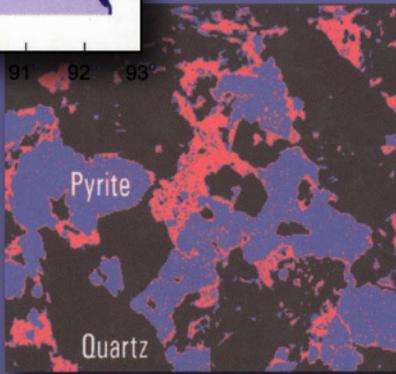
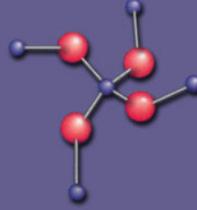
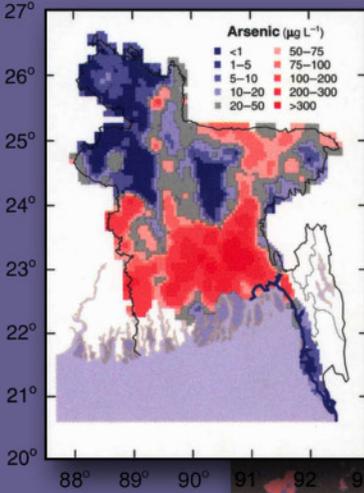


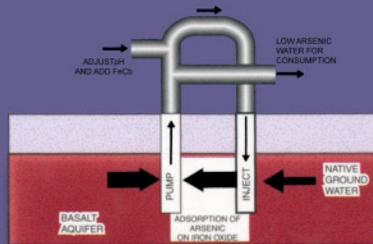
Arsenic in Ground Water Geochemistry and Occurrence



edited by

Alan H. Welch

Kenneth G. Stollenwerk



KLUWER ACADEMIC PUBLISHERS

ARSENIC IN GROUND WATER

This page intentionally left blank

ARSENIC IN GROUND WATER

edited by

Alan H. Welch

U.S. Geological Survey

Kenneth G. Stollenwerk

U.S. Geological Survey

KLUWER ACADEMIC PUBLISHERS

NEW YORK, BOSTON, DORDRECHT, LONDON, MOSCOW

eBook ISBN: 0-306-47956-7
Print ISBN: 1-4020-7317-8

©2003 Kluwer Academic Publishers
New York, Boston, Dordrecht, London, Moscow

Print ©2003 Kluwer Academic Publishers
Dordrecht

All rights reserved

No part of this eBook may be reproduced or transmitted in any form or by any means, electronic, mechanical, recording, or otherwise, without written consent from the Publisher

Created in the United States of America

Visit Kluwer Online at: <http://kluweronline.com>
and Kluwer's eBookstore at: <http://ebooks.kluweronline.com>

Contents

<i>Contributors</i>	<i>vii</i>
<i>Preface</i>	<i>xi</i>

1	Arsenic Thermodynamic Data and Environmental Geochemistry	1
	D. Kirk Nordstrom and Donald G. Archer	
2	Spectroscopic Investigations of Arsenic Species in Solid Phases	27
	Andrea L. Foster	
3	Geochemical Processes Controlling Transport of Arsenic in Groundwater: A Review of Adsorption	67
	Kenneth G. Stollenwerk	
4	Geothermal Arsenic	101
	Jenny G. Webster and D. Kirk Nordstrom	
5	Role of Large Scale Fluid-Flow in Subsurface Arsenic Enrichment	127
	M.B. Goldhaber, R.C. Lee, J.R. Hatch, J.C. Pashin, and J. Treworgy	
6	Arsenic in Ground Water Used for Drinking Water in the United States	165
	Sarah J. Ryker	
7	Arsenic in Groundwater – South and East Asia	179
	Pauline L. Smedley	
8	The Scale and Causes of the Groundwater Arsenic Problem in Bangladesh.....	211
	David G. Kinniburgh, Pauline L. Smedley, Jeff Davies, Chris J. Milne, Irina Gaus, Janice M. Trafford, Simon Burden, S. M. Ihtishamul Huq, Nasiruddin Ahmad, Kazi Matin Ahmed	

9	Mechanisms of Arsenic Release to Water from Naturally Occurring Sources, Eastern Wisconsin.....	259
	M.E. Schreiber, M.B. Gotkowitz, J.A. Simo, and P.G. Freiberg	
10	Arsenic in Southeastern Michigan	281
	Allan Kolker, S. K. Haack, W. F. Cannon, D. B. Westjohn, M.-J. Kim, Jerome Nriagu, and L. G. Woodruff	
11	Occurrence of Arsenic in Ground Water of the Middle Rio Grande Basin, Central New Mexico.....	295
	Laura M. Bexfield and L. Niel Plummer	
12	Arsenic Contamination in the Water Supply of Milltown, Montana.....	329
	Johnnie N. Moore and William W. Woessner	
13	Natural Remediation Potential of Arsenic-Contaminated Ground Water	351
	Kenneth G. Stollenwerk and John A. Colman	
14	Modeling In Situ Iron Removal from Groundwater with Trace Elements such as As	381
	C.A.J. Appelo and W.W.J.M. de Vet	
15	In Situ Arsenic Remediation in a Fractured, Alkaline Aquifer	403
	Alan H. Welch, Kenneth G. Stollenwerk, Douglas K. Maurer and Lawrence S. Feinson	
	References cited	421
	Index.....	471

Contributors

- C.A.J. Appelo
Hydrochemical Consultant
Amsterdam
The Netherlands
- Nasiruddin Ahmad
Department of Public Health
Engineering
Dhaka, Bangladesh
- Kazi Matin Ahmed
Department of Geology
University of Dhaka
Dhaka, Bangladesh
- Donald G. Archer
National Institute of Standards
and Technology
Gaithersberg, MD
- Laura M. Bexfield
U.S. Geological Survey
Albuquerque, NM
- Simon Burden
British Geological Survey
Nottingham
UK
- W.F. Cannon
U.S. Geological Survey
Reston, VA
- John A. Colman
U.S. Geological Survey
Northborough, MA
- Jeff Davies
British Geological Survey
Wallingford, Oxfordshire
UK
- W.W.J.M. de Vet
Hydron-ZH
Gouda
The Netherlands
- Lawrence S. Feinson
U.S. Geological Survey
Carson City, NV
- Michael J. Focazio
U.S. Geological Survey
Reston, VA
- Andrea L. Foster
U.S. Geological Survey
Menlo Park, CA
- Philip Freiberg
Redwood National Park
Orick, CA
- Irina Gaus
British Geological Survey
Wallingford, Oxfordshire
UK
- M.B. Goldhaber
U.S. Geological Survey
Denver, CO

Madeline B. Gotkowitz
Wisconsin Geological And
Natural History Survey
Madison, WI

Chris J. Milne
British Geological Survey
Wallingford, Oxfordshire
UK

S.K. Haack
U.S. Geological Survey
Lansing, MI

Johnnie N. Moore
Department of Geology
University of Montana
Missoula, MT

J.R. Hatch
U.S. Geological Survey
Denver, CO

D. Kirk Nordstrom
U.S. Geological Survey
Boulder, CO

S.M. Ihtishamul Huq
Department of Public Health
Engineering
Dhaka, Bangladesh

Jerome Nriagu
University of Michigan
School of Public Health
Ann Arbor, MI

M. –J Kim
Korea Institute of Science and
Technology
Seoul, South Korea

J.C. Pashin
Geological Survey of Alabama
Tuscaloosa, AL

David Kinniburgh
British Geological Survey
Wallingford, Oxfordshire
UK

L. Neil Plummer
U.S. Geological Survey
Reston, VA

Allan Kolker
U.S. Geological Survey
Reston, VA

Sarah J. Ryker
U.S. Geological Survey
(Present Address)
Carnegie Mellon University
Pittsburgh, PA

R.C. Lee
U.S. Geological Survey
Denver, CO

M.E. Schreiber
Department of Geological
Sciences
Virginia Tech
Blacksburg, VA

Douglas K. Maurer
U.S. Geological Survey
Carson City, NV

J. Antonio Simo
Department of Geology and
Geophysics
University of Wisconsin-
Madison
Madison, WI

Kenneth G. Stollenwerk
U.S. Geological Survey
Denver, CO

Janice M. Trafford
Wallingford, Oxfordshire
UK

J. Treworgy
Earth Science Department
Principia College
Elsahy, IL

Jenny G. Webster
Environmental Chemistry/Water
Quality
School of Environmental &
Marine Science
University of Auckland
Auckland NZ

Alan H. Welch
U.S. Geological Survey
Carson City, NV

D.B. Westjohn
U.S. Geological Survey
Lansing, MI

William W. Woessner
Department of Geology
University of Montana
Missoula, MT

L.G. Woodruff
U.S. Geological Survey
Mounds View, MN

This page intentionally left blank

Preface

Interest in arsenic in ground water has greatly increased in the past decade because of the increased awareness of human health effects and the costs of avoidance or treatment of ground water supplies used for consumption. The goal of this book is to provide a description of the basic processes that affect arsenic occurrence and transport by providing sufficient background information on arsenic geochemistry and descriptions of high-arsenic ground water, both affected and unaffected by human activity.

An understanding of thermodynamics, adsorption, and the speciation of arsenic in solid phases, which are described in first three chapters, is needed to predict the fate of arsenic in ground water systems. Large-scale and deep movement of ground water can and has redistributed arsenic in the near surface environment, as described in the next two chapters. These large-scale systems can affect large volumes of both ground water and surface water, such as in the Yellowstone system, and can produce mineralised zones that subsequently release arsenic to ground water supplies. Regional identification of high-arsenic ground water and its consumption as described in the next three chapters clearly demonstrates a need for increased water-quality monitoring, particularly in south and southeast Asia. Chapters 9-11 provide examples of high arsenic ground water associated with sulfide mineral oxidation and alkaline conditions. Finally, smaller scale studies of the effects of human activities that have produced high-arsenic ground water and methods for attenuation of ground water are presented.

This volume would not have been possible without the financial support of the National Research and National Water-Quality Assessment Programs of the U.S. Geological Survey. The support by these programs is gratefully acknowledged. The able assistance of Nancy Damar, Teresa Foglesong, Chris Stone, and Angie Thacker in the preparation of this volume is greatly appreciated.

Finally, the editors dedicate this book to the victims of arsenic poisoning in the hope that it will help in some small way to lessen the impact of arsenic on humans.

This page intentionally left blank

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 $\text{H}_3\text{AsO}_3^0(\text{aq})$, where the latter value was taken from Naumov et al. (1974). Naumov et al. based their value of $\Delta_f G$ for $\text{H}_3\text{AsO}_3^0(\text{aq})$, 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 $p\epsilon$ - 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 $As_{(\alpha,cr)}$ 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	$(\Delta_f G^\circ; \Delta_r G^\circ)$ / $\text{kJ}\cdot\text{mol}^{-1}$	$(\Delta_f H^\circ; \Delta_r H^\circ)$ / $\text{kJ}\cdot\text{mol}^{-1}$	$(\Delta_r S^\circ; S^\circ)$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$(C_p^\circ; \Delta_r C_p^\circ)$ / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
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