Arsenic behaviour in subsurface hydrogeochemical systems – a Critical review of thermodynamic data for minerals and aqueous species of arsenic

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Abstract

A requirement for modelling the chemical behaviour of groundwater and its quality in sub-surface environments is accurate thermodynamic data for the minerals and aqueous species. This is especially true for pollutant metals. Arsenic is reported as a pollutant element in various aqueous systems in the World. Understanding its behaviour is of crucial importance in order to predict environmental risks and to develop remediation processes. A detailed characterisation of As thermochemical behaviour is crucial to allow evaluation of remediation ways. Thermodynamic models are important tools allowing the optimisation of remediation processes. Unfortunately, the examination of existing thermodynamic data of arsenic reveals dramatic inconsistencies in published data.

Arsenic contamination is a serious problem at many contaminated sites and can pose a significant threat to human health and ecological systems. The aqueous speciation of As influences its solubility, transfer, and toxicity in subsurface waters. Although the fact that As is relatively immobile in subsurface waters as a result of precipitation and adsorption onto iron hydroxides, it can present high concentrations.

In this study, the available literature on the solubility of arsenic minerals in waters is reviewed. Thermodynamic data are compiled and evaluated. The existing conflicts between literature data for some species is tentatively resolved. Although non-exhaustive, the list of minerals and aqueous species of arsenic studied will permit studying the behaviour of arsenic in various hydrogeochemical systems. In this work, we attempted to extend existing thermodynamic databases (as that of the geochemical software, EQ3/6) to permit the exploration of various hydrogeochemical systems from oxidative weathering of mine tailings ($pH < 3.0$, $Eh > 500$ mV), moderate conditions as in the case of soils (pH6-8, Eh = 200 to 500 mV) to alkaline anoxic systems ($pH > 12$, $Eh < 0.0$ mV) as in the case of bottom ash lecheates. All reactions are written in term of the EQ3/6 conventions because this geochemical software is the most used one in BRGM. Individual Gibbs free energy and eventually enthalpy and entropy of each species are given depending to the availability of these data.

The examination of arsenic contents in various hydrothermal and subsurface waters shows that arsenic concentrations are often higher than the SMCL (Second Maximum Contaminant Limit = 0.01 mg/l) fixed by the WHO (World Health Organisation). In many contexts, these polluted waters will be used for agricultural irrigations (rivers, lakes, etc.), therapeutic (thermal sources), etc. Consequently, it is very important to know the behaviour of dissolved arsenic and the main mechanisms controlling its dispersion in the environment.

The aim of this work was to critically compile these data and attempting to reconcile it. The compiled thermochemical data is aimed to improve our knowledge and to help developing trapping process and remediation techniques.

Contents

Introduction

For economic and environmental reasons, the physico-chemical properties of arsenic have been measured and quantified since the beginning of the century. Hydrogeochemical behaviour of arsenic is very complicated due to its affinity to be complexed by ligands of natural waters but also to its involvement in the biota. Consequently, high concentrations of arsenic can be encountered in the environment as a result of mineral dissolution, geothermal activity, meteoric leaching of mine wastes, coal fly ash, and pesticides.

According to the specific Eh-pH conditions of an aqueous system, arsenic can be present either as arsenite, As(III), or arsenate, As(V). Generally, arsenate ($H_3AsO_4^\circ$, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) is the predominant arsenic species in oxidised environments, while arsenite ($H_3AsO_3^\circ$, $H_2AsO_3^-$, and $HAsO_3^{2-}$) predominates under reducing conditions. Arsenate can precipitate when metal cations are present and can also coprecipitate with iron oxyhydroxides. Coprecipitates are stable only under specific conditions and arsenic mobility increases as pH increases. On the other hand, arsenite has a high affinity for metal sulfide compounds. In extreme reducing conditions arsine (AsH_3°) can be formed. Highly volatile methylated species, such as $HAs(CH_3)_2^\circ$ and $As(CH_3)_3^\circ$, can be formed in soils. Some organometallic forms, such as methylarsenic acid $(CH_3)AsO_2H_2^\circ$ and dimethylarsenic acid $(CH_3)_2AsO_2H^\circ$, are reported (Evanko and Dzombak, 1997).

Arsenic can be encountered in natural and anthropogenic hydrogeochemical systems at concentration higher than the WHO (World Health Organisation) Maximum Contaminant Levels (MCL = 0.01 mg/l). Hence, many studies and research works were undertaken in order to understand hydrogeochemical and biogeochemical behaviour of As. The available literature data emphasised the complexity of mechanisms involved in the transfer of that pollutant between phases (water – solid – gas).

In term of pollutant risks from different natural and anthropogenic sources, the challenge is the prediction of the hydrogeochemical behaviour of arsenic. Thermochemical properties of mineral and aqueous species of arsenic will be precisely known.

This report presents a critical compilation of thermodynamic data of about 70 species of arsenic at standard conditions (25°C, 1 bar). The standard state convention for aqueous species adopted in the present study is one of unit activity of the aqueous species in hypothetical one molal solution referenced to infinite dilution (Shock and Helgeson, 1988). All reactions involving arsenic are written as in EQ3/6 database convention. The added reactions were written for new minerals and aqueous species, using $H_2AsO_4^-$, H^+, $O_2(g)$ as "strict basis species" and $H_2AsO_3^-$ as "auxiliary basis species" (see details of these notions in Wolery, 1992). All data for ΔG°_f are in kJ/mol, log K is decimal logarithm of the dimensionless equilibrium constant.

1. Aqueous species of arsenic

Arsenic can be complexed by the hydroxide ion (OH^-) and other inorganic ligands encountered in natural waters. It can also be complexed by cations and especially bivalent cations as Mg^{2+}, Ca^{2+}, etc. Values of available stability constants for more than 50 arsenic aqueous species are critically compiled.

1.1. OXYACIDS

Successive dissociation constants of arsenious acid ($H_3AsO_3^\circ$) and arsenic acid ($H_3AsO_4^\circ$) are well known (Wagman et *al.*, 1982; Johnson et *al.*, 1992; Whiting, 1992).

Arsenite species (As(III))

The standard molal thermodynamic properties at 25°C and 1bar for $H_3AsO_3^\circ$ have been given in Wagman et *al.* (1982) and Shock and Helgeson (1988) compilations. A corroborating measured value (-639.164) of ΔG°_f ($H_3AsO_3^\circ$) was derived by Pokrovski et *al.* (1996) from the precise experimental investigation of solubility of arsenolite and claudetite. A more negative value of the ΔG°_f has been proposed by Sergeyeva and Khodakovskiy (1969), but it leads to a small difference, which doesn't exceed 0.025 in log K of $H_3AsO_3^\circ$ dissociation reaction.

In EQ3/6 database there are two sets of log K for the same forms of orthoarsenous acid, written as:

$HAsO_2^\circ$ and $H_3AsO_3^\circ$ or AsO_2^- and $H_2AsO_3^-$ on the base of Grenthe et *al.* (1992) and Shock and Helgeson (1988) respectively. The use of these couples will lead to overestimation of there concentration. Fortunately, data are consistent as can be seen from log K of oxidation:

$AsO_2^- + H_2O + 0.5O_{2(g)} = H_2AsO_4^-$ log K = 29.08 (1)
$H_2AsO_3^- + 0.5O_{2(g)} = H_2AsO_4^-$ log K = 29.09 (2)

We used the more common second forms.

Using the Ab-initio modelling technique, Tossell (1997) have concluded that the hydrolysis reaction of $HAsO_2^\circ$ to form $As(OH)_3^\circ$ is exothermic by more than 167 kJ/mol. Consequently, the species $HAsO_2^\circ$ is not stable in aqueous solution. He has also evaluated the stability of the species $HAsO(OH)_2^\circ$, in which one proton of $As(OH)_3^\circ$ is transferred from O to As. The energy of this species is about 105 kJ/mol higher than that of $As(OH)_3^\circ$. Hence, the stable neutral monomer species in aqueous solution is certainly $As(OH)_3^\circ$.

The second dissociation reaction of $H_3AsO_3^\circ$ was written by Wolery (1992) through the species $AsO_2(OH)^{2-}$ instead of $HAsO_3^{2-}$, and thermodynamic data were taken from Sergeeva and Khodakovskiy (1969) without corrections. Due to the difference in ΔG°_f values for $H_2AsO_3^-$ between Sergeeva and Khodakovskiy (1969) and EQ3/6 database, the log K_2 was -11.017 (EQ3/6) instead of the well known value, -12.13. Note that the log K_2 and log K_3 of successive dissociation reactions of $H_2AsO_3^-$ have been obtained by Konopik and Leberl (1949) from calorimetric measurements. Hence, the correction is done and the value –12.13 for log K_2 is recommended (Table 1).

The arsenic species AsO^+ and AsO_3^{3-} doesn't present great interest for natural ground and surface waters because their stability field is only at pH<-0.3 or >13.4 respectively (Sergeeva and Khodakovskiy, 1969). However, for some special industrial cases, it will be interesting to know the As speciation in these extreme conditions. We have, therefore, given the thermodynamic constants of the corresponding reactions (Table 1). From Latimer (1954) data ($\Delta G_f^\circ(AsO^+)$ = -163.6) we have computed the stability constant of the reaction

$$H_3AsO_3^\circ = AsO^+ + OH^- + H_2O \qquad \log K = -14.3 \qquad (3)$$

This value is in a close agreement with that of Wagman et *al.* (1982), but some more negative values (Sergeeva and Khodakovski, 1969) can be obtained due to differences in $H_3AsO_3^\circ$ Gibbs free energy. In accordance with the EQ3/6 convention, the following values were obtained for the corresponding reactions using Latimer (1954) value for $\Delta G_f^\circ(AsO^+)$.

$$AsO^+ + 0.5O_2(g) + 2H_2O = H_2AsO_4^- + 2H^+ \qquad \log K = 20.18 \qquad (4)$$
$$AsO_3^{3-} + 2H^+ + 0.5O_2(g) = H_2AsO_4^- \qquad \log K = 54.62 \qquad (5)$$

and the value of $\Delta G_f^\circ(AsO_3^{3-})$ = - 441.415 is taken from Whiting (1992). This value is in a close agreement with that recommended by Akinfiyev et *al.* (1992).

Arsenate species (As(V))

For As(V) species the good choice of an internally consistent $H_3AsO_4^\circ$ successive dissociation constants done by Sergeyeva and Khodakovskiy (1969) is confirmed. These authors have recommended the following thermodynamic constant values for successive dissociation reactions for the arsenate acid $H_3AsO_4^\circ$: -2.20±0.02, -6.97, and -11.51, respectively. The literature search conducted by Whiting (1992) has permitted him to propose the following values for pK_{1-3}: 2.24, 6.96 and 11.5, respectively. The corresponding constants used in EQ3/6 database (taken from Wagman et *a*l., 1982) and Shock and Helgeson (1988) are in good agreement with these values: 2.25, 6.76, 11.60. These values are recommended in the present database.

1.2. SULPHIDE COMPLEXES

Species of As(III)

Various stoichiometries of arsenic sulphide complexes have been proposed and the ground for selection between the dimer such as $As_2S_4^{2-}$ and trimer ($As_3S_6^{3-}$) species are limited. For example, Spycher and Reed (1989a) have shown that solubility data of Mironova and Zotov (1980) can be interpreted equally well by three sets of complexes:

1. $H_2As_2S_4$, $HAs_2S_4^-$, $As_2S_4^{2-}$,
2. $HAsS_2$, AsS_2^-,
3. $H_3As_3S_6$, $H_2As_3S_6^-$, $HAs_3S_6^{2-}$.

Spycher and Reed (1989a) consider the last one (3) best reproduces the solubility data of Mironova and Zotov (1980) and Weissberg et *al.* (1966) together, and are in agreement with the findings of Angeli and Souchay (1960). Spycher and Reed (1989a) evaluated the pK of the following reaction using the data of Mironova and Zotov (1980) and free energy of formation of As_2S_3 from Johnson et *al.* (1980):

$$1.5As_2S_3 + 1.5HS^- + 0.5H^+ = H_2As_3S_6^- \qquad \log K = -2.325 \quad (6)$$

Webster (1990) has determined experimentally the solubility of synthetic, crystalline As_2S_3 in sulphide-bearing solutions ($mS_{tot} = 0.02 \pm 0.005$) as a function of pH (1.45 - 6.75) and considers it's solubility is limited by the same reaction (6) with pK = 3.61± 0.09. Mironova et *al.* (1990) have determined experimentally the solubility of natural, low-temperature orpiment (As_2S_3) at pH 1.2 - 9.0 with sulphide sulphur concentration of 0.002 - 0.04m and consider its solubility is limited by the reactions:

$$As_2S_3 + H_2O = H_2As_2S_3O^\circ \qquad pK = 6.45 \pm 0.05 \qquad (7)$$

$$As_2S_3 + HS^- = HAs_2S_4^- \qquad pK = 1.47 \pm 0.08 \qquad (8)$$

$$As_2S_3 + HS^- + OH^- = As_2S_4^{-2} + H_2O \qquad pK = 4.05 \pm 0.2 \qquad (9)$$

Note that the arsenic concentrations in Webster (1990) are relatively higher than in Mironova et *al.* (1990) even after the recalculations to the equal total sulphur concentration (mS_{tot}). The same observation is reported for dilute O_2-free solutions of Webster (1990) in comparison with Mironova et *al.* (1984). Recall that Mironova et *al.* (1984, 1990) used natural orpiment, consequently, this material can contain impurities which induces this systematically high orpiment solubility.

Mironova et *al.* (1990) simulated the solubility of orpiment on the basis of $As_2S_3^\circ$, $HAs_2S_4^-$, $As_2S_4^{-2}$ Species. The former is represented as a dehydrated molecule, which from the thermodynamic viewpoint is equivalent to the $H_2As_2S_3O^\circ$. This set of species is sufficient to describe the experimental data. Akinfiyev et *al.* (1992) has carried out the thermodynamic analyses of equilibrium in the As(III)-S(II)-O-H system and proposed consistent data for all species involved in this system. These authors have suggested the addition of $As_2S_7^{-2}$ species to interpret the As_2S_3 solubility measurements (Weissbuerg et *al.* 1966; Mironova et *al.*, 1990) at high temperatures.

Discussion about sulphide complexes of arsenic and antimony was continued in Krupp (1990a,b), and Spycher and Reed (1990a,b). Krupp (1990a,b) has strongly argued that the binuclear species are most likely to predominate in sulphide-rich solutions, based on analogy with Sb_2S_3 solubility and analyses of speciations from Angeli and Souchay (1960) and Mironova and Zotov (1980). Spycher and Reed (1990a,b) defend the stability of trimer stoicheometries of sulphide complexes in this kind of systems which agree well with their geological observations (Spycher and Reed, 1989b) and experimental results of Webster (1990) and Eary (1992).

Note that incorrect assignment of molecular formulas can easily lead to orders-of-magnitude errors in predicted solubilities. Helz et *al.* (1995) presented new EXAFS and Raman spectroscopic data, which were interpreted with the aid of the theoretical studies. Their results do not support any of the oligomeric models of thioarsenite speciation and estimated free energies for $AsS(OH)(HS)^-$, $AsS(SH)_2^-$ and $As_3S_4(SH)_2^-$ are presented. So, monomeric thioarsenites could be more important in nature, when sulfidic natural waters are undersaturated with respect to As_2S_3 phases, otherwise, the trimers can be present in saturated solutions. Viewed in another way, increasing HS^- and H^+ favours monomers over trimers, as indicated by the following reaction:

$$As_3S_4(SH)_2^- + HS^- + H^+ = 3AsS(SH)_2^- \qquad (10)$$

The estimated free energies for $AsS(OH)(HS)^-$, $AsS(SH)_2^-$ and $As_3S_4(SH)_2^-$ were integrated in revised EQ3/6 database with auxiliary values of the Gibbs free energy of formation of orpiment (Table 2). Consequently, for reducing environments and moderate $fS_2(g)$ the monomeric species are sufficient to explain the arsenic speciation but for systems at high $fS_2(g)$ and in equilibrium with As_2S_3, dimer and trimer species (reactions 6, 7, 8, and 9) become predominant.

1.3. FLUORIDE COMPLEXES

Stability constants have been determined for the fluoroarsenites by Dutt and Gupta (1961). The reestimation of log K of $HAsO_3F^-$ and $AsO_3F_2^-$ have been done by Whiting (1992). He found that in the original reference the authors did not consider ionic strength effect and the formation of HF_2^- and $H_2F_2^\circ$ when evaluating their experimental results. In addition, the acid dissociation constant values they used for HF°, $H_3AsO_4^\circ$, and $H_2AsO_4^-$, $HAsO_4^{2-}$ differ significantly from that currently accepted (see table 1). The dissociation constant values of arsenic fluoride complexes according to the following reactions:

$$HAsO_3F^- = AsO_3F_2^- + H^+ \qquad \log K = 6.05 \qquad (11)$$

$$HAsO_3F^- + H_2O + H^+ = HF^\circ + H_3AsO_4^\circ \qquad \log K = -0.57 \qquad (12)$$

given by Whiting (1992) are recommended. The initial values (taken from Dutt and Gupta, 1961) in EQ3/6 thermodynamic database have been replaced by these corrected values. Dutt and Gupa (1961) have overestimated the stability constants for $HAsO_3F^-$ and $AsO_3F_2^-$ complexes.

In some applications of arsenic speciation calculations in thermal water (Cézallier, France) with initial thermodynamic database of EQ3/6 have shown that a trace of fluoride can complexe all co-existing dissolved arsenic and the obtained values of saturation index for As minerals (i.e., scorodite, FeAsO4, symplesite, etc., see Table 2) are lower than –10.0. In Cheni tailing leachates (France) the same result is obtained. Furthermore, although it is suggested that in the oxidised zones arsenic is nearly in equilibrium with scorodite or an analogous iron arsenic solid oxide. On the other hand, we noted the absence of any correlation between dissolved As and F. Finally, these new thermodynamic values of stability constants (Whiting, 1992) allows reasonable speciation and equilibrium state of dissolved arsenic when applied to the Cézallier and Cheni fluids.

1.4. METAL COMPLEXES

The stability constants for number of metal arsenate complexes were estimated by Whiting (1992). He applied these thermodynamic constants to explore the behaviour of arsenic in subsurface waters (Sharon Steel, Utah) and the arsenate mineral solubilities. In his evaluation, arsenate complexation constants were computed using two different techniques and sometimes the measured values: BSEP (Brown-Sylva Electronicity Principle, proposed by Brown et *al.* (1985)) and the graphical correlation techniques (consisting in search correlations between log K values of two different but similar systems, such as arsenates and phosphates, that have the same valences). Whiting (1992) have written all reactions with $HAsO_4^{2-}$ or AsO_4^{2-}. Finally, we have rewritten the dissociation reactions of arsenic-metal complexes using $H_2AsO_4^-$ as the basis species of dissolved arsenic (convention adopted in the EQ3/6 databases). All values of ΔG°_f for concerned cations and CrO_4^{2-} used in EQ3/6 are from Shock and Helgeson (1988) and that of Al^{3+} from Pokrovskii and Helgeson (1994). Obtained data are compiled in Table 1. Note that data of Whiting (1992) are in reasonable agreement with those of Mironov et *al.* (1995) for $CaH_2AsO_4^+$, $CaHAsO_4^\circ$, and $CaAsO_4^-$ given at 40°C. The following values are proposed by Whiting (1992) 1.06, 2.69, and 6.22 at 25°C, and by Mironov et *al.* (1995) 1.39, 2.75, and 4.3 at 40°C, respectively.

Species	ΔG^0_f	ΔH^0_f	S^0	Reaction	log K	Réf.
$H_3As(aq)$	99.58	45.61	51.04	$H_3As(aq) + 1.5O_2(g) = H^+ + H_2AsO_3^-$	120.30	a, b, e
$CH_3AsO_3H_2^\circ$	-	-	-	$CH_3AsO_3H_2^\circ = CH_3AsO_3H^- + H^+$	-4.19	i
$CH_3AsO_3H^-$	-	-	-	$CH_3AsO_3H^- = CH_3AsO_3^{2-}$	-8.77	i
$(CH_3)_2AsO_3H^\circ$	-	-	-	$(CH_3)_2AsO_3H^\circ = (CH_3)_2AsO_3^- + H^+$	-6.27	i
$H_3AsO_3^\circ$	-639.68	-742.20	194.97	$H_3AsO_3^\circ = H^+ + H_2AsO_3^-$	-9.20	a, b, f
$H_2AsO_3^-$	-587.14	-714.49	110.46	$H_2AsO_3^- + 0.5O_2 = H_2AsO_4^-$	29.09	a, b, f
$AsO_2(OH)^{2-}$	-517.90	-	-	$AsO_2(OH)^{2-} + H^+ = H_2AsO_3^-$	12.13	a, b
AsO_3^{3-}	-441.42	-	-186.6	$AsO_3^{3-} + 2H^+ + 0.5O_2 = H_2AsO_4^-$	54.615	*
AsO^+	-163.60	-	-	$AsO^+ + 0.5O_{2(g)} + 2H_2O = H_2AsO_4^- + 2H+$	20.18	*
H_3AsO_4	-766.00	-902.50	184.00	$H_3AsO_4 = H^+ + H_2AsO_4^-$	-2.249	a, b, c
$H_2AsO_4^-$	-753.16	-909.56	117.15	BS		a, b, f
$HAsO_4^{2-}$	-713.43	-906.34	-1.67	$HAsO_4^{2-} + H^+ = H_2AsO_4^-$	6.96	a, b
AsO_4^{3-}	-647.79	-888.14	-162.8	$AsO_4^{3-} + 2H^+ = H_2AsO_4^-$	18.46	a, b
$HAsO_3F^-$	-831.90			$HAsO_3F^- + H_2O = F^- + H^+ + H_2AsO_4^-$	-5.99	*
AsO_3F^{2-}	-797.37			$AsO_3F^{2-} + H_2O = F^- + H_2AsO_4^-$	0.06	*
$AsS(OH)(SH)^-$	-245.11	-	-	$AsS(OH)(SH)^- + 2H_2O = H_2AsO_3^- + 2HS^- + 2H^+$	-27.38	* h
$AsS(SH)_2^-$	-38.00	-	-	$AsS(SH)_2^- + 3H_2O = H_2AsO_3^- + 3HS^- + 3H^+$	-34.74	* h
$As_3S_4(SH)_2^-$	-127.19			$As_3S_4(SH)_2^- + 9H_2O = 3H_2AsO_3^- + 6HS^- + 8H^+$	-100.3	* h
$H_2As_2S_3O^\circ$	-284.56			$H_2As_2S_3O^\circ + 5H_2O = 2H_2AsO_3^- + 3HS^- + 5H^+$	-58.18	* d
$HAs_2S_4^-$(*)	-63.83			$HAs_2S_4^- + 6H_2O = 2H_2AsO_3^- + 4HS^- + 5H^+$	-63.16	* d
$As_2S_4^{2-}$(*)	-15.46			$As_2S_4^{2-} + 6H_2O = 2H_2AsO_3^- + 4HS^- + 4H^+$	-54.68	* d
$FeH_2AsO_4^+$	-861.0			$Fe^{2+} + H_2AsO_4^- = FeH_2AsO_4^+$	2.86	* g
$FeHAsO_4^0$	-825.14			$Fe^{2+} + H_2AsO_4^- = FeHAsO_4^0 + H^+$	-3.42	* g
$FeAsO_4^-$	-779.59			$Fe^{2+} + H_2AsO_4^- = FeAsO_4^- + 2H^+$	-11.04	* g
$FeH_2AsO_4^{2+}$	-793.57			$Fe^{3+} + H_2AsO_4^- = FeH_2AsO_4^{2+}$	4.06	* g
$FeHAsO_4^+$	-786.38			$Fe^{3+} + H_2AsO_4^- = FeHAsO_4^+ + H^+$	2.8	* g
$FeAsO_4^0$	-772.62			$Fe^{3+} + H_2AsO_4^- = FeAsO_4^0 + 2H^+$	0.39	* g
$Fe(AsO_4)_2^{3-}$	-1483.5			$Fe^{3+} + 2H_2AsO_4^- = Fe(AsO_4)_2^{3-} + 4H^+$	-7.01	* g
$AlAsO_4^\circ$	-1215.9			$Al^{3+} + H_2AsO_4^- = AlAsO_4^\circ + 2H^+$	-4.36	* g
$AlHAsO_4^+$	-1242.7			$Al^{3+} + H_2AsO_4^- = AlHAsO_4^+ + H^+$	0.33	* g
$AlH_2AsO_4^{2+}$	-1258.3			$Al^{3+} + H_2AsO_4^- = AlH_2AsO_4^{2+}$	3.07	* g
$CrHAsO_4^0$	-912.79			$CrO_4^{3-} + H_2AsO_4^- + 4H^+ = CrHAsO_4^0 + 0.75O_{2(g)} + 2.5H_2O$	-16.43	* g
$MnHAsO_4^0$	-962.81			$Mn^{2+} + H_2AsO_4^- = MnHAsO_4^0 + H^+$	-3.22	* g
$MnAsO_4^-$	-910.81			$Mn^{2+} + H_2AsO_4^- = MnAsO_4^- + 2H^+$	-12.33	* g
$CuHAsO_4^0$	-668.86			$Cu^{2+} + H_2AsO_4^- = CuHAsO_4^0 + H^+$	-3.28	* g
$NiHAsO_4^0$	-775.59			$Ni^{2+} + H_2AsO_4^- = NiHAsO_4^0 + H^+$	-4.06	* g
$CoHAsO_4^0$	-784.95			$Co^{2+} + H_2AsO_4^- = CoHAsO_4^0 + H^+$	-3.96	* g
$ZnHAsO_4^0$	-879.03			$Zn^{2+} + H_2AsO_4^- = ZnHAsO_4^0 + H^+$	-3.75	* g
$CdHAsO_4^0$	-806.61			$Cd^{2+} + H_2AsO_4^- = CdHAsO_4^0 + H^+$	-4.24	* g
$MgH_2AsO_4^+$	-1215.8			$Mg^{2+} + H_2AsO_4^- = MgH_2AsO_4^+$	1.52	* g
$MgHAsO_4^0$	-1183.7			$Mg^{2+} + H_2AsO_4^- = MgHAsO_4^0 + H^+$	-4.10	* g
$MgAsO_4^-$	-1137.96			$Mg^{2+} + H_2AsO_4^- = MgAsO_4^- + 2H^+$	-12.12	* g
$CaH_2AsO_4^+$	-1312.00			$Ca^{2+} + H_2AsO_4^- = CaH_2AsO_4^+$	1.06	* g
$CaHAsO_4^0$	-1281.58			$Ca^{2+} + H_2AsO_4^- = CaHAsO_4^0 + H^+$	-4.27	* g
$CaAsO_4^-$	-1236.08			$Ca^{2+} + H_2AsO_4^- = CaAsO_4^- + 2H^+$	-12.24	* g
$PbHAsO_4^0$	-754.68			$Pb^{2+} + H_2AsO_4^- = PbHAsO_4^0 + H^+$	-3.92	* g
$PbH_2AsO_4^+$	-785.78			$Pb^{2+} + H_2AsO_4^- = PbH_2AsO_4^+$	1.53	* g

Tab.1 - Thermodynamic parameters of aqueous species of arsenic. *, recomputed in this study (see text); a, Wolery (1992); b, Wolery- (1997); c, Wagman et al. (1982); d, Mironova et al. (1990); e, Sergeeva and Khodakovskiy (1969); f, Shock and Helgeson (1988); g, Whiting (1992); h, Helz et al. (1995); i, reported by Jackson and Miller (1999); BS, basis species of arsenic; this species is the basis species for As in all mineral and aqueous reactions.

2. Arsenic Minerals

A review of the thermochemical data of arsenic minerals and the thermodynamic equilibrium constant for their hydrolysis and eventually oxidation reactions are given in Table 1. Values given are those adopted in this study otherwise indicated. Discussions and eventually other existing values are dressed in the text.

As(s)

At standard conditions (25°C, 1 bar), the equilibrium constant of hydrolysis and oxidation reaction of As(s) given in Table 2 is only dependent on the Gibbs energy of water and on $H_2AsO_3^-$; those of As(s) and $O_2(g)$ are set to zero (by principle). Initial data in EQ3/6 thermodynamic database for As(s) are adopted.

2.1. OXIDE AND SULPHIDE AS MINERALS

As_2O_3, Arsenolite (oct) and Claudetite (mono)

The standard Gibbs free energy of arsenolite As_2O_3 at 25°C (-575.96) was derived from the electrochemical measurements of As/As_2O_3 potential performed by Schulmann (1924) and Kirschning and Plieth (1955). This value was adopted in all references. The recent solubility measurements of arsenolite (Pokrovski et *al.*, 1996) are in close agreement with previously published data. These authors have also derived the free energy of arsenolite to claudetite transition reaction (ΔG_{tr}) from the solubility measurements. Consequently, a small correction (-0.125) of log K for the hydrolysis reaction of claudetite

$$As_2O_3\ (mon) + 3H_2O <==> 2H^+ + 2H_2AsO_3^- \qquad \log K = -19.89 \qquad (13)$$

has been performed.

As_2O_5

The accurate calorimetric measurements of Beezer et *al.* (1965) was adopted in all thermochemical compilations (Robie et *al.*, 1978; Wolery, 1992). We have adopted these data in the calculation of the hydrolysis reaction of As_2O_5 given in our compilation (Table 2).

As_4O_6 (mono, cubic)

Thermodynamic data for these solid phases given in EQ3/6 were taken from Grenthe et *al.* (1992). These phases have not a great interest because the form As_2O_3 is the most cited and used in practical studies.

As_2S_3, Orpiment(mono)

Literature data reveal a dramatic disagreement in the Gibbs free energy of As_2S_3. A very low value (-168.6) of the Gibbs free energy value of orpiment was given by Wagman et *al.* (1982) and adopted in the initial thermodynamic data accompagning EQ3/6. We have adopted the new value of ΔG_f^0 (-84.19±1.25) which has been derived from Webster (1990) solubility experiments with synthetic orpiment in dilute and sulphide-bearing fluids at 25 and 90°C. Using the SUPCRT92 (Johnson et *al.*, 1992) data for other species ($H_2AsO_3^-$, HS^- and H_2O) a new value of log K of the hydrolysis reaction

$$As_2S_3 + 6H_2O = 2H_2AsO_3^- + 3HS^- + 5H^+ \qquad \log K = -64.63 \qquad (14)$$

is obtained (Table 2). Some more negative thermodynamic properties of orpiment were given by Johnson et *al.* (1980) based on their measurement results and data from the literature. The energies of combustion of vitreous As_2S_3 in fluorine were measured using bomb calorimeter techniques, but Johnson et *al.* (1980) did not measure the enthalpy increment for crystalline orpiment. They used, instead, the value of 35.0±2.0 kJ/mol for stibnite (Sb_2S_3) given by Bryndzia and Kleppa (1988). The latter authors have published the first directly determined value (23.33±0.65 kJ/mol) for the enthalpy of the crystal-to-glass transition for As_2S_3 allotropes. These authors have determined a value of -83.0±3.8 kJ/mol for the standard Gibbs free energy of formation of orpiment, As_2S_3. This value is in agreement with that of Mironova et *al.* (1984; -85.899) used by Pokrovski et *al.* (1996) but in serious disagreement with that of Johnson et *al.* (1980; -91.6±4.8).

More recently, Eary (1992) determined experimentally the solubility of amorphous arsenic sulphide $As_2S_3(am)$ from 25 to 90°C in acidic, sulphide-deficient solutions (field of $H_3AsO_3^\circ$ predominance) and in acidic solutions with excess sulphide (field of $H_2As_3S_6^-$ predominance). The respective logarithms of stoichiometric equilibrium constants (designed with asterisk (*) in the text) for corresponding reactions at 25°C and 0.1 ionic strength are:

$$1/2As_2S_3(am) + 3H_2O = H_3AsO_3^\circ + 3/2H_2S^\circ \qquad \log K^* = -11.3\pm0.3 \qquad (15)$$

$$3/2As_2S_3(am) + 3/2H_2S^\circ = H_2As_3S_6^- + H^+ \qquad \log K^* = -5.0\pm0.3 \qquad (16)$$

The solubility data indicate that $As_2S_3(am)$ is from 5 to 16 times more soluble than orpiment between 25 and 90°C and that it does not readily convert to orpiment in the time scale of laboratory experiments. The occurrence of orpiment with $As_2S_3(am)$ is reported for some present-day hot spring deposits in New Zeland and Kamchatka fields (Eary, 1992).

AsS (Realgar, mono)

There are extremely large differences between published free energy values for realgar. The adopted Gibbs free energy value (-70.32) of AsS in EQ3/6 is taken from Robie et *al.* (1978). This too low value is based on the oxygen-bomb calorimetric determination of Britske et *al.* (1934). We selected the recent higher value of Johnson et *al.* (1980) for which analytical methods and thermodynamic data are well documented. Spycher and Reed (1989a) and Heinrich and Edington (1986) have also adopted these more recent data.

In Johnson and co-authors work, the energies of combustion of β-As_4S_4 in fluorine were measured in a bomb calorimeter. Based on the measurement results and data from the literature, the thermodynamic data of the mineral realgar, α-As_4S_4 (with $\Delta G_f(AsS) = -32.9\pm6.8$), are in agreement with experimental investigation results of Barton (1969) and especially with the results of calorimetric studies of reaction $4As(s) + 4S_{orth,\ mon,\ liquid} = As_4S_{4\beta,\alpha}$ by Mah (1982). This value of Gibbs free energy is consistent with the value of log K (-8.9) recommended in IVTANTERMO databank (Moscow, V.P. Glushko editor).

Bryndzia and Kleppa (1988) determined the standard molal enthalpies of formation of realgar (α-AsS) and orpiment (As_2S_3) at 768 K by high-temperature direct-synthesis calorimetry, well above the melting temperature of either minerals. Their values are systematically less negative than values previously obtained by fluorine combustion calorimetry. For example in comparison with the value -34.53±6.7 of the Gibbs free energy from Johnson et *al.* (1980) Bryndzia and Kleppa (1988) propose a value of -28.1 ±3.1 kJ/mol for realgar. The authors suppose that the standard molal enthalpies of formation of sulphides determined by fluorine combustion calorimetry are systematically in error. But as we can see from data for orpiment, there is an agreement between values obtained by different methods: thermochemistry (Johnson et *al.*, 1980), equilibria in Fe-S-As dry system (Barton,1969) and the solubility experiments in aqueous solutions (Webster,1990 and Pokrovski et *al.*, 1996). Consequently, we recommend (Table 2) the value –32.9 obtained by Johnson et *al.* (1980).

FeAsS (Arsenopyrite)

Proposed thermochemical data for arsenopyrite continue to conflict and are debated in various literature sources. Apparently, the Gibbs free energy value (-50.0) quoted by Wagman et *al.* (1982) and included in database EQ3/6 (Wolery, 1992) is seriously in error. Dove and Rimstidt (1985) have used some more negative Gibbs free energy value for FeAsS (-125.70) from Barton (1979). Davis et *al.* (1996) used the value -127.254 from the compilation of Delany and Lunden (1991). Recently, G. Pokrovski (unpublished data) calculated, from his in progress experimental work, a free energy value of formation of FeAsS is somewhat about 20 kJ/mol lower than that commonly used in the literature, *e.g.* Barton (1969). The debate continues and it is difficult to conclude definitely because of the lack of more independent measurement data.

Consequently, we recommend (Table 2) thermodynamic data of Barton (1969). These data have been used by Naumov et *al.* (1974) in their Handbook and up today they are the most used data (Spycher and Reed, 1989b; Vink, 1996; and reference therein). Solubility measurements and aqueous speciation characterisations (G. Pokrovski, work in progress) will permit to improve the situation.

2.2. ARSENATE MINERALS

With the environmental problems and the mine activities, unusual and unstable arsenic minerals can form in oxidised zone of mineral deposits and of waste heaps. In order to constrain the behaviour of arsenic and its transfer mechanisms it is necessary to extend our thermodatabases including these kinds of components.

Note that lammerite $Cu_3(AsO_4)_2$ and kottigite $Zn_3(AsO_4)_2{\cdot}8H_2O$ can form under extreme conditions (low pH, high metal and arsenate concentrations). Masscheleyn et *al.* (1991) suggested that Fe, Ca, Pb and Mn arsenates are the most likely minerals that control As in soils, based on thermodynamic data presented by Sadiq et *al.* (1983). However, a main problem is that these minerals tend to dissolve incongruently (Rimstidt and Dove, 1987) and it is a very difficult task to find real log Ks value for well-characterised (crystalline) arsenate solids. Then some of them can easily be replaced by carbonates even at atmospheric CO_2 partial pressure (the phase $Pb_3(AsO_4)_2$ has not been identified as mineral probably because of cerusite control on Pb^{2+} concentrations). In acid-near neutral solutions with an increase in concentrations of sulphate the stable areas of arsenites and arsenates are reduced by formation of insoluble metal sulphate, such as barium sulphate.

$FeAsO_4{:}2H_2O$, Scorodite

The solubility of scorodite $FeAsO_4{:}2H_2O$ was investigated experimentally in the first extensive study by Chykhlantsev (1956) and more recently by Dove and Rimstidt (1985), Robins (1987), and Krause and Etell (1988). The solubility product pKs ($Fe^{3+}AsO_4^{3-}$) calculated by these authors ranges from 20.24 to 24.41. Last value have been derived by Krause and Etell (1988) from the precise experimental investigation of solubility of synthetic crystalline scorodite at 23±1°C over the pH range 0.97-7.92. Data of Krause and Etell (1988) have been adopted in the EQ3/6 database, and ΔG°_f ($FeAsO_4{:}2H_2O$) (-1278.73) was calculated using the consistent data for Fe^{3+} and AsO_4^{3-}. Moreover, Whiting (1992) corrected the Ks of scorodite for complexation and ionic strength effects using the stability constant values for metal-arsenate complexes. He obtained a pKs value of 25.87±0.18 corresponding to the value of (-1287.06) for ΔG°_f ($FeAsO_4{:}2H_2O$). The latter values are adopted in our database.

It should be mentioned here that scorodite has a very low solubility under oxidizing conditions, but when the Eh drops below ~ 100 mV, dissolved As values can increase dramatically due to reductive dissolution of both Fe and As. Krause and Ettel (1988) conclude that crystalline scorodite is approximately 100 times less soluble than the apparently amorphous form.

Other Arsenate and Arsenite Minerals (Zn, Cu, Ni, Mg, Ca, Ba, Mn, Pb, Ca, Fe, Al, Sr)

Over the last few years the solubility product constants (pK_S) have been determined experimentally for a large number of arsenate compounds: for Zn^{2+}, Cu^{2+}, Ni^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+} in Nishima et *al.* (1988), for Cu^{2+}, Zn^{2+}, Pb^{2+} in Magalhaest et *al.* (1988), for Mn^{2+}, Pb^{2+}, Ca^{2+}, Fe^{3+}, Al^{3+} in Hess and Blanchar (1976). Other solubility data for a series of arsenates are given in Chukhlantsev (1956) and Naumov et *al.* (1974). But oversimplification in Chukhlantsev's calculations resulted in published solubility products being almost 10 times higher than that of other authors. In Rochette et *al.* (1998) the behaviour of five arsenates was explored experimentally under oxic and anoxic conditions. The apparent solubility of arsenates decreased in the order $CaHAsO_4 = Na_2HAsO_4{\cdot}7H_2O > AlAsO_4{\cdot}2H_2O > MnHAsO_4 > FeAsO_4{\cdot}2H_2O$ under oxic conditions. Under anoxic conditions the order is: $FeAsO_4{\cdot}2H_2O > CaHAsO_4 = Na_2HAsO_4{\cdot}7H_2O > AlAsO_4{\cdot}2H_2O > MnHAsO_4$. Moreover, computed equilibrium concentration of dissolved arsenic for natural waters is greatly overestimated than that effectively measured due to the sorption processes involving both arsenate and arsenite.

An empirical method have been developed by Essington (1988a) for estimating the standard free energy of formation of solid phases of metal arsenates, selenates, and selenites. A free energy function of a solid phase is found to be linearly correlated to a function of the metal oxide $\Delta G°_f$ and the aqueous metal ion free energy for the compound groups examined. He stated that the values estimated by this method are, on average, within ±10.9 kJ/mol of the experimental arsenate values and for hydrated arsenates within ±23.7 kJ/mol. Basset (1977) observed that the free energy of formation of hydrated mineral phases are related to the free energy of formation of the corresponding anhydrous phase by: $\Delta G°_f$ (hydrated) = $\Delta G°_f$ (anhydrous) - 242.46 kJ/mol. Whiting (1992) have calculated the pKs data for weilite ($CaHAsO_4$), schultenite ($PbHAsO_2$), sterlinghillite ($Mn_3(AsO_4)_2{:}8H_2O$) and scorodite with considering estimated arsenate-metal complexation and experimental data of different authors (Hess and Blanchar, 1976; Nishimura et *al.*, 1988; Krause and Ettel, 1988; Clara et *al.*, 1988). Davis et *al.* (1996) performed solubility calculations of solid-solution series: scorodite-strengite, $FeAsO_4{:}2H_2O$ - $FePO_4{:}2H_2O$; mimetite - pyromorphite, $Pb_5(AsO_4)_3Cl$ - $Pb_5(PO_4)_3Cl$; symplesite - vivianite, $Fe_3(AsO_4)_2{:}8H_2O$ - $Fe_3(PO_4)_2{:}8H_2O$.

In Magalhaest et *al.* (1988) equilibrium solubility studies have been carried out mainly on natural arsenate minerals combined to the X-ray powder diffraction and SEM X-ray analyse techniques. In this paper analytical methods and thermodynamic data are well documented, solubility products and free energy of formation have been derived for 11 minerals and these data have been used in turn to construct stability field diagrams illustrating the chemical conditions under which the various minerals can occur in nature. Results of these equilibrium calculations, using their computer program COMICS, are then compared with several natural occurrences of the arsenates and good agreement is obtained between observed and calculated paragenetic sequences.

In our compilation, the values of log Ks from Clara et *al.* (1988) have been adopted for 7 arsenates of Cu, Zn, Pb and Ca (Table 2). The $\Delta G°_f$ of these minerals were derived from the values of log Ks using the SUPCRT92 values of $\Delta G°_f$ for involved aqueous species. The difference between primary values of $\Delta G°_f$ (given by Clara et *al.*, 1988) and those derived in the present study doesn't exceed 2 kJ/mol.

In Nishimura et *al.* (1988) metal oxide or hydroxide (Zn, Cu, Ca, Sr, Ba) solubility was measured. Special experiments have been conducted to clarify the effect of sulphate and carbonate ions. After the experiments, metals and arsenic (III, V) in filtrates and precipitates were determined, the precipitates were identified by X-ray powder diffraction and chemical analysis. From these solubility data, the constants of solubility equilibria were derived. The standard free energies of formation for these metal arsenites and arsenates were calculated (Nishimura et *al.*, 1988) using the $\Delta G°_f$ for species from Wagman et *al.* (1968, 1982), assuming that activity coefficients of all species were unity.

Some values of $\Delta G°_f$ and log K from Nishimura et *al.* (1988) are the same or higher than in frequently quoted paper of Chykhlantsev (1956) for $Zn_3(AsO_4)_2{\cdot}8H_2O$, $Ni_3(AsO_4)_2{\cdot}8H_2O$, $Co_3(AsO_4)_2{\cdot}8H_2O$ and for Ba-arsenates in comparison with results of Essington (1988). The data of Nishimura et *al.* (1988) should be used with caution, because they have a tendency to overestimate olivenite and adamite solubilities. The equilibrium constant values (in log units) of corresponding reactions (Table 2) are 2.39 and 3.0 for olivenite and 5.71 and 7.02 for adamite, obtained respectively by Clara et *al.* (1988) and Nishimura et *al.* (1988).

Values of solubility for weillite ($CaHAsO_4$) were given by Nishimura et *al.* (1988), Robins (1985) and Ball and Nordstrom (1991). In experimental work of Mahapatra et *al.* (1986) calcium hydrogen arsenate ($CaHAsO_4$) has been precipitated from aqueous medium and its solubility isotherms were studied in the pH range 4.0-8.0 and temperature range 35-50°C. The thermodynamic solubility product has been determined after taking into account the formation of the aqueous ion pairs $CaHAsO_4^°$ and $CaH_2AsO_4^+$ in the system. The pKs obtained from the data of Mahapatra et *al.* (1986) has a value of 4.6 at 25°C. The stability constants of the ion pairs and the thermodynamic solubility product exhibit a similar negative temperature dependence. (1986).

Hess and Blanchar (1976) synthesised Al, Ca, Fe, Mn and Pb arsenate solid compounds. Based on the results of the X-ray analyses, all of the arsenates were amorphous; but the correct mineral stoichiometry has been established. They performed solubility experiments during 7 days at 25°C in dilute HCl or NaOH solutions varying pH values from 2 to 8. Each arsenate was tested for congruent dissolution after the resulting solutions were analysed for Me, As, Eh and pH. All arsenates did not undergo congruent dissolution. Then samples from Sharpsburg and Menfro soils were equilibrated with the analogous solutions and the pKs (pIAP) were computed. The values of the ionic activity products indicated that equilibrium solutions from both soils were undersaturated with respect to Al, Fe and Ca and that Pb and Mn arsenates were stable in the Sharpsburg and Menfro soils.

The lowest log Ks($Mn_3(AsO_4)_2*8H_2O$) value was derived from these experiments =-33.73 (maximum stability). Due to the Eh under which the experiments were performed (~0.57 V) sterlinghillite ($Mn_3(AsO_4)_2*8H_2O$) tends to dissolve incongruently because bixbyite, Mn_2O_3, and hausmannite, Mn_3O_4, were precipitated. A value of -29.44±0.44 was obtained by Whiting (1992) after the rerunning of the raw experimental data of Hess and Blanchar (1976) and correction of aqueous speciation in these experimental solutions. Moreover, Whiting (1992) have plotted the conditions of the Menfro soil on an Eh-pH diagram. The experimental conditions of Hess and Blanchar (1976) fall within the bixbyite field, very near its boundaries with the sterlinghillite and rhodocrosite (using a $pCO_2 = 10^{-2}$ atm). The value of -29.44±0.44 was used in our thermodynamic database in addition to $MnHAsO_4^\circ$ and $MnAsO_4^-$ aqueous species from Whiting (1992). In the framework of this new interpretation (Whiting, 1992) the $\Delta G^\circ_f(Mn_3(AsO_4)_2*8H_2O)$ have the value of -4045.17 which is very close to that used in Rochette et *al*. (1998).

The mineral mansfieldite, $AlAsO_4{:}2H_2O$, is similar to scorodite and has the similar conditions of formation. Particularly, it is unstable at high pH and dissolves incongruently to form amorphous $Al(OH)_3$. The solubility products pKs ($Al^{3+}AsO_4^{3-}$) obtained by different authors range from 15.84 (Chukhlantsev, 1956) to 22.7 (Whiting, 1992). The latter value is adopted in the present database.

Thermodynamic data for symplesite, $Fe_3(AsO_4)_2{:}8H_2O$, and mimetite, $Pb_5(AsO_4)_3Cl$, have been taken from Davis et *al*. (1996).

The data of $Ba_3(AsO_4)_2$, $BaHAsO_4{:}H_2O$ and $Sr_3(AsO_4)_2$ are given by Essington (1988) and Reddy et *al*.(1987).

Mineral	ΔG°f	ΔH°f	S°	Reaction	log K	Réf.
As(s) Arsenic	-	-	35.10	$As + 1.5H_2O + 0.75O_2 = H^+ + H_2AsO_3^-$	40.53	a, b
As_2O_3 Arsenolite	-575.96	-656.97	107.41	$As_2O_3 + 3H_2O = 2H^+ + 2H_2AsO_3^-$	-19.83	a, b, c
As_2O_3 Claudetite	-576.26	-655.21	113.34	$As_2O_3 + 3H_2O = 2H^+ + 2H_2AsO_3^-$	-19.89	*
As_2O_5	-782.45	-924.87	-105.4	$As_2O_5 + 3H_2O = 2H^+ + 2H_2AsO_4^-$	2.16	a, b, h
AsS Realgar	-32.9	-34.53		$AsS+2.5H_2O+0.25O_2 = H_2AsO_3^- + HS^- + 2H^+$	-8.90	l
As_2S_3(s) Orpiment	-84.19	-	-	$As_2S_3 + 6H_2O = 2H_2AsO_3^- + 3HS^- + 5H^+$	-64.63	* s
FeAsS Arsenopyrite	**-109.62** -127.25	-105.44	108.37	$FeAsS + H^+ + H_2O + O_2 = Fe^{3+} + H_2AsO_3^- + HS^-$	**43.03** 39.94	e, f * g
$FeAsO_4*2H_2O$ Scorodite	**-1278.7** -1287.1	- -	- -	$FeAsO_4*2H_2O + 2H^+ = Fe^{3+} + H_2AsO_4^- + 2H_2O$	**-5.95** -7.41	* n m
$PbHAsO_4$ Schultenite	-807.93			$PbHAsO_4 + H^+ = Pb^{2+} + H_2AsO_4^-$	-5.41	* o
$PbCuAsO_4(OH)$ Duftite	-959.92			$PbCuAsO_4(OH) + 3H^+ = Pb^{2+} + Cu^{2+} + H_2AsO_4^- + H_2O$	-1.975	* o
$Cu_2AsO_4(OH)$ Olivenite	-845.52			$Cu_2AsO_4(OH) + 3H^+ = 2Cu^{2+} + H_2AsO_4^- + H_2O$	2.39	* o
$Cu_3AsO_4(OH)_3$ Clinoclase	-1209.48			$Cu_3AsO_4(OH)_3 + 5H^+ = 3Cu^{2+} + H_2AsO_4^- + 3H_20$	10.10	* o
$Zn_2AsO_4(OH)$ Adamite	-1252.29			$Zn_2AsO_4(OH) + 3H^+ = 2Zn^{2+} + H_2AsO_4^- + H_2O$	5.71	* o
$CaCuAsO_4(OH)$ Conichalcite	-1470.17			$CaCuAsO_4(OH) + 3H^+ = Ca^{2+} + Cu^{2+}\ H_2AsO_4^- + H_2O$	1.29	* o
$CaZnAsO_4(OH)$ Austinite	-1651.13			$CaZnAsO_4(OH) + 3H^+ = Zn^{2+} + Ca^{2+}\ H_2AsO_4^- + H_2O$	6.88	* o
$CaHAsO_4$ weillite	-1292.48			$CaHAsO_4 + H^+ = Ca^{2+} + H_2AsO_4^-$	2.36	* p
$CaHAsO_3$	-	-	-	$CaHAsO_3 + H^+ + 0.5\ O2(g) = Ca^{2+} + H_2AsO_4^-$	34.25	* r
$Mn_3(AsO_4)_2*8H_2O$ Sterlinghillite	**-4045.17** -4069.66			$Mn_3(AsO_4)_2*8H_2O + 4H^+ = 3Mn^{2+} + 2H_2AsO_4^- + 8H_2O$	**7.42** 3.18	* m * k
$AlAsO_4*2H_2O$ Mansfieldite	**-1730.78** -1739.34			$AlAsO_4*2H_2O + 2H^+ = Al^{3+} + H_2AsO_4^- + 2H_2O$	**-2.74** -4.24	* m
$Ba_3(AsO_4)_2$	-3101.20			$Ba_3(AsO_4)_2 + 4H^+ = 3Ba^{2+} + 2H_2AsO_4^-$	15.32	j
$BaHAsO_4*H_2O$	-1585.60			$BaHAsO_4*H_2O + H^+ = Ba^{2+} + H_2AsO_4^- + H_2O$	-6.04	j
$Sr_3(AsO_4)_2$	-3080.10			$Sr_3(AsO_4)_2 + 4H^+ = 3Sr^{2+} + 2H_2AsO_4^-$	20.63	q
$Fe_3(AsO_4)_2*8H_2O$ Symplesite	-3687.23			$Fe_3(AsO_4)_2*8H_2O + 4H^+ = 3Fe^{2+} + 2H_2AsO_4^- + 8H_2O$	-1.57	i
$Pb_5(AsO_4)_3Cl$ Mimetite	-2616.25			$Pb_5(AsO_4)_3Cl + 6H^+ = 5Pb^{2+} + 3H_2AsO_4^- + Cl^-$	-19.80	i

Tab.2 - Critically Evaluated Standard Thermodynamic Data for Arsenic minerals. *, values recomputed in this study; a, Wolery (1992); b, Wolery (1998); c, Robie et al. (1978); e, Barton (1969); f, Naumov et al. (1974); g, Delany and Lunden (1991); h, Wagman et al. (1982); i, Davis et al. (1996); j, Essington (1988); k, Hess and Blanchar (1976); l, Johnson et al. (1980); m, Whiting (1992); n, Krause and Ettel (1988); o, Clara et al. (1988); p, Mahapatra et al. (1986); q, Reddy et al. (1987); r, Dutré and Vandecasteele (1998); s, Webster (1990). When two values are given for the same mineral, the bold one is recommended.

Table 2 presents minerals for which thermodynamic data seem to be correctly established.

3. Arsenic volatility

The volatility of arsenic is not of great interest for remediation problems. We have just mentioned some arsine and methyl-arsine species frequently detected in soil fluids.

$AsH_3(g)$

The value of $\Delta G°_f(AsH_3(aq))$ have been derived in Sergeyeva and Khodakovskiy (1969) from recalculation by the methods of least squares of old Jung's experimental data (1939). This value (99.58 kJ/mol) was adopted in EQ3/6 thermodynamic database. The log K of reaction $AsH_3(g) \Leftrightarrow AsH_3(aq)$ from Sergeyeva and Khodakovskiy (1969) is -5.35±0.3; whereas, Spycher and Reed (1989b) proposed the value -5.86. The free energy of formation of $AsH_3(g)$, 77.94 kJ/mol (Sergeyeva and Khodakovskiy, 1969) is used to calculate log K for the following reaction

$$AsH_3(g) + 1.5O_2(g) = H^+ + H_2AsO_3^- \qquad \log K = 116.52 \pm 0.3 \qquad (17)$$

Other volatile organic species (i.e., methyl arsines $(CH_3)_nAsH_{3-n}$) have been reported in soils (Jackson and Miller, 1999) but their thermodynamic parameters are not well established.

4. Arsenic concentrations in natural waters

Sources of As in the environment include geothermal springs, acid mine drainage, basin–fill deposits, and the application of various agriculturally compounds (Rochette et *al.*, 1998). Figure 1 shows that waters contaminated with arsenic can be encountered in different hydrogeochemical systems. When concentrations of arsenic are given in the scientific papers, more than 80 % of the samples have concentrations higher than MCL (0.01 mg/l). Recent studies of Nimick *et al.* (1998) and Nimick (1998) showed that geothermal waters from Yellowstone National Park (YNP) have high As concentrations (up to 0.4 mg/l) in the Madison and Missouri rivers. Furthermore, these authors have demonstrated that dissolved As is transported largely conservatively in the Madison and Missouri rivers from source in YNP for a distance higher than 300 km. This observation illustrates the problem of public health risks due to the mobility of arsenic in ground waters.

Dissolved total As concentrations in pore waters (PW, Fig. 1) from Puget Sound, Lake Washington, the Washington Coast and Saanich Inlet (USA) are presented (Peterson and Carpenter, 1986). Figure 1 shows that the new MCL (SMCL = 0.01 mg/l) allows reconsideration of the state of a major part of pore and river waters of the Washington region. The situation is also true for rivers located in eastern California and western Nevada (USA) when As concentrations given by Johannesson et *al.* (1997) is considered'(RIV-USA, in Fig. 1).

A compilation of the arsenic behaviour in geothermal systems was realized by Ballantyne and Moore (1988). They showed that geothermal fluids may contain as much as 50 mg/l of As (indicated by HT in Fig. 1). Consequently, the geothermal systems can be a source of As contaminations of river and lake waters (as in the Owens River and Lake Crowly: Wilkie and Hering, 1998; Madisson and Missouri Rivers: Nimick et *al.*, 1998).

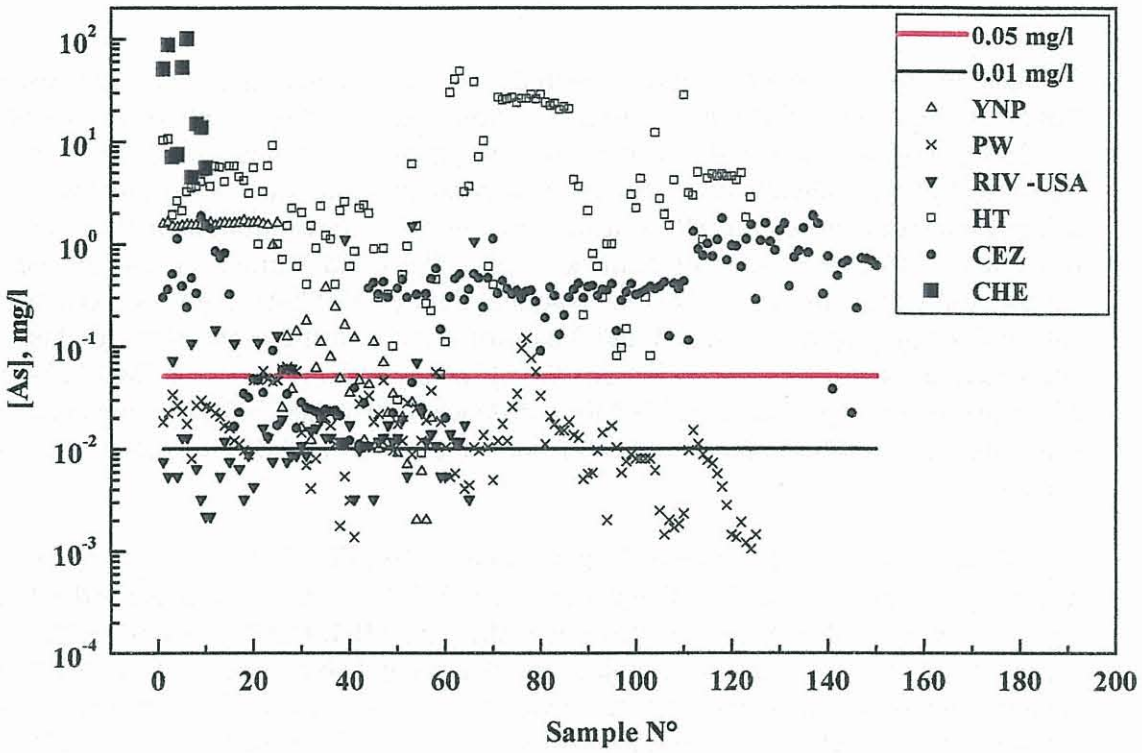

Fig.1 - Arsenic concentrations in natural waters. Lines at 0.05 and 0.01 mg/l represent Maximum Contaminant Limit (MCL = 0.05 mg/l) and Second Maximum Contaminant Limit (SMCL = 0.01 mg/l) recently fixed by the WHO (World Health Organization). Other symbols correspond to As Concentration in waters from different sources. YNP: Yellowstone National Park, Woming, USA (Stauffer and Thompson (1984), Nimick et al. (1998)). PW: Porewater of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, B.C. USA (Peterson and Carpenter, 1986). RIV- USA: Eastern Sierra Nevada Rivers, USA (Johannesson et al., 1997). HT: High Temperature Geothermal Systems (T > 100°C) given in the compilation by Ballantyne and Moore (1984). CEZ: Thermomineral springs from Cezallier, Massif Central, France (Criaud and Fouillac, 1986a,b; Beaucaire et al., 1987; This study). CHE: lecheate from Cheni tailing (France).

In France, CO_2-rich spring waters associated with a crystalline environment (gneiss) are inventoried in Cézallier (Central Massif) (Criaud and Fouillac, 1986; Beaucaire et *al.*, 1987; Criaud and Fouillac, 1989; and BRGM studies in progress). The arsenic concentrations in Cézallier fluids (CEZ in Fig. 1) are systematically higher than the SMCL.

We have also examined the As behaviour in lecheate from Cheni's tailings (France) of a gold ore mining from sulphide-quartz veins. High concentrations of As (up to 85 mg/l) were measured in waters from saturated zone (BRGM study in progress; Glaskova et *al.*, 1999).

5. Arsenic Eh-pH diagram

Figure 2 shows the equilibrium speciation of As in the hypothetical system As-Fe-S-H2O at 25°C and 1 bar (Piantone et *al.*, 1997). The stability field of various aqueous and mineral arsenic species are delimited. But in natural systems, the situation is more complicated. Several studies have reported that most aquatic redox systems are far from equilibrium because energetically-favoured redox reactions are kinetically slow (Tallman and Shaikh, 1980; Lindberg and Runnells, 1984; Glaskova et *al.*, 1999).

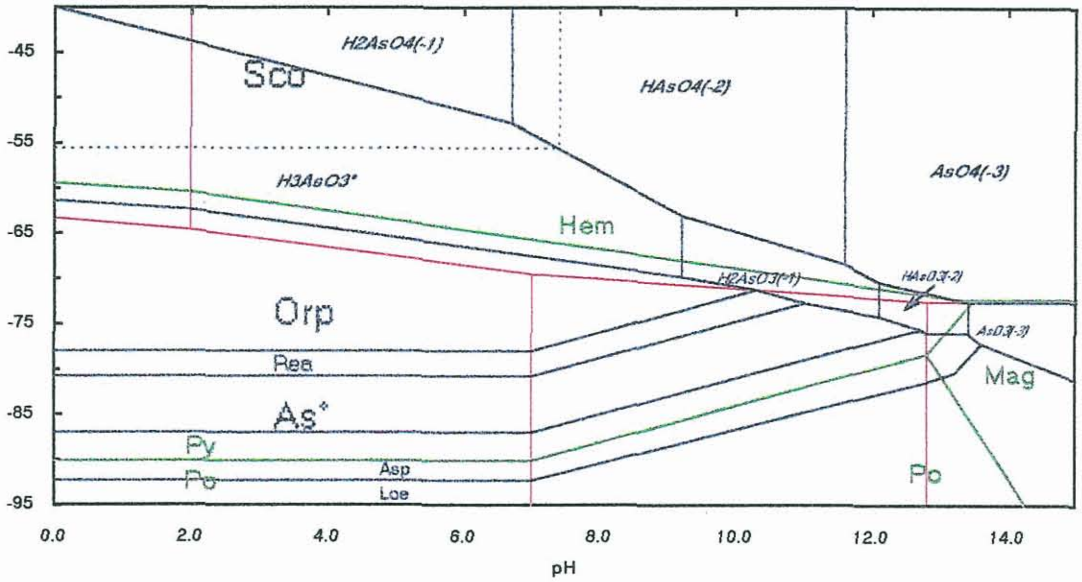

Fig. 2 - Diagram of log fO_2 vs. pH for S-H-O-As-Fe system. Fixed activities : $a_{As} = 10^{-3}$, for As_{total}, $a_S = 0.01$. Abbreviations have the meaning: Asp, arsenopyrite; $As_{(cr)}$, native arsenic; Rea, realgar; Orp, orpiment; Sco, scorodite; Po, pyrrhotite; Py, pyrite; Hem, hematite; Mag, magnetite; Loe, loellingite. The aqueous species are written in italic.

Consequently, in several systems, As(V) is found at unexpectedly high levels in permanently anaerobic regions of lake (Aurilio *et al.*, 1994) and in other aerobic systems As(III) is predominant (Ascue and Nriagu, 1994). Oscaron et *al.* (1983) have examined three manganese dioxides MnO_2 (birnessite, cryptomelane, and pyrolusite) for their ability to oxide As(III) in water. These authors have concluded that the depletion of As(III) at pH7 by manganese dioxides followed a first-order kinetics and the effectiveness of Mn dioxides to sorb As is related to the specific surface area. These anomalies can be caused by the presence or absence of iron, manganese, sulphide or microbes (Harrington *et al.*, 1998).

6. Adsorption-desorption of As to mineral surfaces

Although the high number of arsenic minerals can be formed in soils and hydrothermal conditions (see Table 2), measured As concentrations in natural waters are controlled by adsorption-desorption reactions and biological activity. Due to the low SMCL established by WHO methods for removing arsenic from water are essentially based on the adsorption–precipitation reactions. The review of Korte and Fernands (1991) reported that a variety of adsorbents, including phyllosilicates, silica and hydrous oxides of Fe and Al were explored. Iron oxides, e.g., ferrihydrite, have strong affinity for both arsenite and arsenate. Apparently, ferrihydrite exhibits a relatively higher retention of arsenate at lower pH values, whereas arsenite is more strongly retained at higher pH value (Jaim et *al.*, 1999). Arsenic (V) is much more effectively removed than arsenic (III) because the former exists in natural water as monovalent or divalent anions ($H_2AsO_4^-$ and $HAsO_4^{2-}$), whereas the latter exists predominantly in a neutral form ($H_3AsO_3^\circ$). Jones et *al.* (1997) showed that soluble As levels in several representative mine tailing samples were correlated with solution pH. All solutions are undersaturated with respect to the expected solid phases (scorodite, Ca-arsenates, etc.) in these environments.

Among the various adsorption models available that account for the effects of surface charge the diffuse double layer (DDLM) model (Dzombak and Mored, 1990) is the most used to model the adsorption of metals to mineral surfaces. This model describes the sorption of solutes at oxide surfaces as a chemical reaction with specific surface sites. For each sorption reaction at equilibrium, the concentrations of sorbate, sorbent, and surface sites satisfy a mass law equation. The default values for the specific surface area (600 m^2/g) and the concentration of adsorption sites (equivalents per mol of oxides) is 0.2 for iron oxyhydroxides (Dzombak and Morel, 1990). Table 3 summarises the intrinsic adsorption thermodynamic constants.

Reaction	log K	Réf.
$\equiv FeOOH \Leftrightarrow \equiv FeOO^- + H^+$	-8.82	a
	-10.60	b
$\equiv FeOOH + H^+ \Leftrightarrow \equiv FeOOH^{2+}$	7.18	a
	5.97	b
$\equiv FeOOH + AsO_4^{3-} + 2\ H^+ \Leftrightarrow \equiv FeH_2AsO_4^\circ + H_2O$	29.31	a
$\equiv FeOOH + AsO_4^{3-} + 3\ H^+ \Leftrightarrow \equiv FeHAsO_4^- + H_2O$	23.51	a
$\equiv FeOOH + AsO_4^{3-} \Leftrightarrow \equiv FeOHAsO_4^{3-}$	10.58	a
$\equiv FeOOH + H_3AsO_3^\circ \Leftrightarrow \equiv FeH_2AsO_3^\circ + H_2O$	5.41	a
$2 \equiv FeOOH + H_3AsO_3^\circ \Leftrightarrow \equiv Fe_2HAsO_3^\circ + 2\ H_2O$	9.22	b
$2 \equiv FeOOH + H_3AsO_3^\circ \Leftrightarrow \equiv Fe_2AsO_3^- + 2\ H_2O + H^+$	0.51	b

Tab.3 - Thermodynamic constants for DDLM (A) and CCM (B) models. A, Dzombak and Morel (1990); b, Manning et al. (1998).

Manning et *al.* (1998) used the Constant Capacitance Model (CCM) developed by stumm et *al.* (1980) to describe the As(III) adsorption on goethite (α-FeOOH). The CCM model was successfully applied to study the adsorption of As(III) and As(V) on clay minerals (Manning and Goldberg, 1997). Manning et *al.* (1998) have shown that surface complexation models with monodentate and bidentate As surface complex permitted a satisfactory interpretation of As adsorption on goethite surface. They also demonstrated that As(III) species are more strongly bound on iron oxide surfaces than As(V) at neutral to alkaline pH. In fact, the retention of both arsenite and arsenate is strongly pH-dependant, but with opposite trends. The effects of pH on the transport of As(V) is consistent with the pH dependence of surface complexation reactions describing AsO_4 sorption by oxide minerals (Darland and Inskeep, 1997).

Some geochemical models including, PHREEQC (Parkhurst et *al.*, 1995), WATEQF (Ball and Nordstrom, 1991), MINTEQ2 and MICROQL (Allison et *al.*, 1991, etc.), have the capability to deal with complexation surface reactions. The Diffuse Double Layer Model (DDLM) is the most used approach. In some recent studies the surface complexation models were satisfactory applied to the transport and reaction of arsenic in water-saturated soils and shallow waters (PHREEQC: Welch and Lico, 1998; MINTEQ2: Smith and Jaffé, 1998; MICROQL: Carrillo and Drever, 1997).

The recent spectroscopic (X-ray Adsorption Fine Structure, EXAFS and Infrared, IR) studies (Sun and Doner, 1996; Manning et *al.*, 1998) have provided evidence that arsenite and arsenate are adsorbed on iron oxide surfaces as bidentate binuclear complexes. These observations combined to theoretical treatments (Felmy and Rustad, 1998) allow a great improvement of the surface complexation models applied to the transport of pollutant metals in aquatic systems.

7. Arsenic biogeochemistry

Micro-organisms capable of direct As(III) oxidation and direct As(V) reduction have been reported (Ahmann et *al.*, 1997). Leblanc et *al.* (1996) have described the formation of bacterial stromatolite at Carnoules (France) accumulating arsenic in a mineral form (Fe^{3+} arsenate) via direct or indirect microbial action. The authors have identified acidophile bacteria, *Thiobacillus ferrooxidans.* DRX scorodite ($FeAsO_4$:$2H_2O$), hematite with sometimes bukovskyite ($Fe_2AsO_4SO_4OH.7H_2O$), angelellite ($Fe_4As_2O_{11}$), and beudantite ($PbFe_3AsO_4SO_4(OH)_6$). Ahmann et *al.* (1997) reported some arsenate-respiring bacteria known in freshwater sediments and in gold mine waters. The activity of these bacteria allows rapid arsenic mobilization from aquatic sediments as observed in field studies (Harrington et *al.*, 1998). The involvement of bacteria in oxidation and reduction of arsenic is confirmed by experimental studies in progress in BRGM.

8. Mechanisms of As immobilization in soils, mine tailings, and removal from polluted waters

Arsenic retention in soils is related to the content of Fe and Al oxides, exchangeable Ca, and the type and content of clay in the soil (Onken and Adriano, 1997). Kaolinite sorbs more As from solution than vermiculite, which sorbs more As than montmorillonite (Dickens and Hiltbold, 1967).

Under the highly reduced, neutral pH conditions, arsenic can be precipitated by sulphide (Seyler and Martin, 1989). Under the oxidising conditions (nearer the surface), coprecipitation of arsenic with iron and manganese oxihydroxides lowers its concentration in water. Near the redox boundary, arsenic is predominantly as As(III) and appears to be more mobile (Korte and Fernando, 1991). Consequently, the presence or absence of iron or manganese, sulphide, or microbial transformants is the key condition controlling As mobility. Furthermore, arsenate solid phases are generally unstable in surface soils, due to their relatively high solubility. The effects of pH-Eh conditions on As mobility in soils are essentially due to surface complexation reactions rather than to precipitation-dissolution reactions (Jones et *al.*, 1997).

Mechanisms for removing arsenic from water include adsorption-coprecipitation with hydrolysing metals such as Al or Fe(III), adsorption on activated alumna or activated carbon, ion exchange (reported by Bajpai and Chaudhuri, 1999), and clay minerals (Manning and Goldberg, 1997). Bajpai and Chaudhuri (1999) developed a removal process based on manganese dioxide-coated sand.

Finally, available results do not permit to propose removal and trapping mechanisms based directly on arsenic mineral depositions. Due to the diversity of As pollution sources including mine tailings ($pH < 3$, $Eh > 300$ mV), herbicides (variable pH and Eh), bottom ash leachates ($pH > 12$, $Eh < 300$ mV), the behavior of As is not well known. In order to anticipate the behavior of As by numerical modelling of reaction paths and mass transfer approaches, many points must be improved.

- The compilation of thermochemical properties of arsenic minerals and especially for arsenic aqueous species.
- The understanding of the action mechanisms of biological activity.
- The development of approaches taking into account the arsenic oxidation and reduction reaction kinetics including organic and inorganic inhibiting/catalyst agents.
- The understanding the mechanisms of surface complexation in order to understand the relation between As and reactive sites of oxide surfaces.
- The determination of the stability of solid adsorbates under various Eh-pH conditions.

Conclusion

Inorganic species of arsenite and arsenate are highly toxic and thus represent a potential threat to the environment and human health. In the environment, the fate of arsenic is often complex. It can be adsorbed by soils, uptake by plants, leached by waters, transported via erosion phenomena, or reduced to volatile arsines. Consequently, it is important to know the speciation and transformations of arsenic in aquatic environments and soils to optimise strategies for its immobilization in solids or removal from contaminated waters. The aim of this work was to establish a state of the art and critically compile thermochemical data for arsenic mineral and aqueous species.

Published standard thermodynamic properties of minerals and aqueous species of arsenic were collected and critically reviewed. A set of Gibbs free energy and equilibrium constants of reactions written according to the Wolery (1992) convention is recommended for applications to the industrial and environmental problems at 25°C and 1 bar.

The most important results concerns the following points:

i) The stability constant values of arsenite fluoride complexes ($HAsO_3F^-$ and $AsO_3F_2^-$) was in error in Wagmann et *al.* (1982) and Wolery (1992) thermodynamic databases. Data of Whiting (1992) are recommended.

ii) The thermochemical properties of orpiment, loellingite and arsenopyrite were in error in the precedent thermodynamic databases. A reconciliation of these state of data was possible after the examination of several experimental calorimetric and solubility results. A set of recommended data is proposed in Table 2.

iii) The possible formation of metal-arsenate complexes and arsenate minerals can be simulated.

iv) A brief review of the surface complexation reaction models is presented. Although the fact that surface complexation reactions seem to be the key for understanding the mobility of As, thermodynamic stability constants for these solide – water interface reactions are scarce. A tentatively compiled database is proposed for iron oxyhydroxide solids.

v) The involvement of bacteria in the mobility of arsenic is clearly established. The biota activity must be taken into account in the numerical models.

A significant improvement of our ability to remediate the arsenic polluted aqua systems is anticipated. Theoretically, the critical review of existing thermodynamic data will permit enlargement of target solid phases for trapping the excedent of arsenic in surface waters under various redox and pH conditions. Nevertheless, with the new SMCL (0.01 mg/l), arsenic minerals of surface and soil environments cannot allow As concentrations lower than this SMCL. Other mechanisms potentially controlling As transfer processes (e.g., adsorption on oxyhydroxide surfaces, biological activity, etc.) are potentially more attractive and are being used in remediation process development. Arsenic adsorption on a wide variety of adsorbents, including clay minerals (Manning and Goldberg, 1997), manganese dioxide-coated sand (Bajpai and Chaudhuri, 1999), aluminum oxides, and iron oxides (see review of Jain et *al.*, 1999), has been explored.

Primary applications of this thermodynamic database to some natural and anthropic As-rich waters were realised. The updated Eh-pH diagram for some arsenic systems shows that in subsurface waters (Tallman and Shaikh, 1980; Lindberg and Runnells, 1984; Glaskova et *al.*, 1999), the redox equilibrium is not attained. Consequently, the fate of arsenic during transport in shallow aquifers could not be predicted by thermodynamic considerations alone. The redox disequilibrium and kinetic processes must be taken into account in numerical models.

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Fig.1 - Arsenic concentrations in natural waters. Lines at 0.05 and 0.01 mg/l represent Maximum Contaminant Limit (MCL = 0.05 mg/l) and Second Maximum Contaminant Limit (SMCL = 0.01 mg/l) recently fixed by the WHO (World Health Organization). Other symbols correspond to As Concentration in waters from different sources. YNP: Yellowstone National Park, Woming, USA (Stauffer and Thompson (1984), Nimick et *al.* (1998)). PW: Porewater of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, B.C. USA (Peterson and Carpenter, 1986). RIV- USA: Eastern Sierra Nevada Rivers, USA (Johannesson et *al.*, 1997). HT: High Temperature Geothermal Systems (T > 100°C) given in the compilation by Ballantyne and Moore (1984). CEZ: Thermomineral springs from Cezallier, Massif Central, France (Criaud and Fouillac, 1986a,b; Beaucaire et *al.*, 1987; This study). CHE: lecheate from Cheni tailing (France).

Fig. 2 - Diagram of $\log fO_2$ vs. pH for S-H-O-As-Fe system. Fixed activities : $a_{As} = 10^{-3}$, for As_{total}, $a_S = 0.01$. Abbreviations have the meaning: Asp, arsenopyrite; $As_{(cr)}$, native arsenic; Rea, realgar; Orp, orpiment; Sco, scorodite; Po, pyrrhotite; Py, pyrite; Hem, hematite; Mag, magnetite; Loe, loellingite. The aqueous species are written in italic

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Tab.1 - Thermodynamic parameters of aqueous species of arsenic.*, recomputed in this study (see text); a, Wolery (1992); b, Wolery- (1997); c, Wagman et *al.* (1982); d, Mironova et *al.* (1990); e, Sergeeva and Khodakovskiy (1969); f, Shock and Helgeson (1988); g, Whiting (1992); h, Helz et *al.* (1995); i, reported by Jackson and Miller (1999); BS, basis species of arsenic; this species is the basis species for As in all mineral and aqueous reactions.

Tab.2 - Critically Evaluated Standard Thermodynamic Data for Arsenic minerals. *, values recomputed in this study; a, Wolery (1992); b, Wolery (1998); c, Robie et *al.* (1978); e, Barton (1969); f, Naumov et *al.* (1974); g, Delany and Lunden (1991); h, Wagman et *al.* (1982); i, Davis et *al.* (1996); j, Essington (1988); k, Hess and Blanchar (1976); l, Johnson et *al.* (1980); m, Whiting (1992); n, Krause and Ettel (1988); o, Clara et *al.* (1988); p, Mahapatra et *al.* (1986); q, Reddy et *al.* (1987); r, Dutré and Vandecasteele (1998); s, Webster (1990). When two values are given for the same mineral, the bold one is recommended

Tab.3 - Thermodynamic constants for DDLM (A) and CCM (B) models. A, Dzombak and Morel (1990); b, Manning et *al.* (1998).

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