some thermodynamic compilations. The significance of a lack of confidence in the thermodynamic properties of arsenic acid is that they contribute to the formation properties of the arsenate ions, $\text{H}_2\text{AsO}_4^-_{(\text{aq})}$, $\text{HAsO}_4^{2-}_{(\text{aq})}$ and $\text{AsO}_4^{3-}_{(\text{aq})}$ and also to the thermodynamic properties of crystalline arsenate compounds.

3.6 Discrepancies in the arsenic sulfide system

Some tabulations of thermodynamic properties of arsenic compounds list the enthalpies of formation for $\text{AsS}_{(\text{cr})}$ and $\text{As}_2\text{S}_{3(\text{cr})}$ to be of the order of -71 and $-169 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. These values, when accompanied with reasonable values of the entropies of the crystalline phases, and the elements, lead to Gibbs energies of formation of the same magnitude. Those enthalpies were obtained from oxygen combustion measurements performed by Britzke et al. (1933). The products of the combustion were a mixture of arsenic oxides and SO_x compounds. (It was recognized some time ago that there are two crystalline forms of each of $\text{AsS}_{(\text{cr})}$ and $\text{As}_2\text{S}_{3(\text{cr})}$ and that each pair has an equilibrium interconversion temperature substantially above room temperature.) Barton (1969) examined the phase behavior of the $\text{As}+\text{S}$ system as a subset of his work on the $\text{Fe}+\text{As}+\text{S}$ system and concluded that the enthalpies of formation were much too negative and that better values were on the order of -36 and $-95 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{AsS}_{(\text{cr})}$ and $\text{As}_2\text{S}_{3(\text{cr})}$, respectively. Johnson et al. (1980) measured the enthalpy of fluorine combustion of samples of the high-temperature form of AsS and of glassy As_2S_3 . They combined those values with other measured properties and some estimates to obtain enthalpies of formation of -33 ± 1.6 and $-91.6 \pm 4.8 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{AsS}_{(\alpha, \text{cr})}$ and $\text{As}_2\text{S}_{3(\beta, \text{cr})}$, respectively. Subsequently Bryndzia and Kleppa (1988) used direct-synthesis calorimetry and obtained enthalpies of formation of -28.1 ± 0.38 and $-83.0 \pm 3.8 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{AsS}_{(\alpha, \text{cr})}$ and $\text{As}_2\text{S}_{3(\beta, \text{cr})}$, respectively. The differences between these two more recent enthalpy determinations for these two arsenic sulfide minerals, (-5 and -9) $\text{kJ}\cdot\text{mol}^{-1}$, remain large for the purpose of calculating equilibria in a system containing arsenic, sulfur, water and other potential components. Bryndzia and Kleppa (1988) observed previously that enthalpies of formation of other materials determined by means of fluorine combustion disagreed with both observed phase behavior and high-temperature solution calorimetry, e.g., the case of chalcopyrite. Nonetheless, the fluorine reactions for these materials apparently went to completion with well-defined end products and a cavalier dismissal of them would not be wise.

Fortunately, for at least orpiment, there is additional information available that helps to clarify the picture. In a separate study, Webster (1990) measured the solubility of synthetic orpiment in water and her value gives $\Delta_r G = -131.91 \text{ kJ}\cdot\text{mol}^{-1}$ for the reaction:



at 298.15 K . This value is in very good agreement with the enthalpy of formation determined by Bryndzia and Kleppa (1988). Based on the lack of

agreement of the Gibbs energy of orpiment determined from fluorine combustion measurements with that obtained from 298.15 K equilibrium data, we gave insignificant weight to the fluorine combustion results for both orpiment and realgar.

Helz et al. (1995) interpreted differences between the solubility determinations made independently by Webster (1990) and by Mironova et al. (1984) as being due to differences in the Gibbs energies of formation of the crystalline orpiment samples used in the respective studies. Webster (1990) used a synthetic orpiment and Mironova et al. (1984) used a naturally occurring orpiment crystal. Helz et al. (1995) concluded that the sample used by Webster (1990) was less stable than the naturally occurring orpiment by approximately $3 \text{ kJ}\cdot\text{mol}^{-1}$. The Gibbs energy of formation obtained from Webster's solubility determinations for the synthetic crystal is, however, in very good agreement with the enthalpy of formation determined by Bryndzia and Kleppa (1988) and the entropy determined from low-temperature adiabatic calorimetry. The latter two values were obtained from natural orpiment crystals. We also note the following. Bryndzia and Kleppa (1988) determined the enthalpy of fusion of natural orpiment to be $23.33 \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K. Myers and Felty (1970) determined the enthalpy of fusion of natural orpiment to be $28.7 \pm 1.3 \text{ kJ}\cdot\text{mol}^{-1}$ at 588 K. Adjustment of that value to 298.15 K gave $21.6 \pm 2.6 \text{ kJ}\cdot\text{mol}^{-1}$, using the enthalpy increment for vitreous As_2S_3 from Johnson et al. (1980) and the enthalpy increment for orpiment from Blachnik et al. (1980). Blachnik et al. (1980) measured the enthalpy of fusion of a synthetic orpiment. Their enthalpy of fusion, when adjusted to 298.15 K, was $23.34 \pm 2.5 \text{ kJ}\cdot\text{mol}^{-1}$. These results suggest thermodynamic equivalence of some synthetic orpiments with some natural orpiments within about $\pm 2 \text{ kJ}\cdot\text{mol}^{-1}$, or less. Finally, we note that the uncertainty in the Gibbs energy of reaction for 298.15 K from Mironova et al. (1984) was $\pm 3 \text{ kJ}\cdot\text{mol}^{-1}$, and thus represents the entire difference between the Gibbs energies of reaction from Mironova et al. (1984) and that from Webster (1990). Thus, it is not so clear that the differences in the solubility determinations must have arisen from differences in the stabilities of the different crystal samples rather than having arisen from differences in the solubility determinations per se (i.e. systematic error).

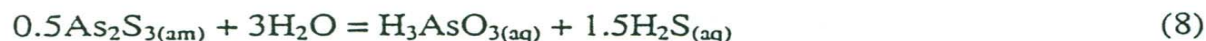
For orpiment, the solubility data and the entropy determined from calorimetric measurements support Bryndzia and Kleppa's (1988) determination of its enthalpy of formation. This might lead one to accept their value for the enthalpy of formation of realgar also. However, if one also takes Bryndzia and Kleppa's value for the enthalpy of formation for realgar and an entropy value determined from calorimetric values, the resulting Gibbs energy of formation of realgar has a fugacity of $S_{2(g)}$ that is larger than that of orpiment, which is the opposite of what is expected on the basis of chemography or on the basis of Barton's (1969) phase diagram for

the As + S system. Therefore, calorimetric measurements failed to provide information of sufficient accuracy to predict a reasonable phase diagram for the arsenic + sulfur phase diagram and other considerations must be applied. We obtained thermodynamic properties of the realgar phases by accepting Barton's value for the chemical potential of the reaction:



the entropy of $\text{AsS}_{(\beta, \text{realgar})}$ from Weller and Kelley (1964), and the enthalpy of transition for the transition of $\text{AsS}_{(\alpha, \text{realgar})}$ to $\text{AsS}_{(\beta, \text{realgar})}$ at 540 K. The enthalpy of formation calculated by this method is $3.2 \text{ kJ}\cdot\text{mol}^{-1}$ more exothermic than that obtained by Bryndzia and Kleppa (1988). These calculations presume that the entropy obtained from Weller and Kelley's (1964) calorimetric measurements from 52 K to 300 K, the assumption of a non-degenerate ground state for the β -form of realgar at 0 K, and the assumption that no phase transition occurs between 0 K and 52 K are correct.

Eary (1992) prepared an amorphous sample of As_2S_3 by precipitation of the sulfide from an aqueous solution of NaAsO_2 , buffered at pH 4.0, to which was added an excess of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. The precipitate was aged 1 to 3 days, and washed with water to remove the buffer. X-ray analysis showed no realgar, orpiment, crystalline sulfur or crystalline arsenic. Eary determined the solubility of this material at 298.15 K, 313.15 K, 333.15 K, and 363.15 K in solutions with the presence and absence of added sulfide. He gave equilibrium constants for the reaction:



at the four temperatures. The heat capacity of the reaction was estimated, $\Delta_r C_p = (180 \pm 100) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, from values of the heat capacities given in Archer and Nordstrom (in press), and where we have assumed that the heat capacity of the amorphous material is approximately equal to that of the crystalline material. These values were used to calculate:

$$\Delta_r G(T) - \Delta_r C_p \{T - T_r - T \ln(T/T_r)\} = \Delta_r G(T_r) - \Delta_r S(T - T_r) \quad (9)$$

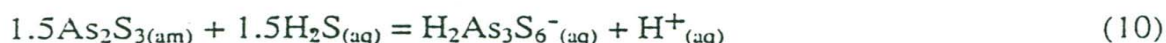
This relation was used to determine the entropy of reaction, $\Delta_r S = 66 \pm 30 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The entropy of reaction corresponds to an entropy of $\text{As}_2\text{S}_{3(\text{am})}$ of $(200 \pm 60) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. We note that there is a lower bound to the uncertainty of the amorphous material, that being the entropy of crystalline orpiment, approximately $165 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Therefore, a symmetrical uncertainty cannot be assigned in this case and we give $S(\text{As}_2\text{S}_{3(\text{am})}, 298.15$

K) = (200 +60/-35) J·K⁻¹·mol⁻¹. The Gibbs energy of reaction was $\Delta_r G(298.15 \text{ K}) = 68.08 \pm 0.85 \text{ kJ} \cdot \text{mol}^{-1}$, which when combined with other Gibbs energies of formation for the species in equation (9) leads to $\Delta_f G = -76.8 \text{ kJ} \cdot \text{mol}^{-1}$.

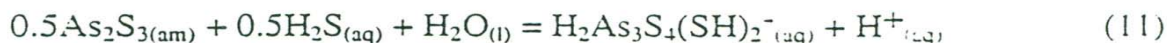
3.7 Thioarsenites

There has been some debate as to the identity of the aqueous arsenic species that are present in an aqueous solution in equilibrium with As₂S₃ where that solution contains an excess of sulfide over that which would be present from dissolution of As₂S₃ alone (see e.g. Krupp, 1990; Spycher and Reed, 1989). We had believed this controversy to have been settled recently by Helz et al. (1995) who utilized spectroscopy, molecular orbital calculations, and the solubility studies to arrive at the conclusion that the principal aqueous species in excess-sulfidic solutions are H₂As₃S₆⁻(aq) and AsO(SH)₂⁻(aq).

Helz et al. (1995) fitted the solubility measurements determined by Eary (1992) to obtain $pK = 5.5$ for the reaction:



This value leads to $\Delta_f G(\text{As}_3\text{S}_4(\text{SH})_2^-(\text{aq})) = -125.6 \text{ kJ} \cdot \text{mol}^{-1}$. They also obtained $pK = 7.9$ for the reaction:



This value leads to $\Delta_f G(\text{H}_2\text{AsS}_2\text{O}^-(\text{aq})) = -244.4 \text{ kJ} \cdot \text{mol}^{-1}$. Clarke and Helz (2000) analyzed phase behavior in the copper + arsenic + sulfur + water system and obtained a somewhat different value for the equilibrium constant for eq 11. They obtained $pK = -8.23 \pm 0.32$. This value leads to $\Delta_f G(\text{H}_2\text{AsS}_2\text{O}^-(\text{aq})) = -242.5 \text{ kJ} \cdot \text{mol}^{-1}$. The minimum uncertainty in this value, and presumably the immediately previous value is at least 1.8 kJ·mol⁻¹. We took the former value that arose solely from the treatment of Eary's solubility determinations over those obtained in the mixed arsenic + copper aqueous sulfidic system, because of difficulties in establishing the activity of arsenic sulfide in the latter system.

3.8 Hydrolysis constants for arsenious acid

Ivakin et al. (1979) determined the second and third ionization constants of arsenious acid in NaCl and KCl solutions. The pK values were determined by two methods, potentiometric and spectrophotometric. The solutions had

ionic strength 1 M and the temperature of the measurements was 293.15 K. The individual pK values were:

$$pK_2 = 13.54 \pm 0.03 \quad pK_3 = 13.99 \pm 0.04 \quad \text{NaCl(aq) potentiometric} \quad (12)$$

$$pK_2 = 13.65 \pm 0.05 \quad pK_3 = 13.75 \pm 0.04 \quad \text{KCl(aq) spectrophotometric} \quad (13)$$



where the subscript to the equilibrium constant identifies the deprotonation step. We adjusted these values for the ionic strength effect, obtaining $pK_2 = 14.2 \pm 0.1$ and $pK_3 = 15.1 \pm 0.22$. We used estimates of the entropies of reactions (14) and (15) (-125 and $-167 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively), to calculate the Gibbs energies for 298.15 K. These values led to Gibbs energies of reaction of $80.3 \pm 0.1 \text{ kJ}\cdot\text{mol}^{-1}$ and $85.6 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$, for reactions (14) and (15), respectively. These values are entered in Table 1b parenthetically because there is only one investigation and estimates had to be used to derive the values.

4. CONCLUSIONS

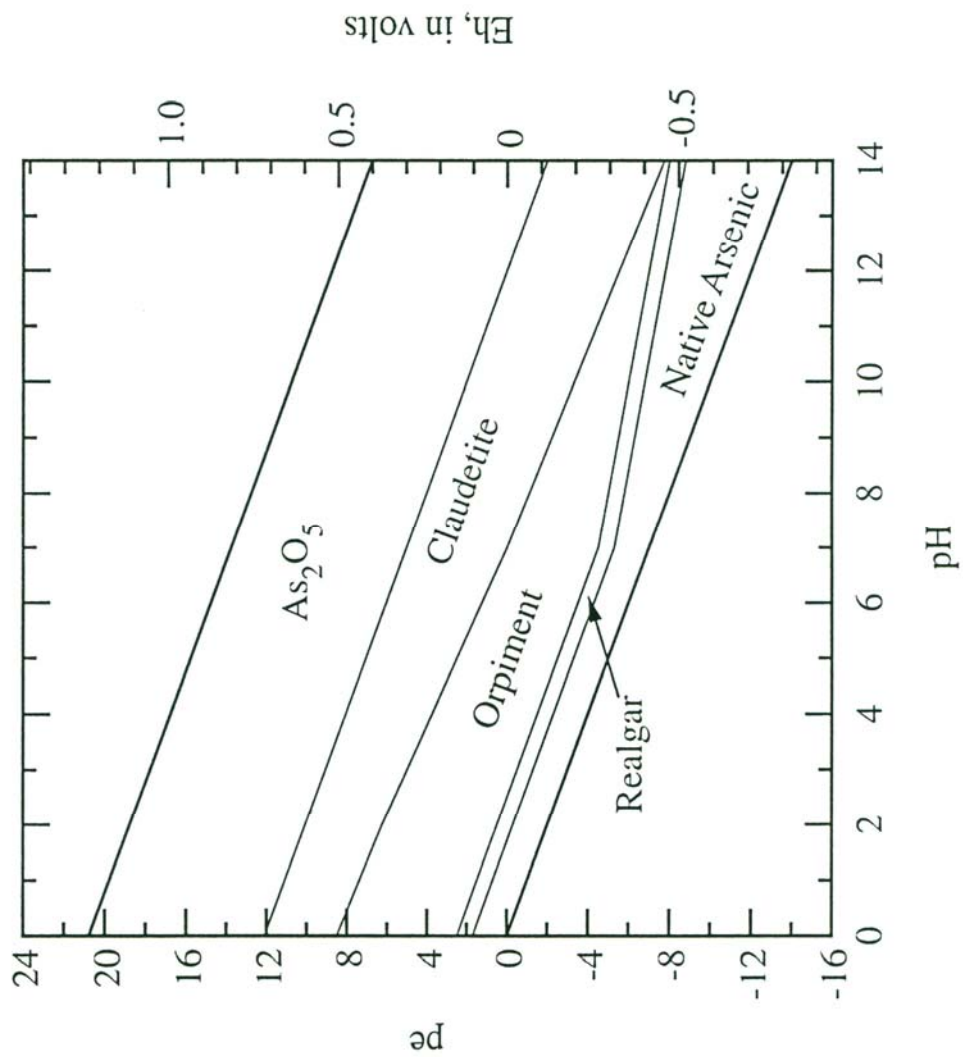
Sufficient physicochemical measurements exist to evaluate the thermodynamic properties for the simple arsenic minerals: native arsenic, arsenolite, claudetite, α -realgar, β -realgar, crystalline orpiment, and amorphous orpiment. The evaluation has been done by examining the available literature, screening and selecting the data, and performing a simultaneous weighted multiple least-squares regression on substances and reactions of arsenic, its oxides, its sulfides, and their aqueous hydrolysis products. These results have been combined with known occurrences and mineral transformations observed in nature to provide a coherent framework for mineral reactions in the As-S-O-H₂O system. The results show the following:

1. Claudetite is the most stable phase of arsenic trioxide under standard state conditions.
2. Claudetite and arsenolite are products of weathering of several arsenic sulfide minerals, of native arsenic, and of scorodite.

3. Claudetite and arsenolite are stable in equilibrium with waters of high pH.
4. Orpiment is more stable than realgar at standard state conditions and is stable in equilibrium with waters of low pH.
5. Orpiment and realgar can form under a wide variety of conditions that include hydrothermal mineralization, hot spring environments, mine fire sublimates, and fumarolic encrustations.
6. Realgar appears to be more stable than orpiment in high temperature environments (100-200°C).
7. Native arsenic is stable only under strongly reducing conditions and although it appears as a stable phase under standard state conditions, field observations indicate it only forms under hydrothermal conditions.
8. New polymorphs of realgar, pararealgar and alacrinite, have been characterized and reported in the literature and appear to form under earth's surface conditions. Pararealgar forms by visible light radiation of realgar. No thermodynamic data exist for these phases.

ACKNOWLEDGEMENTS

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corrected version of figure 3.

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