

Chapter 1

Arsenic thermodynamic data and environmental geochemistry

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

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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