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ORIGINAL ARTICLE

Prediction of the thermodynamic properties of metal–arsenate and metal–arsenite aqueous complexes to high temperatures and pressures and some geological consequences

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Abstract The standard thermodynamic properties at 25°C, 1 bar (ΔG_f^o, ΔH_f^o, S^o, C_P^o, V^o, ω) and the coefficients of the revised Helgeson–Kirkham–Flowers equations of state were evaluated for several aqueous complexes formed by dissolved metals and either arsenate or arsenite ions. The guidelines of Shock and Helgeson (Geochim Cosmochim Acta 52:2009–2036, 1988) and Sverjensky et al. (Geochim Cosmochim Acta 61:1359–1412, 1997) were followed and corroborated with alternative approaches, whenever possible. The SUPCRT92 computer code was used to generate the log K of the destruction reactions of these metal–arsenate and metal–arsenite aqueous complexes at pressures and temperatures required by the EQ3/6 software package, version 7.2b. Apart from the $AlAsO_4^o$ and $FeAsO_4^o$ complexes, our log K at 25°C, 1 bar are in fair agreement with those of Whiting (MS Thesis, Colorado School of Mines, Golden, CO, 1992). Moreover, the equilibrium constants evaluated in this study are in good to fair agreement with those determined experimentally for the Ca–dihydroarsenate and Ca–hydroarsenate complexes at 40°C (Mironov et al., Russ J Inorg Chem 40:1690, 1995) and for Fe(III)–hydroarsenate complex at 25°C (Raposo et al., J Sol Chem 35:79–94, 2006), whereas the disagreement with the log K measured for the Ca–arsenate complex at 40°C (Mironov et al., Russ J Inorg Chem 40:1690, 1995) might be due to uncertainties in this measured value. The implications of aqueous complexing between dissolved metals and arsenate/arsenite ions were investigated for seawater, high-temperature geothermal liquids and acid mine drainage and aqueous solutions deriving from mixing of acid mine waters and surface waters.

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Introduction

Today arsenic requires a high level of concern owing to its distribution in different geo-environmental matrices (e.g., surface waters, groundwaters, soils and stream sediments) as a result of both natural processes and anthropogenic pollution. The latter is chiefly caused by (1) widespread use of As compounds as parasiticides in agriculture and for wood preservation, (2) disposal of As-bearing wastes from mining, ore processing and metallurgy and (3) other industrial activities.

Not surprisingly, a huge number of geochemical researches devoted to As have been carried out in the last decades, especially during the last one [see reviews by Cullen and Reimier (1989) and Smedley and Kinniburgh (2002) and references therein]. Particular attention has been paid to the abundance and the redox state of dissolved As in natural waters, especially those intended for human consumption. Indeed, As-rich groundwaters have been identified in several countries, including Argentina, Chile, Mexico, Hungary, China, Vietnam, Bangladesh and West Bengal

(India), with over 40 million people drinking high-As waters in the last area (Smedley and Kinniburgh 2002 and references therein).

An other geochemical research topic of major interest concerns the sorption of As aqueous species by mineral surfaces like clays, metal oxides and hydrous oxides of Al, Fe and Mn (e.g., Stumm and Morgan 1981; Dzomback and Morel 1990). Quite obviously, the accurate knowledge of As speciation in the aqueous phase is required inter alia for modeling the interactions between dissolved As species and mineral surfaces in aquatic and soil systems (e.g., Sverjensky and Fukushi 2006).

However, most authors (e.g., Vink 1996; Sadiq 1997; Cullen and Reimier 1989; Smedley and Kinniburgh 2002 and references therein) describe the speciation of dissolved As in terms of the products of the progressive dissociation of both arsenic acid (H_3AsO_4) ,i.e., $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} ions and arsenious acid (H_3AsO_3),i.e., $H_2AsO_3^-$ and $HAsO_3^{2-}$ ions, depending on the pH and redox conditions of the considered system (e.g., Fig. 1). In our opinion, this consolidated procedure is not satisfactory since the aqueous complexes formed through association of arsenate and arsenite anions and inorganic cations are totally neglected. Among these aqueous complexes, those involving the ions $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} are expected to be present in a wide pH interval under (relatively) oxidising conditions, whereas those containing the ions $H_2AsO_3^-$ and $HAsO_3^{2-}$ should be important under strongly reducing conditions and above pH 8–9 only, owing to the high pK_1 values of arsenious acid ionisation (Fig. 1). This pH threshold for the formation of arsenite complexes could be somewhat lower at high temperature, based on the pK_1 values (7.80 at 150°C, 7.40 at 200°C, 7.21 at 250°C, and 7.11 at 300°C) which were recently determined for H_3AsO_3 by Zakaznova-Herzog et al. (2006).

As discussed in the following section, the complexation reactions involving arsenate and arsenite anions and inorganic cations have received little attention in the previous literature and the stability of these aqueous complexes at high temperatures and pressures is totally unknown.

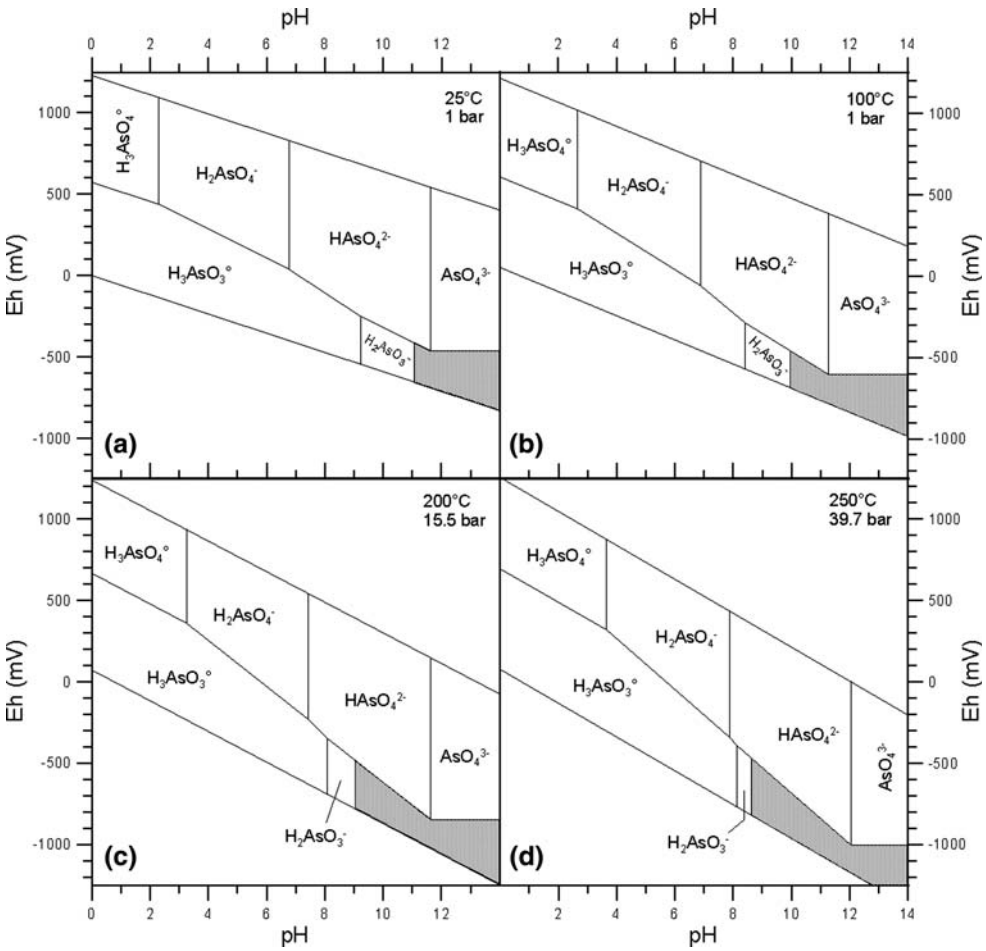

Fig. 1 Eh-pH diagram for aqueous As species in the system As–O_2–H_2O at **a** 25°C and 1 bar total pressure, **b** 100°C and 1 bar total pressure, **c** 200°C and 15.5 bar total pressure (P_{sat} for pure water), and **d** 250°C and 39.7 bar total pressure (P_{sat} for pure water). Predominance fields and isoactivity lines are drawn on the basis of the thermodynamic data reported by Shock et al. (1997). Mutual relationships between aqueous As species are uncertain at high pH values and strongly reducing conditions (*shaded areas*). The left limit of these shaded areas is represented by the $H_2AsO_3^-/HAsO_3^{2-}$ isoactivity line, i.e., the pK of $H_2AsO_3^-$ ion from Sergeyeva and Khodakovsky (1969)

In order to try to fill this gap, we decided to review this matter, by re-estimating the standard partial molal Gibbs free energy of arsenate and arsenite aqueous complexes at 25°C, 1 bar and evaluating other standard partial molal thermodynamic properties—enthalpy, entropy, isobaric heat capacity and volume—at the reference temperature and pressure as well as all the parameters involved in the revised Helgeson–Kirkham–Flowers (HKF) equations of state (Helgeson et al. 1981; Tanger and Helgeson 1988; Shock and Helgeson 1988).

These data were inserted in the code SUPCRT92 (Johnson et al. 1992), which calculates the thermodynamic properties of the reactions of interest up to 5 kbar and 1,000°C. The log K of the destruction reactions of arsenate and arsenite aqueous complexes were thus computed at established P, T conditions (1.013 bar and 0.01, 25, 60, 100°C; saturation pressure and 150, 200, 250 and 300°C) and inserted in the database of the EQ3/6 software package, version 7.2b (Wolery 1979, 1992; Wolery and Daveler 1992).

Finally, speciation calculations for some kinds of natural waters were carried out to draw some possible consequences and implications deriving from the formation of arsenate and arsenite aqueous complexes.

Of course, our estimates of the thermodynamic properties of these species represent provisional results that must be verified through suitable laboratory experiments. Anyway, these preliminary data can be of help for setting up these experiments.

Previous data on the stability of arsenate and arsenite aqueous complexes

Lowenthal et al. (1977) suggested that dissolved arsenate may undergo significant ion association with cations other than Na^+ (such as Mg^{2+} and Ca^{2+} and perhaps K^+ and Sr^{2+} ions) in seawater. This inference was based on the different values they observed for the arsenic acid dissociation constants in NaCl solutions and artificial seawater media of the same ionic strength. However, they did not substantiated this deductions by means of speciation calculations.

Whiting (1992) evaluated the stability constants, βs (also known as formation constants or association constants) of the arsenate complexes involving several cationic constituents (Mg^{2+}, Ca^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}) based on the Electronicity Principle (Brown and Sylva 1987) and by means of log–log plots in which the stability constants of the arsenate complexes were compared with those of the corresponding phosphate complexes. Both the stability constants of H_3AsO_4, $H_2AsO_4^-$, and $HAsO_4^{2-}$ as well as those of $FeH_2AsO_4^{2+}$, $FeHAsO_4^+$, and $FeAsO_4^o$ reported by Robins (1990) were used by Whiting (1992) to construct these log–log plots, although the reliability of Robins' data on Fe(III)–arsenate complexes could not be evaluated.

It must be noted that these log $\beta_{arsenate}$–log $\beta_{phosphate}$ plots are fully equivalent to diagrams in which the standard Gibbs free energies of the reactions (ΔG_r^o) of association of the arsenate complexes are compared with those of the phosphate complexes, owing to the fundamental equation:

$$\Delta G_r^o = -RTlnK \quad (1)$$

where R is the universal gas constant, T is the absolute temperature (in Kelvin), and K the thermodynamic equilibrium constant of the considered reaction (for the association reaction of any aqueous complex: $K = \beta$).

The stability constants obtained by Whiting (1992) were used by Langmuir and coworkers (1999, 2006) in a series of very interesting papers (e.g., Mahoney et al. 2005) as well as by other few authors (e.g., Donahue and Hendry 2003; Apollaro et al. 2006). However, these log β values refer to 25°C, 1 bar. Besides, those of $FeAsO_4^o$ and $AlAsO_4^o$ complexes are at variance with similar estimates carried out in this work (see Comparison of the destruction constants of arsenate complexes with previous data).

During the last few years, experimental studies were carried out to constrain the thermodynamic properties of arsenous acid and its first acid ionization constant up to 300°C (Pokrovski et al. 1996, 2002; Zakaznova-Herzog et al. 2006), but contrasting results were obtained at high temperatures (see Fig. 14 of Zakaznova-Herzog et al. 2006).

The stability of the As(III)–carbonate complex $As(OH)_2CO_3^-$ at 25°C, 1 bar was investigated by Neuberger and Helz (2005). Note that the formation of this complex implies the basic dissociation of arsenous acid, whereas the production of metal–arsenite complexes is related with its acid dissociation. Therefore, the results of Neuberger and Helz (2005) are of little interest for the purposes of our study.

Also the As(III)–sulfide complexes, e.g., $HAs_2S_4^-$ and $As_2S_4^{2-}$ (Zotov et al. 1994), are not relevant for the aim of this communication.

Recently, the stability of the $FeHAsO_4^+$ complex species at 25°C was determined by means of UV-vis spectrophotometry by Raposo et al. (2006), who obtained a log β value of 9.21 ± 0.01, which is in fair agreement with the value of 9.86 computed by Whiting (1992) from free energies reported by Robins (1990).

Mironov et al. (1995) evaluated the formation constants of the aqueous complexes $CaH_2AsO_4^+$, $CaHAsO_4^o$, and $CaAsO_4^-$ at 40°C by means of potentiometric measurements with a membrane electrode reversible to calcium, obtaining log β values of 1.39 ± 0.08, 2.75 ± 0.05, and 4.30 ± 0.1, respectively.

The theoretical predictions of Whiting (1992) and the experimental data by Mironov et al. (1995) and Raposo et al. (2006) will be considered in Comparison of the destruction constants of arsenate complexes with previous data.

Estimation of the thermodynamic properties of arsenate and arsenite aqueous complexes at 25°C, 1 bar

Following Helgeson et al. (1981), for aqueous species other than water, the standard state convention adopted here is the hypothetical one molal solution referenced to infinite dilution at any pressure and temperature.

Thermodynamic properties of aqueous species other than water are conventional standard partial molal properties (Helgeson et al. 1981).

All the thermodynamic properties of arsenate and arsenite aqueous complexes estimated in this work are reported in Table 1 (see also the electronic supplement file http://www.supcrt_patch.dat), whereas the procedures utilized to this purpose are discussed in the following subsections of Estimation of the thermodynamic properties of arsenate and arsenite aqueous complexes at 25°C, 1 bar.

Gibbs free energy at 25°C, 1 bar

The standard Gibbs free energies of formation (ΔG_f^o) of aqueous complexes at 25°C, 1 bar were evaluated by means of linear free energy plots (LFEPs) which are somewhat different from the log $\beta_{arsenate}$–log $\beta_{phosphate}$ plots used by Whiting (1992).

Our choice is based on a preliminary comparison of the ΔG_f^o of well known aqueous complexes of homologous ligands (e.g., Marsicano and Hancock 1978 and Langmuir 1979), such as the LFEPs of fluoride versus chloride complexes and sulfate versus selenate complexes (Fig. 2). These LFEPs display the ΔG_f^o values which were obtained from several data sources (Smith and Martell 1976; Lemire and Tremaine 1980; Hogfelt 1982; Wagman et al. 1982; Jackson and Helgeson 1984; Lemire 1984; Rard 1985; Ruaya and Seward 1987; Sverjensky 1987; Martell and Smith 1989; Shock et al. 1989; Grenthe et al. 1992; Silva et al. 1995; Sverjensky et al. 1997).

These data fit the linear regression equations shown in Fig. 2 with very high values of the squared regression coefficients and relatively low standard errors on both the slope and intercept (obtained by means of the software code OriginPro v. 6.1), especially in the case of the fluoride and chloride complexes. Besides, the slope of these linear relations does not differ significantly from 1 and the pairs HCl/HF and HSO_4^-/$HSeO_4^-$ plot along the regression lines together with the other aqueous complexes in Fig. 2a,b, respectively.

Based on these findings, the ΔG_f^o of arsenate and arsenite complexes were obtained by means of similar LFEPs, in which the known ΔG_f^o values of phosphate and borate complexes are used as a term of comparison.

The choice of phosphate as homologous of arsenate is supported by the similarity in both the structure, which is better represented by $PO(OH)_3$ and $AsO(OH)_3$, and the successive pK_a values of phosphoric acid and of arsenic acid, 2.2, 7.2, and 12.4 against 2.2, 6.9, and 11.5, respectively, at 25°C, 1 bar (e.g., Lowenthal et al. 1977; Baes and Mesmer 1976).

The ionization behavior of arsenous acid, with pK_a values of 9.2, 12.1, and 13.4 (at 25°C, 1 bar), closely resembles that of boric acid (Baes and Mesmer 1976) and supports the choice of the latter as a chemical isomorph of the former (Raposo 2003). Besides, the $As(OH)_3$-type structure of arsenous acid was proven as the more likely by Raman spectroscopy (Loehr and Plane 1968) and quantuum-mechanical (Tossell 2005) studies.

As a further similarity between P and As, it must be underscored that the properties of the AsF_6^- ion are quite similar to those of the PF_6^- ion. For instance, the potassium–hexafluorophosphate complex has a log β of 0.38 at 25°C, 1 bar, which is close to that of the potassium–hexafluoroarsenate complex, 0.25 (Smith and Martell 1976).

Again, the data of phosphate complexes were taken from several sources (Nriagu 1972a, 1972b; Truesdell and Jones 1974; Smith and Martell 1976; Langmuir 1979; Mattigod and Sposito 1979; Hogfeldt 1982; Shock and Helgeson 1988; Martell and Smith 1989; Hummel et al. 2002), whereas the ΔG_f^o values of the borate complexes were derived from Bassett (1980).

Note that the slope of the linear relation in LFEPs was forced to be equal to 1, representing a sort of limiting value (as suggested by the LFEPs involving fluoride and chloride complexes and sulfate and selenate complexes, see above), and the intercept was constrained by the well known ΔG_f^o values of either (1) $H_3AsO_4^o$, $H_2AsO_4^-$, and $HAsO_4^{2-}$—for the arsenate complexes containing the $H_2AsO_4^-$, $HAsO_4^{2-}$, and

Table 1 Estimated standard partial molal thermodynamic properties of arsenate and arsenite complexes at 25°C, 1 bar and estimated equation-of-state parameters for calculation of the corresponding properties at high temperatures and pressures

Complex	ΔG_f^o (cal mol^{-1})	ΔH_f^o (cal mol^{-1})	S^o (cal mol^{-1} K^{-1})	C_P^o (cal mol^{-1} K^{-1})	V^o (cm^3 mol^{-1})	$a_1 \times 10$ (cal mol^{-1} bar^{-1})	$a_2 \times 10^{-2}$ (cal mol^{-1})	a_3 (cal K mol^{-1} bar^{-1})	$a_4 \times 10^{-4}$ (cal K mol^{-1})	c_1 (cal mol^{-1} K^{-1})	$c_2 \times 10^{-4}$ (cal K mol^{-1})	$\omega \times 10^{-5}$ (cal mol^{-1})
$NaH_2AsO_4^o$	–240179	–272608	41.2	37.8	41.1	7.3772	10.2353	1.1421	–3.2022	29.1998	4.6508	–0.0380
$KH_2AsO_4^o$	–244935	–274352	54.5	21.9	52.4	8.9277	14.0226	–0.4840	–3.3587	19.5032	1.4059	–0.0380
$MgH_2AsO_4^+$	–290910	–332717	–10.4	50.7	18.3	4.5105	3.2335	4.1483	–2.9127	30.2446	7.2785	0.7009
$CaH_2AsO_4^+$	–314170	–348007	18.5	45.8	22.2	4.8949	4.1724	3.7452	–2.9515	31.2714	6.2748	0.2639
$SrH_2AsO_4^+$	–315896	–347841	27.3	40.1	22.9	4.9488	4.3041	3.6887	–2.9570	29.0527	5.1198	0.1301
$MnH_2AsO_4^+$	–236482	–270828	14.5	53.5	23.3	5.0617	4.5799	3.5702	–2.9684	35.4116	7.8469	0.3244
$FeH_2AsO_4^+$	–205693	–243719	1.0	44.9	17.6	4.3531	2.8490	4.3134	–2.8968	28.3283	6.1052	0.5283
$CoH_2AsO_4^+$	–193388	–232357	–1.5	45.2	13.9	3.8628	1.6516	4.8275	–2.8473	28.1142	6.1511	0.5664
$NiH_2AsO_4^+$	–193146	–233785	–7.1	36.4	10.0	3.3580	0.4185	5.3569	–2.7963	21.9883	4.3636	0.6516
$CuH_2AsO_4^+$	–166866	–204382	4.1	49.9	14.9	3.9712	1.9164	4.7138	–2.8583	31.7749	7.1135	0.4813
$ZnH_2AsO_4^+$	–215927	–255372	–0.3	50.7	15.3	4.0397	2.0836	4.6420	–2.8652	31.6623	7.2831	0.5485
$PbH_2AsO_4^+$	–187896	–215577	44.7	34.1	25.0	5.1359	4.7611	3.4924	–2.9759	27.8453	3.9053	–0.1328
$AlH_2AsO_4^{2+}$	–299978	–350717	–57.0	34.9	–7.1	1.4491	–4.2440	7.3587	–2.6036	9.1062	4.0580	1.9508
$FeH_2AsO_4^{2+}$	–189949	–235535	–39.9	66.2	1.1	2.4901	–1.7013	6.2670	–2.7087	30.5209	10.4288	1.6927
$NaHAsO_4^-$	–234026	–272938	19.4	11.0	16.4	4.4640	3.1200	4.1970	–2.9080	0.3285	–0.8014	1.3274
$KHAsO_4^-$	–238754	–275247	30.7	3.9	26.1	5.7282	6.2078	2.8713	–3.0357	–2.4032	–2.2436	1.1561
$MgHAsO_4^o$	–282655	–326456	–17.1	–3.4	–0.5	1.6885	–3.6591	7.1076	–2.6278	4.1421	–3.7347	–0.0380
$CaHAsO_4^o$	–306038	–344341	3.5	–5.6	2.0	2.0228	–2.8426	6.7570	–2.6615	2.8090	–4.1808	–0.0380
$SrHAsO_4^o$	–307750	–344917	9.8	–8.1	2.4	2.0851	–2.6905	6.6917	–2.6678	1.2751	–4.6941	–0.0380
$MnHAsO_4^o$	–229564	–268033	0.7	–2.1	2.7	2.1148	–2.6180	6.6606	–2.6708	4.8969	–3.4821	–0.0380
$FeHAsO_4^o$	–196961	–237958	–8.9	–5.9	–0.9	1.6263	–3.8112	7.1729	–2.6215	2.5838	–4.2562	–0.0380
$CoHAsO_4^o$	–187516	–229240	–10.7	–5.8	–3.2	1.3102	–4.5832	7.5044	–2.5896	2.6447	–4.2358	–0.0380
$NiHAsO_4^o$	–185083	–227995	–14.7	–9.7	–5.7	0.9749	–5.4021	7.8559	–2.5557	0.2707	–5.0302	–0.0380
$CuHAsO_4^o$	–160044	–200797	–6.7	–3.7	–2.6	1.3964	–4.3727	7.4140	–2.5983	3.9229	–3.8080	–0.0380
$ZnHAsO_4^o$	–209827	–252128	–9.9	–3.4	–2.4	1.4251	–4.3025	7.3838	–2.6012	4.1482	–3.7327	–0.0380
$PbHAsO_4^o$	–180119	–214509	22.2	–10.7	3.7	2.2585	–2.2670	6.5099	–2.6853	–0.3380	–5.2339	–0.0380
$AlHAsO_4^+$	–295884	–343378	–46.1	–37.3	–8.2	1.0572	–5.2011	7.7697	–2.5640	–28.3000	–10.6450	1.2420
$FeHAsO_4^+$	–188188	–232211	–34.7	–23.4	–4.9	1.4545	–4.2306	7.3530	–2.6042	–18.2487	–7.8136	1.0694
$NaAsO_4^{2-}$	–223700	–253943	48.5	–38.4	–17.0	0.2824	–7.0935	8.5822	–2.4858	–40.6586	–10.8762	2.5085
$KAsO_4^{2-}$	–228428	–249049	84.0	–45.5	–9.64	1.1121	–5.0669	7.7120	–2.5696	–40.0201	–12.3184	1.9714
$MgAsO_4^-$	–271474	–305167	16.9	–55.0	–25.98	–1.3284	–11.0278	10.2713	–2.3232	–40.1942	–14.2425	1.3662
$CaAsO_4^-$	–294913	–323076	37.5	–57.2	–25.50	–1.3685	–11.1259	10.3134	–2.3191	–38.6424	–14.6886	1.0531
$SrAsO_4^-$	–296243	–323239	43.9	–59.7	–25.41	–1.3889	–11.1758	10.3349	–2.3170	–39.2835	–15.2019	0.9562
$MnAsO_4^-$	–218289	–251397	18.7	–53.7	–25.37	–1.2541	–10.8464	10.1934	–2.3307	–39.1883	–13.9899	1.3390
$FeAsO_4^-$	–186668	–218541	21.7	–57.5	–26.07	–1.3653	–11.1181	10.3101	–2.3194	–41.0801	–14.7639	1.2932
$CoAsO_4^-$	–177190	–210481	17.6	–57.4	–26.53	–1.4073	–11.2205	10.3541	–2.3152	–41.5926	–14.7436	1.3555
$NiAsO_4^-$	–176304	–211320	11.8	–61.3	–27.01	–1.4432	–11.3083	10.3918	–2.3116	–44.7770	–15.5380	1.4434
$CuAsO_4^-$	–151743	–183607	23.1	–55.3	–26.40	–1.4178	–11.2463	10.3651	–2.3141	–39.5414	–14.3158	1.2716
$ZnAsO_4^-$	–200121	–233853	18.9	–55.0	–26.36	–1.3907	–11.1799	10.3366	–2.3169	–39.9077	–14.2404	1.3358
$PbAsO_4^-$	–169793	–194437	54.9	–62.3	–25.16	–1.4108	–11.2291	10.3577	–2.3148	–39.3690	–15.7417	0.7904
$AlAsO_4^o$	–285558	–330398	–37.2	–60.2	–9.75	0.4180	–6.7624	8.4400	–2.4995	–30.4558	–15.3128	–0.0380
$FeAsO_4^o$	–177862	–218904	–24.7	–84.8	–13.09	–0.0391	–7.8787	8.9193	–2.4533	–45.4298	–20.3238	–0.0380

Table 1 Continued

Complex	ΔG_f^o (cal mol^{-1})	ΔH_f^o (cal mol^{-1})	S^o (cal mol^{-1} K^{-1})	C_P^o (cal mol^{-1} K^{-1})	V^o (cm^3 mol^{-1})	$a_1 \times 10$ (cal mol^{-1} bar^{-1})	$a_2 \times 10^{-2}$ (cal mol^{-1})	a_3 (cal K mol^{-1} bar^{-1})	$a_4 \times 10^{-4}$ (cal K mol^{-1})	c_1 (cal mol^{-1} K^{-1})	$c_2 \times 10^{-4}$ (cal K mol^{-1})	$\omega \times 10^{-5}$ (cal mol^{-1})
$NaH_2AsO_3^o$	–203270	–228832	39.7	28.4	32.7	6.2236	7.4178	2.3518	–3.0857	23.4841	2.7381	–0.0380
$AgH_2AsO_3^o$	–123526	–147071	44.3	25.8	33.0	6.2709	7.5332	2.3022	–3.0905	21.8954	2.2064	–0.0380
$MgH_2AsO_3^+$	–251410	–286183	–11.3	41.3	9.9	3.3617	0.4276	5.3530	–2.7967	24.3996	5.3658	0.7149
$CaH_2AsO_3^+$	–274922	–301872	17.1	36.4	13.8	3.7486	1.3726	4.9473	–2.8358	25.3584	4.3621	0.2853
$SrH_2AsO_3^+$	–275601	–300702	25.8	30.7	14.5	3.8032	1.5060	4.8900	–2.8413	23.1189	3.2071	0.1538
$BaH_2AsO_3^+$	–276315	–297936	40.1	25.6	19.9	4.4634	3.1185	4.1977	–2.9080	22.0326	2.1758	–0.0628
$CuH_2AsO_3^+$	–134368	–164924	3.0	40.5	6.5	2.8237	–0.8865	5.9172	–2.7424	25.8958	5.2008	0.4990
$PbH_2AsO_3^+$	–153138	–174063	42.8	24.7	16.5	3.9918	1.9667	4.6922	–2.8603	21.8705	1.9925	–0.1047
$AlH_2AsO_3^{2+}$	–266611	–309612	–55.5	25.5	–15.6	0.2882	–7.0795	8.5761	–2.4864	3.5909	2.1453	1.9290
$FeH_2AsO_3^{2+}$	–154392	–192413	–39.1	56.8	–7.3	1.3321	–4.5295	7.4813	–2.5918	24.9248	8.5160	1.6797

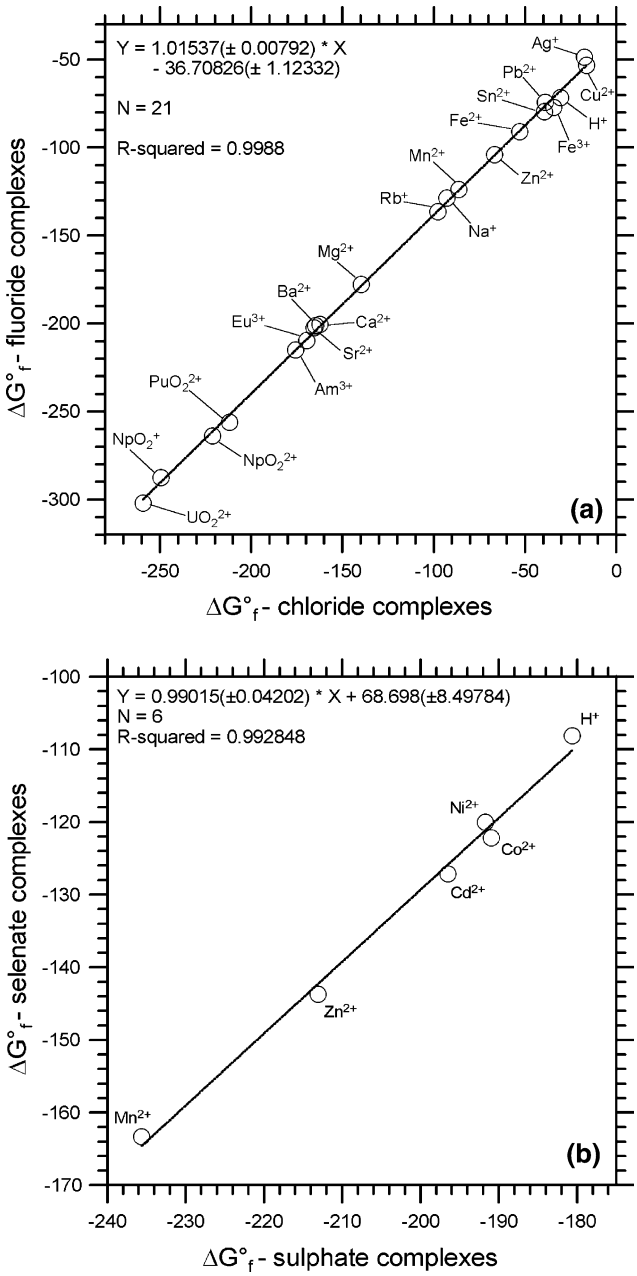

Fig. 2 LFEPs for **a** fluoride versus chloride complexes and **b** selenate versus sulfate complexes. Standard partial molal Gibbs free energies of formation are at Tr = 25°C and Pr = 1 bar

AsO_4^{3-} ions, respectively—or (2) $H_3AsO_3^o$ for the arsenite complexes involving the $H_2AsO_3^-$ ion. The ΔG_f^o values of these species were taken from Shock et al. (1997). We refrained from using the ΔG_f^o values of Fe(III)–arsenate complexes (Robins 1990), as the reliability of these data is uncertain (see Previous data on the stability of arsenate and arsenite aqueous complexes).

It can be easily shown that, the unit value of the slope makes the relation

$$\Delta G^{o}_{f,MA} = \Delta G^{o}_{f,MP} + n, \quad (2)$$

totally equivalent to the equation

$$\Delta G^{o}_{r,MA} = \Delta G^{o}_{r,MP} + q, \quad (3)$$

where M is a generic cation, A and P are one of the arsenate anions (or the arsenite ion $H_2AsO_3^-$) and the corresponding phosphate anion (or the borate ion $H_2BO_3^-$), respectively,

$$n = \Delta G^{o}_{f,HA} - \Delta G^{o}_{f,HP}, \quad (4)$$

and

$$q = \Delta G^{o}_{r,HA} - \Delta G^{o}_{r,HP}. \quad (5)$$

In Eqs. (4) and (5), HA and HP represent the protonated forms of A and P, respectively. Therefore, under the hypothesis of slope equal to 1, the log $\beta_{arsenate}$–log $\beta_{phosphate}$ plots are also completely equivalent to the LFEPs based on the ΔG^{o}_{f}.

Of course, the procedure outlined above allows one to estimate the ΔG^{o}_{f} of arsenate complexes corresponding to phosphate complexes whose ΔG^{o}_{f} is known. For instance, since the ΔG^{o}_{f} is known for the $KHPO_4^-$ complex but it is not for the $KH_2PO_4^o$ and KPO_4^{2-} complexes, it is possible to evaluate the ΔG^{o}_{f} for the $KHAsO_4^-$ complex but it is impossible to estimate the ΔG^{o}_{f} for the $KH_2AsO_4^o$ and $KAsO_4^{2-}$ complexes. The ΔG^{o}_{f} of arsenate complexes whose corresponding phosphate complexes have unknown ΔG^{o}_{f} was obtained in a second step by means of LFEPs between the ΔG^{o}_{f} of $MH_2AsO_4^{(n-1)+}$, $MHAsO_4^{(n-2)+}$, and $MAsO_4^{(n-3)+}$ complexes. In this way it was possible to constrain the ΔG^{o}_{f} of all the arsenate complexes of the considered metals, although the errors of the second step of the adopted procedure are somewhat higher than those of the first step. The LFEPs involving the $MH_2PO_4^{(n-1)+}$, $MHPO_4^{(n-2)+}$, and $MPO_4^{(n-3)+}$ complexes (whose ΔG^{o}_{f} is obviously known) provide evidence in favor of the approach used in the second step. Again, the linear regression equations shown in Fig. 3 have slopes very close to 1, very high values of the squared regression coefficients and comparatively low standard errors on both the slope and intercept.

Note that this second step cannot be applied to arsenite complexes, since the only borate complexes are those involving the $H_2BO_3^-$ ion.

The errors on the ΔG^{o}_{f} values of arsenate and arsenite complexes depend both on those of corresponding phosphate and borate complexes and on those of the adopted method of estimation. The unknown uncertainties on the ΔG^{o}_{f} of phosphate (and borate) complexes are probably larger than those determined by LFEPs (Whiting 1992).

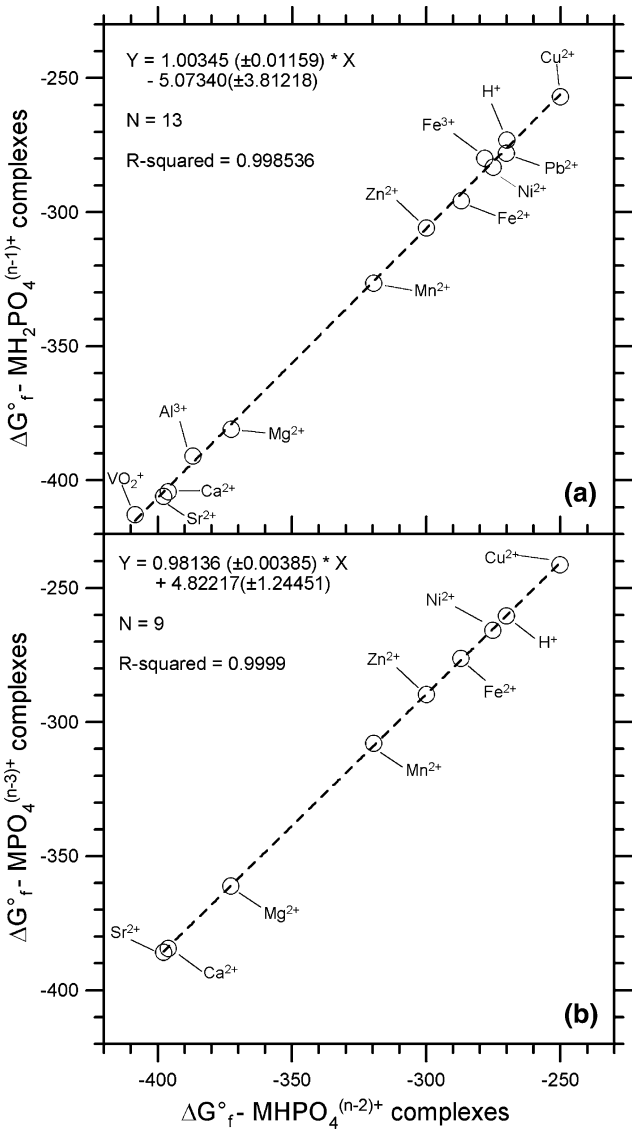

Fig. 3 LFEPs for **a** $MH_2PO_4^{(n-1)+}$ versus $MHPO_4^{(n-2)+}$ complexes and **b** $MHPO_4^{(n-2)+}$ versus $MPO_4^{(n-3)+}$ complexes

Entropy, isobaric heat capacity and volume

Standard partial molal entropies, isobaric heat capacities and volumes at 25°C, 1 bar for aqueous complexes ML containing monovalent and divalent ligands were evaluated chiefly following the procedure by Sverjensky et al. (1997). The standard partial molal entropies, isobaric heat capacities, and volumes of cations and anions required in these calculations were taken from Shock et al. (1997).

Standard partial molal entropies at 25°C, 1 bar

Following Sverjensky et al. (1997), the evaluation of the standard partial molal entropy (S^o_{ML}) of aqueous complexes involving monovalent ligands (e.g., the $H_2AsO_4^-$ and $H_2AsO_3^-$ ions) or divalent ligands (e.g., the $HAsO_4^{2-}$ ion) requires first the estimation of the standard partial molal entropy of association (ΔS^o_r) and then use of the relationship:

$$S^o_{ML} = \Delta S^o_r + S^o_M + S^o_L, \tag{6}$$

where the pedices M and L identify a generic cation and a generic ligand, respectively. As suggested by Sverjensky et al. (1997), the ΔS^o_r was obtained by means of different equations, depending on the charge of both the ligand (Z_L) and the aqueous complex (Z_{ML}). For aqueous complexes of charge $Z_{ML} = 0$ or $Z_{ML} = +1$, containing monovalent ligands, the standard partial molal entropy of association was estimated by means of the relation:

$$\Delta S^o_r = \alpha_{Z_{ML}} S^o_M + \beta_{Z_{ML}}. \tag{7}$$

For neutral complexes involving monovalent ligands and monovalent cations, the parameters $\alpha_{Z_{ML}}$ and $\beta_{Z_{ML}}$ are constrained by (S^o_L in cal mol^{-1} K^{-1}):

$$\alpha_{Z_{ML}=0} = -0.000479 S^o_L + 0.3185 \tag{8}$$

$$\beta_{Z_{ML}=0} = -0.05757 S^o_L - 3.4494 \tag{9}$$

whereas for complexes of charge +1 formed by monovalent ligands and divalent cations, the parameters $\alpha_{Z_{ML}}$ and $\beta_{Z_{ML}}$ are given by (S^o_L in cal mol^{-1} K^{-1}):

$$\alpha_{Z_{ML}=1} = 0.015762 S^o_L + 0.03874 \tag{10}$$

$$\beta_{Z_{ML}=1} = 0.10344 S^o_L + 7.5807. \tag{11}$$

For aqueous complexes of charge $Z_{ML} = +2$ formed by monovalent ligands and trivalent cations, the standard partial molal entropy of association was computed by using the equation (ΔS^o_r, S^o_L and S^o_M in cal mol^{-1} K^{-1}):

$$\Delta S^o_r = (0.032003 S^o_L - 0.40104) S^o_M + 0.58208 S^o_L + 14.8826. \tag{12}$$

Among the complexes containing divalent ligands, thermodynamic data are known only for those involving CO_3^{2-} and SO_4^{2-} ions. Since the latter has the same number of O atoms of the $HAsO_4^{2-}$ ion, the standard partial molal entropies of association of the complexes containing the $HAsO_4^{2-}$ ion were computed following the approach of Sverjensky et al. (1997) for the sulfate complexes, namely equation (7), in which:

$$\alpha_{Z_{ML}} = -0.055 Z_{ML} + 0.055 \tag{13}$$

$$\beta_{Z_{ML}} = 13.84 Z_{ML} + 18.16. \tag{14}$$

Standard partial molal entropies of the charged complexes containing either the $H_2AsO_4^-$ ion or the $HAsO_4^{2-}$ ion were also estimated by means of a different procedure, comprising:

1. Calculation of the electrostatic radius, $r_{e,ML,Pr,Tr}$(Å), of known aqueous complexes containing monovalent and divalent ligands, at 1 bar, 25 °C, through the relation (Shock and Helgeson 1988):

$$r_{e,ML,Pr,Tr} = \frac{Z^2_{ML}(\eta Y_{Pr,Tr} - 100)}{S^o_{ML} - 71.5|Z_{ML}|}, \tag{15}$$

where η is a constant equal to 166,027 Å cal mol^{-1} and the Born function Y is defined as (Helgeson and Kirkham 1974):

$$Y = \frac{1}{\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P, \tag{16}$$

where ε is the dielectric constant of water. Y takes the value of -5.802×10^{-5} K^{-1} at 25°C, 1 bar. Values of S^o_{ML} (cal mol^{-1} K^{-1}) were taken from Shock and Koretsky (1993, 1995), Sverjensky et al. (1997), and Shock et al. (1997).
2. Linear fitting of the $r_{e,ML,Pr,Tr}$ values containing a given cation against the $r_{e,L,Pr,Tr}$ values of the involved ligands (Shock and Helgeson 1988). This step was applied separately to all the considered monovalent and divalent cations, i.e., Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}.
3. Calculation of the $r_{e,ML,Pr,Tr}$ of the arsenate and arsenite complexes with $Z \neq 0$ by introducing the $r_{e,L,Pr,Tr}$ values of arsenate and arsenite ions in the linear regression equations obtained in the previous step 2.
4. Computation of the standard partial molal entropy of arsenate and arsenite complexes by inserting their $r_{e,ML,Pr,Tr}$ values in Eq. (15) solved for S^o_{ML}.

The standard partial molal entropies obtained in this way for the $M(II)H_2AsO_4^+$ and $M(I)HAsO_4^-$ complexes are compared with the corresponding S^o_{ML} values evaluated by means of the procedure of Sverjensky

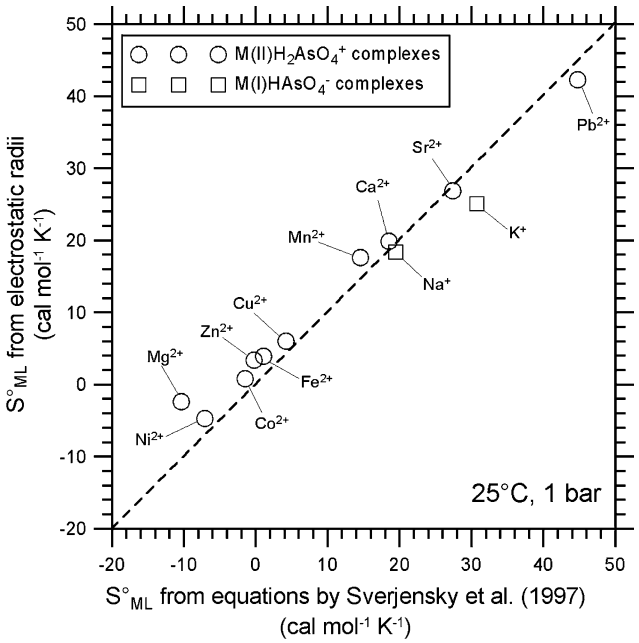

Fig. 4 Correlation plot between the standard entropies for the M–$H_2AsO_4^-$ and M–$HAsO_4^{2-}$ complexes evaluated by means of the procedure of Sverjensky et al. (1997) and the corresponding S^o_{ML} obtained based on linear correlations involving the electrostatic radii

et al. (1997, see above) in the correlation plot of Fig. 4. This diagram shows that the differences between the S^o_{ML} values obtained by means of the two approaches are generally of 0.5–3.1 cal mol^{-1} K^{-1}, apart from the complexes $MgH_2AsO_4^+$, $KHAsO_4^-$, and $ZnH_2AsO_4^+$, presenting deviations of 8.0, 5.6, and 3.7 cal mol^{-1} K^{-1}, respectively.

Owing to these encouraging results, the approach based on the electrostatic radius versus entropy correlation was used to compute the S^o_{ML} values of the complexes containing the trivalent AsO_4^{3-} ion. The standard error on the estimated S^o_{ML} values is of 0.1–2.5 cal mol^{-1} K^{-1}, apart from the complex $MgAsO_4^-$, for which the standard error on the estimated S^o_{ML} is of 5.0 cal mol^{-1} K^{-1}. This error on entropy leads to uncertainties on the log K of the $MgAsO_4^-$ complex of 0.2 log-units at 100°C, 0.4 log-units at 200°C and 0.5 log-units at 300°C.

However, this approach cannot be applied to the neutral complexes $AlAsO_4^o$ and $FeAsO_4^o$, whose standard partial molal entropy was computed through linear regression of the S^o_{ML} values of the complexes containing the AsO_4^{3-} ion against the standard partial molal entropy of the corresponding cations and insertion of the S^o_M value of Al^{3+} and Fe^{3+} ions in the obtained linear regression equation.

Standard partial molal isobaric heat capacities at 25°C, 1 bar

Similarly to the estimation of standard partial molal entropy (see Standard partial molal entropies at 25°C, 1 bar), evaluation of the standard partial molal isobaric heat capacity ($C^o_{P,ML}$) for aqueous complexes involving monovalent ligands (such as the $H_2AsO_4^-$ ion) was carried out, following Sverjensky et al. (1997), through: (1) estimation of the standard partial molal isobaric heat capacity of the association reaction ($\Delta C^o_{P,r}$) by means of the equation ($\Delta C^o_{P,r}$ and $C^o_{P,ML}$ in cal mol^{-1} K^{-1}):

$$\Delta C^o_{P,r} = 1.25 C^o_{P,M} + 45.3 Z_M - 27.3. \quad (17)$$

and (2) use of the equation:

$$C^o_{P,ML} = \Delta C^o_{P,r} + C^o_{P,M} + C^o_{P,L}. \quad (18)$$

In an alternative attempt, the $C^o_{P,ML}$ values of aqueous complexes containing the $H_2AsO_4^-$ ion were estimated assuming that the $\Delta C^o_{P,r}$ of the isocoulombic reactions:

$$M(I)H_2AsO_4^o + OH^- = M(I)OH^o + H_2AsO_4^- \quad (19)$$

and

$$M(II)H_2AsO_4^+ + OH^- = M(II)OH^+ + H_2AsO_4^- \quad (20)$$

are equal to those of the reference isocoulombic reactions:

$$M(I)L^o + OH^- = M(I)OH^o + L^- \quad (21)$$

and

$$M(II)L^+ + OH^- = M(II)OH^+ + L^-, \quad (22)$$

respectively, where M(I) is a generic monovalent metal, M(II) a generic divalent metal, and L^- a generic monovalent ligand, such as F^-, Cl^-, Br^-, I^-, HCO_3^-, $HSiO_3^-$, $HCOO^-$, and CH_3COO^-. The $C^o_{P,ML}$ values of the $M(I)L^o$, $M(II)L^+$, $M(I)OH^o$, and $M(II)OH^+$ aqueous complexes and of the anionic species involved in reactions (19)–(22) were taken from Johnson et al. (1992), Shock and Koretsky (1993, 1995), Sverjensky et al. (1997), and Shock et al. (1997).

The two series of $C^o_{P,ML}$ values are compared in the binary diagram of Fig. 5a, in which the average values of the standard partial molal isobaric heat capacities evaluated based on the isocoulombic approach are reported together with an error bar corresponding to one standard deviation on both sides. Vertical error

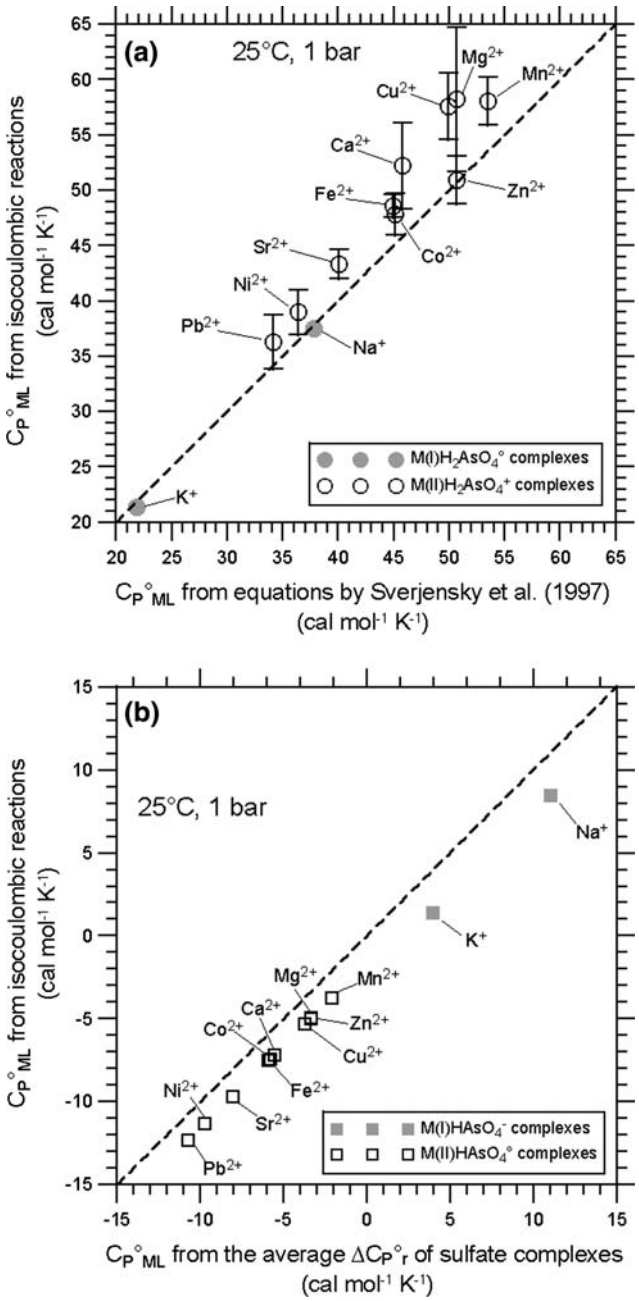

Fig. 5 **a** Correlation plot of the standard partial molal isobaric heat capacities of aqueous complexes containing the $H_2AsO_4^-$ ion evaluated both by means of the procedure of Sverjensky et al. (1997) and based on the isocoulombic approach and **b** correlation plot of the standard partial molal isobaric heat capacities of aqueous complexes containing the $HAsO_4^{2-}$ ion evaluated both from the average $\Delta C^{\circ}_{P,r}$ of sulfate complexes and based on the isocoulombic approach

bars are not shown for the aqueous complexes $NaH_2AsO_4^{\circ}$ and $KH_2AsO_4^{\circ}$ as they are comparable in size with the graphical symbols. This plot shows that the differences between the two series of $C^{\circ}_{P,ML}$ values are generally of 0.3–3.7 cal mol^{-1} K^{-1}, apart from the complexes $MgH_2AsO_4^+$, $CaH_2AsO_4^+$, $CuH_2AsO_4^+$, and $MnH_2AsO_4^+$, which exhibit deviations of 7.6, 6.5, 7.8, and 4.6 cal mol^{-1} K^{-1}, respectively. The agreement is especially striking for the $NaH_2AsO_4^{\circ}$ and $KH_2AsO_4^{\circ}$ complexes, whose $C^{\circ}_{P,ML}$ values computed using Eqs. (17) and (18) are 37.8 and 21.9 cal mol^{-1} K^{-1}, respectively, whereas those estimated on the basis of reactions (19) and (21) are 37.5 ± 0.4 and 21.4 ± 0.8 cal mol^{-1} K^{-1}, respectively. The $C^{\circ}_{P,ML}$ values of the complexes $NaH_2AsO_4^{\circ}$ and $KH_2AsO_4^{\circ}$ can also be estimated assuming $\Delta C^{\circ}_{P,r} = 0$ for the isocoulombic reaction:

$$H_3AsO_4^{\circ} + M^+ = M(I)H_2AsO_4^{\circ} + H^+. \quad (23)$$

In this way, $C^{\circ}_{P,ML}$ values of 34.9 and 27.8 cal mol^{-1} K^{-1} are obtained for the complexes $NaH_2AsO_4^{\circ}$ and $KH_2AsO_4^{\circ}$, respectively. These figures are somewhat different from the values estimated based on reactions (19) and (21) and from those computed using Eqs. (17) and (18), suggesting that the approach based on reaction (23) determines uncertainties on the estimated $C^{\circ}_{P,ML}$ values of 3–6 cal mol^{-1} K^{-1} which are still acceptable.

In the absence of guidelines by Sverjensky et al. (1997), the standard partial molal isobaric heat capacity ($C^{\circ}_{P,ML}$) of aqueous complexes involving the divalent ligand $HAsO_4^{2-}$ was evaluated by means of two different approaches.

In a first attempt, the $\Delta C^{\circ}_{P,r}$ was taken equal to either 49.459 for the aqueous complexes involving monovalent cations ($Z_{ML} = -1$) and divalent cations ($Z_{ML} = 0$) or 42.695 for those containing trivalent cations ($Z_{ML} = +1$). These values represent the average $\Delta C^{\circ}_{P,r}$ of the sulfate complexes with the same charges, based on the $C^{\circ}_{P,ML}$ values given by Johnson et al. (1992), Haas et al. (1995), Sassani and Shock (1998), and Murphy and Shock (1999).

The second, isocoulombic approach applies to complexes involving monovalent and divalent cations only and it is different depending on the Z_M value. The $C^{\circ}_{P,ML}$ values of aqueous complexes formed by monovalent cations and the $HAsO_4^{2-}$ ion was estimated assuming $\Delta C^{\circ}_{P,r} = 0$ for the isocoulombic reaction:

$$H_2AsO_4^- + M^+ = M(I)HAsO_4^- + H^+. \quad (24)$$

Note the similarity between this approach and that based on reaction (23), see above.

The $C^{\circ}_{P,ML}$ values of the aqueous complexes formed by divalent cations and the $HAsO_4^{2-}$ ion was evaluated by means of a two-step procedure. In the first step it was assumed that the isocoulombic reactions:

$$CaHAsO_4^o + SO_4^{2-} = CaSO_4^o + HAsO_4^{2-} \quad (25)$$

and

$$CaHAsO_4^o + CO_3^{2-} = CaCO_3^o + HAsO_4^{2-} \quad (26)$$

have the same $\Delta C^o_{P,r}$ of the isocoulombic reaction:

$$CaCO_3^o + SO_4^{2-} = CaSO_4^o + CO_3^{2-}, \quad (27)$$

which is equal to –3.52 cal mol^{-1} K^{-1}. In this way, the $C^o_{P,ML}$ of the aqueous complex $CaHAsO_4^o$ was estimated to be –7.1 ± 2.5 (1σ) cal mol^{-1} K^{-1}. Then (in the second step), it was assumed $\Delta C^o_{P,r} = 0$ for the isocoulombic reaction:

$$CaHAsO_4^o + M^{2+} = Ca^{2+} + M(II)HAsO_4^o \quad (28)$$

to compute the $C^o_{P,ML}$ of the aqueous complexes $M(II)HAsO_4^o$.

The differences between the two series of $C^o_{P,ML}$ values for the aqueous complexes involving the divalent ligand $HAsO_4^{2-}$ are of 1.6–2.6 cal mol^{-1} K^{-1}, as shown in the binary diagram of Fig. 5b.

Stemming from the good results given by the isocoulombic approach, it was used to compute the $C^o_{P,ML}$ values of the complexes containing the trivalent AsO_4^{3-} ion. The $C^o_{P,ML}$ values of the complexes $NaAsO_4^{2-}$ and $KAsO_4^{2-}$ was computed assuming $\Delta C^o_{P,r} = 0$ for the isocoulombic reaction:

$$HAsO_4^{2-} + M^+ = MAsO_4^{2-} + H^+. \quad (29)$$

The $C^o_{P,ML}$ values of the aqueous complexes formed by divalent cations and the AsO_4^{3-} ion was calculated assuming $\Delta C^o_{P,r} = 0$ for the isocoulombic reaction:

$$M(II)HAsO_4^o + OH^- = M(II)AsO_4^- + H_2O. \quad (30)$$

The $C^o_{P,ML}$ values of the complexes $AlAsO_4^o$ and $FeAsO_4^o$ was computed assuming $\Delta C^o_{P,r} = 0$ for the isocoulombic reaction:

$$H_3AsO_4^o + HM(III)O_2^o = M(III)AsO_4^o + 2H_2O. \quad (31)$$

Standard partial molal volumes at 25°C, 1 bar

Likewise S^o_{ML} and $C^o_{P,ML}$ (see Standard partial molal entropies at 25°C, 1 bar and Standard partial molal isobaric heat capacities at 25°C, 1 bar), the prediction of the standard partial molal volume (V^o_{ML}) for aqueous complexes involving monovalent and divalent ligands (such as the $H_2AsO_4^-$ and the $HAsO_4^{2-}$ ions) was performed, following Sverjensky et al. (1997), by using the equation:

$$V^o_{ML} = \Delta V^o_r + V^o_M + V^o_L, \quad (32)$$

after estimation of the standard partial molal volume of association (ΔV^o_r), through the following relationship (ΔV^o_r and V^o_M in cm^3 mol^{-1}):

$$\Delta V^o_r = 0.11419 V^o_M + 8.9432, \quad (33)$$

for the complexes containing monovalent ligands, and by means of the equation (ΔV^o_r and V^o_M in cm^3 mol^{-1}):

$$\Delta V^o_r = \gamma_Z V^o_M + \delta_Z, \quad (34)$$

for the complexes containing divalent ligands, where

$$\gamma_Z = -0.25Z - 0.3 \quad (35)$$

$$\delta_Z = -2.88Z + 3.32. \quad (36)$$

In an alternative approach (similar to that adopted for estimating the $C^o_{P,ML}$ values of aqueous complexes containing the $H_2AsO_4^-$ ion, see Standard partial molal isobaric heat capacities at 25°C, 1 bar), the V^o_{ML} values of aqueous complexes containing the $H_2AsO_4^-$ ion were evaluted assuming that the ΔV^o_r values of the isocoulombic reactions (19) and (20) are equal to those of the reference isocoulombic reactions (21) and (22), respectively (data from Johnson et al. 1992; Shock and Koretsky 1993, 1995; Sverjensky et al. 1997; Shock et al. 1997). Again, the two sets of V^o_{ML} values are compared in the correlation plot of Fig. 6, where the average values of the isocoulombic-based standard partial molal volumes are reported together with an error bar corresponding to one standard deviation on both sides. The differences between the two sets of V^o_{ML} values are generally of 0.3–0.8 cm^3 mol^{-1}, apart from the complex $KH_2AsO_4^o$, for which the difference between the two V^o_{ML} values is 1.6 cm^3 mol^{-1}.

In the absence of guidelines for the prediction of the standard partial molal volume of the aqueous complexes containing trivalent anions, the V^o_{ML} values of the complexes involving the AsO_4^{3-} ion were computed through linear regression, for each metal, of the V^o_{ML} values of the complexes containing the $H_2AsO_4^-$ and $HAsO_4^{2-}$ ions against the standard partial molal volume of the corresponding ligands and insertion of the V^o_L value of the AsO_4^{3-} ion in the obtained linear regression equation. Since the uncertainty associated with this approach is completely unknown, the thermodynamic properties of the complexes involving the AsO_4^{3-} ion should not be computed at pressures exceeding some hundreds bar.

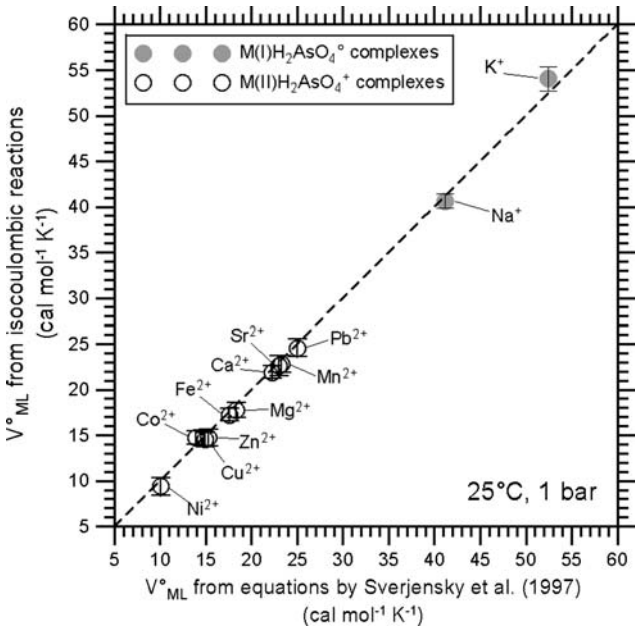

Fig. 6 Correlation plot of the standard partial molal volumes of aqueous complexes containing the $H_2AsO_4^-$ ion evaluated both by means of the procedure of Sverjensky et al. (1997) and based on the isocoulombic approach

Standard enthalpy of formation at 25°C, 1 bar

The standard enthalpies of formation (ΔH_f^o) of aqueous complexes at 25°C, 1 bar were computed through the fundamental thermodynamic relationship $\Delta G_f^o = \Delta H_f^o - T \cdot \Delta S_f^o$. The standard entropies of formation (ΔS_f^o) at 25°C, 1 bar were calculated from the standard partial molal entropies of the aqueous complexes (see Standard partial molal entropies at 25°C, 1 bar) and the standard entropies of the elements in their stable state of aggregation at Pr, Tr [data from Schumm et al. (1973) for Sr, Ba, Mn, Fe, Co, Ni, As and from Cox et al. (1989) for $H_{2,g}$, $O_{2,g}$, Na, K, Mg, Ca, Al, Cu, Zn, Ag, and Pb) and adopting for the ''aqueous electron'' an effective molal entropy of 15.617 cal mol^{-1} K^{-1} (Cox et al. 1989).

Parameters of the revised HKF equations of state

The revised HKF equations of state for the aqueous complex ML can be written as (Tanger and Helgeson 1988):

$$V^o_{ML,P,T} = \hat{C}\left[a_{1,ML} + \frac{a_{2,ML}}{\Psi + P} + \frac{a_{3,ML}}{T - \Theta} + \frac{a_{4,ML}}{(\Psi + P)(T - \Theta)} - \omega_{ML} Q - \left(1 - \frac{1}{\varepsilon}\right)\left(\frac{\partial \omega_{ML}}{\partial P}\right)_T\right], \quad (37)$$

and

$$C^o_{P,ML,Pr,T} = \omega_{ML} TX + 2TY\left(\frac{\partial \omega_{ML}}{\partial T}\right)_P - T\left(\frac{1}{\varepsilon} - 1\right)\left(\frac{\partial^2 \omega_{ML}}{\partial T^2}\right)_P + c_{1,ML} + \frac{c_{2,ML}}{(T - \Theta)^2}, \quad (38)$$

where $\hat{C}$ (41.84 bar cm^3 cal^{-1}) is a conversion factor, Ψ (2,600 bar) and Θ (228 K) are constants characteristic of the solvent, and the solvent Born functions Q, Y, and X (Helgeson and Kirkham 1974) are defined by:

$$Q = \frac{1}{\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial P}\right)_T, \quad (39)$$

equation (16), and by:

$$X = \frac{1}{\varepsilon}\left[\left(\frac{\partial^2 \ln \varepsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P^2\right], \quad (40)$$

respectively. Moreover, in the equations of state (37) and (38), ω_{ML} is the conventional Born coefficient of the aqueous complex ML and $a_{1,ML}$, $a_{2,ML}$, $a_{3,ML}$, $a_{4,ML}$, $c_{1,ML}$, and $c_{2,ML}$ are equation of state coefficients independent of P and T and specific for the aqueous complex ML. These solute-characteristic parameters have to be suitably obtained for each aqueous complex of interest in order to compute its thermodynamic properties at high temperatures and pressures by means of the revised HKF model. Calculation of these solute-characteristic parameters is an easy task (Shock and Helgeson 1988; Sverjensky et al. 1997), knowing the standard partial molal entropy, isobaric heat capacity and volume at 25°C, 1 bar.

For charged aqueous complexes, whose electrostatic radius at 25°C, 1 bar is known (Eq. 15), the conventional Born coefficient at 25°C, 1 bar is computed by means of the equation:

$$\omega_{ML,Pr,Tr} = \eta\left(\frac{Z^2_{ML}}{r_{e,ML,Pr,Tr}} - \frac{Z_{ML}}{3.082}\right) \quad (41)$$

whereas it is assumed that the $\omega_{ML,\ Pr,\ Tr}$ for all neutral aqueous complexes is equal to that of $NaCl^o$, which takes the value of –3,800 cal mol^{-1} at 25°C, 1 bar.

Knowing the value of the conventional Born coefficient at 25°C, 1 bar for the aqueous complex ML, the solvation volume ($\Delta V^o_{s,ML}$) at Pr, Tr is computed from:

$$\Delta V^o_{s,ML,Pr,Tr} = -\hat{C}\omega_{ML,Pr,Tr} Q_{Pr,Tr}, \quad (42)$$

where the Born function Q takes the value of 5.903×10^{-7} bar^{-1} at 25°C, 1 bar.

The non-solvation volume at 25°C, 1 bar is then calculated from:

$$\Delta V^{o}_{n,ML,Pr,Tr} = V^{o}_{ML,Pr,Tr} - \Delta V^{o}_{s,ML,Pr,Tr} \quad (43)$$

The non-solvation volume permits calculation of the equation of state coefficients $a_{1,ML}$ (cal mol^{-1} bar^{-1}), $a_{2,ML}$ (cal mol^{-1}), $a_{3,ML}$ (cal K mol^{-1} bar^{-1}), $a_{4,ML}$ (cal K mol^{-1}) by means of the relations ($\Delta V^{o}_{n,ML,\ Pr,\ Tr}$ in cm^3 mol^{-1}):

$$a_{1,ML} = 0.013684\Delta V^{o}_{n,ML,Pr,Tr} + 0.1765 \quad (44)$$

$$a_{2,ML} = 33.423\Delta V^{o}_{n,ML,Pr,Tr} - 347.23 \quad (45)$$

$$a_{3,ML} = -0.1435\Delta V^{o}_{n,ML,Pr,Tr} + 7.0274 \quad (46)$$

$$a_{4,ML} = -138.17\Delta V^{o}_{n,ML,Pr,Tr} - 26355 \quad (47)$$

Finally, the equation of state coefficients $c_{1,ML}$ (cal mol^{-1} K^{-1}), and $c_{2,ML}$ (cal K mol^{-1}) are obtained through the relations ($C^{o}_{P,ML,\ Pr,\ Tr}$ in cal mol^{-1} K^{-1}, $\omega_{ML,\ Pr,\ Tr}$ in cal mol^{-1}):

$$c_{1,ML} = 0.6087C^{o}_{P,ML,Pr,Tr} + \omega_{ML,Pr,Tr}298.15X_{Pr,Tr} + 5.85 \quad (48)$$

and

$$c_{2,ML} = 2037C^{o}_{P,ML,Pr,Tr} - 30460, \quad (49)$$

where $X_{Pr,\ Tr} = -3.09 \times 10^{-7}$ K^{-2}.

Calculation of the destruction constants of arsenate and arsenite aqueous complexes at high temperatures and pressures

As anticipated in Introduction, the estimated standard partial molal thermodynamic properties of arsenate and arsenite complexes at 25°C, 1 bar and the estimated equation-of-state parameters were inserted in the code SUPCRT92 (Johnson et al. 1992) for calculating the logarithms of thermodynamic constants of the destruction reactions of arsenate and arsenite aqueous complexes at high pressures and temperatures.

To be consistent with the requirements of the EQ3/6 software package (Wolery 1992; Wolery and Daveler 1992), the destruction reactions of aqueous complexes containing arsenate and arsenite ions are as follows:

$$MH_2AsO_4^{(n-1)+} = M^{n+} + H_2AsO_4^- \quad (50)$$

$$MHAsO_4^{(n-2)+} + H^+ = M^{n+} + H_2AsO_4^- \quad (51)$$

$$MAsO_4^{(n-3)+} + 2H^+ = M^{n+} + H_2AsO_4^- \quad (52)$$

$$MH_2AsO_3^{(n-1)+} = M^{n+} + H_2AsO_3^-. \quad (53)$$

The log K of these reactions at 0.01, 25, 60, 100°C (and 1.013 bar total pressure) and 150, 200, 250 and 300°C (and saturation pressure for pure water) are reported in Table 2 (see also the electronic supplement file http://www.eq36_patch.dat). The four decimal digits are really too many with respect to the uncertainties of these data, but they are consistent with the EQ3/6 formats.

Again, as anticipated in Introduction, the log K listed in Table 2 were inserted in the database COM of the EQ3/6 software package, version 7.2b for geochemical modeling of some aquatic environments, as discussed in Consequences of arsenic complexing in different aquatic environments.

Comparison of the destruction constants of arsenate complexes with previous data

Most log K of the destruction reactions of $MH_2AsO_4^{(n-1)+}$, $MHAsO_4^{(n-2)+}$ and, $MasO_4^{(n-3)+}$ complexes at 25°C and 1 bar obtained in this study differ from the corresponding log K of Whiting (1992) by less than 0.4 log-units, except for the $MnHAsO_4^o$ complex, whose log K value deviates by 0.85 log-units (Fig. 7). Larger discrepancies are found for the $AlAsO_4^o$ and $FeAsO_4^o$ complexes, whose log K values differ by 3.0 and 5.0 log-units, respectively.

Summing up, there is in general a fair agreement between our estimates and those of Whiting (1992), apart from a few cases, essentially the $AlAsO_4^o$ and $FeAsO_4^o$ complexes. This fair agreement between the two series of data is quite expected owing to the similar approaches used to estimate thermodynamic constants at 25°C and 1 bar.

The discrepancies for the $AlAsO_4^o$ and $FeAsO_4^o$ complexes may be due to the fact that Whiting's evaluations are influenced by the stability constants of the $AlPO_4^o$ and $FePO_4^o$ complexes derived by Langmuir (1979) whereas our estimates are independent of these data. Indeed, the stability constants of $AlPO_4^o$ and $FePO_4^o$ complexes of Langmuir (1979), 14.86 and 19.62, respectively, appears to be too high of 2.2 and 3.7 log-units based on a log β–log β plot for the $MHPO_4^{(n-2)+}$ and $MPO_4^{(n-3)+}$ complexes (not reported).

Sverjensky and Fukushi (2006) proposed for the destruction of the $NaH_2AsO_3^o$ complex at 25°C, 1 bar a log K of –0.57, which is 0.32 log-units lower than the value estimated in this study, –0.25.

Table 2 Logarithms of thermodynamic constants of the reactions of destruction (as required by the software package EQ3/6) of the aqueous complexes containing arsenate and arsenite ions at temperatures ranging from 0 to 300°C and saturation pressure for pure water

Complex	T (°C)							
	0.01	25	60	100	150	200	250	300
$NaH_2AsO_4^o$	1.8900	1.7753	1.5729	1.3316	1.0256	0.7007	0.3242	–0.1767
$KH_2AsO_4^o$	2.0931	1.8948	1.6176	1.3202	0.9685	0.6159	0.2260	–0.2741
$MgH_2AsO_4^+$	–2.0719	–1.7555	–1.4953	–1.3372	–1.2744	–1.3332	–1.5201	–1.8878
$CaH_2AsO_4^+$	–1.6019	–1.4953	–1.4878	–1.5872	–1.8172	–2.1466	–2.5892	–3.2060
$SrH_2AsO_4^+$	–0.8142	–0.8254	–0.9513	–1.1665	–1.5019	–1.9067	–2.4052	–3.0678
$MnH_2AsO_4^+$	–1.0980	–1.0057	–1.0223	–1.1447	–1.3953	–1.7387	–2.1911	–2.8132
$FeH_2AsO_4^+$	–3.1309	–2.7950	–2.5118	–2.3396	–2.2754	–2.3464	–2.5559	–2.9545
$CoH_2AsO_4^+$	–0.3982	–0.2771	–0.2394	–0.2897	–0.4427	–0.6835	–1.0291	–1.5390
$NiH_2AsO_4^+$	–1.9144	–1.6390	–1.4089	–1.2686	–1.2172	–1.2818	–1.4717	–1.8414
$CuH_2AsO_4^+$	–2.0859	–1.8552	–1.6937	–1.6314	–1.6739	–1.8286	–2.1066	–2.5632
$ZnH_2AsO_4^+$	–0.6658	–0.5256	–0.4747	–0.5176	–0.6661	–0.9047	–1.2492	–1.7586
$PbH_2AsO_4^+$	–1.5417	–1.5950	–1.7726	–2.0415	–2.4406	–2.9094	–3.4775	–4.2246
$AlH_2AsO_4^{2+}$	–3.6690	–3.1952	–2.7232	–2.3391	–2.0168	–1.8383	–1.8068	–1.9732
$FeH_2AsO_4^{2+}$	–4.7471	–4.2654	–3.8402	–3.5484	–3.3688	–3.3470	–3.4774	–3.8049
$NaHAsO_4^-$	6.4254	6.2855	6.175	6.1463	6.2073	6.3332	6.4923	6.6611
$KHAsO_4^-$	6.5993	6.4255	6.2692	6.1831	6.1653	6.207	6.2788	6.3572
$MgHAsO_4^o$	4.4410	4.2954	4.1206	3.9565	3.7651	3.5430	3.2341	2.7484
$CaHAsO_4^o$	4.6509	4.4655	4.2454	4.0304	3.7756	3.4934	3.1309	2.5973
$SrHAsO_4^o$	5.3988	5.1457	4.8479	4.5684	4.2618	3.9516	3.5788	3.0485
$MnHAsO_4^o$	4.2108	4.0653	3.8906	3.7220	3.5198	3.2843	2.9618	2.4625
$FeHAsO_4^o$	3.6992	3.6057	3.4909	3.3770	3.2284	3.0344	2.7446	2.2717
$CoHAsO_4^o$	4.1573	4.0271	3.8703	3.7179	3.5308	3.3052	2.9883	2.4915
$NiHAsO_4^o$	4.4198	4.2712	4.0935	3.9221	3.7161	3.4754	3.1459	2.6387
$CuHAsO_4^o$	3.2016	3.1453	3.0811	3.0229	2.9399	2.8071	2.5738	2.1534
$ZnHAsO_4^o$	4.0675	3.9458	3.7979	3.6564	3.4853	3.2781	2.9812	2.5053
$PbHAsO_4^o$	4.2770	4.1056	3.9018	3.7085	3.4879	3.2473	2.9334	2.4545
$AlHAsO_4^+$	–0.1146	–0.1942	–0.2185	–0.1728	–0.0779	–0.0049	–0.0188	–0.2154
$FeHAsO_4^+$	–3.1545	–2.9745	–2.7121	–2.4132	–2.0768	–1.8196	–1.6884	–1.7656
$NaAsO_4^{2-}$	15.3369	13.8545	12.3687	11.2507	10.4333	10.053	9.9877	10.2001
$KAsO_4^{2-}$	15.9889	13.9946	11.8984	10.1882	8.7386	7.8073	7.2419	6.9748
$MgAsO_4^-$	14.1402	12.4912	10.7706	9.3779	8.1924	7.3958	6.8319	6.3958
$CaAsO_4^-$	14.3003	12.6202	10.851	9.3879	8.0967	7.1808	6.4865	5.9019
$SrAsO_4^-$	15.3543	13.5804	11.6995	10.1357	8.7498	7.7640	7.0163	6.3859
$MnAsO_4^-$	13.6649	12.3299	10.9689	9.8986	9.0218	8.4613	8.0829	7.7942
$FeAsO_4^-$	12.6188	11.1505	9.6346	8.4204	7.3986	6.7196	6.2408	5.8641
$CoAsO_4^-$	13.0583	11.5962	10.0900	8.8879	7.8820	7.2195	6.7582	6.4017
$NiAsO_4^-$	12.0485	10.7063	9.3418	8.2738	7.4063	6.8599	6.5001	6.2367
$CuAsO_4^-$	10.5112	9.2300	7.9360	6.9326	6.1277	5.6274	5.2985	5.0494
$ZnAsO_4^-$	12.4821	11.0603	9.5989	8.4394	7.4792	6.8567	6.4312	6.1064
$PbAsO_4^-$	13.257	11.6746	10.0068	8.6291	7.4153	6.5531	5.8910	5.3095
$AlAsO_4^o$	8.3275	7.3748	6.3474	5.4577	4.5884	3.8417	3.0951	2.2214
$FeAsO_4^o$	5.3509	4.5945	3.8788	3.3556	2.9355	2.6194	2.2822	1.7933
$NaH_2AsO_3^o$	–0.3210	–0.2502	–0.2393	–0.2760	–0.3664	–0.5100	–0.7352	–1.1144
$AgH_2AsO_3^o$	–1.3174	–1.1840	–1.0978	–1.0672	–1.0948	–1.1913	–1.3779	–1.7212
$MgH_2AsO_3^+$	–2.1977	–1.8818	–1.6213	–1.4523	–1.3635	–1.3895	–1.5440	–1.8873
$CaH_2AsO_3^+$	–1.9392	–1.8063	–1.7674	–1.8272	–2.0023	–2.2756	–2.6661	–3.2409
$SrH_2AsO_3^+$	–0.3158	–0.3689	–0.5417	–0.7887	–1.1393	–1.5430	–2.0336	–2.6902
$BaH_2AsO_3^+$	–1.3810	–1.4274	–1.5947	–1.8473	–2.2206	–2.6607	–3.1997	–3.9205
$CuH_2AsO_3^+$	–7.8177	–7.114	–6.4083	–5.8383	–5.3656	–5.1013	–5.0341	–5.2077
$PbH_2AsO_3^+$	–5.4812	–5.1972	–4.9860	–4.8885	–4.9108	–5.0689	–5.3780	–5.9108
$AlH_2AsO_3^{2+}$	–8.6542	–7.8170	–6.9284	–6.1551	–5.4372	–4.9371	–4.6422	–4.5955
$FeH_2AsO_3^{2+}$	–7.9940	–7.2819	–6.5924	–6.0502	–5.6108	–5.3738	–5.3264	–5.5111

The reactions of destruction of the aqueous complexes are as follows:

$MH_2AsO_4^{(n-1)+} = M^{n+} + H_2AsO_4^-$

$MHAsO_4^{(n-2)+} + H^+ = M^{n+} + H_2AsO_4^-$

$MAsO_4^{(n-3)+} + 2H^+ = M^{n+} + H_2AsO_4^-$

$MH_2AsO_3^{(n-1)+} = M^{n+} + H_2AsO_3^-$

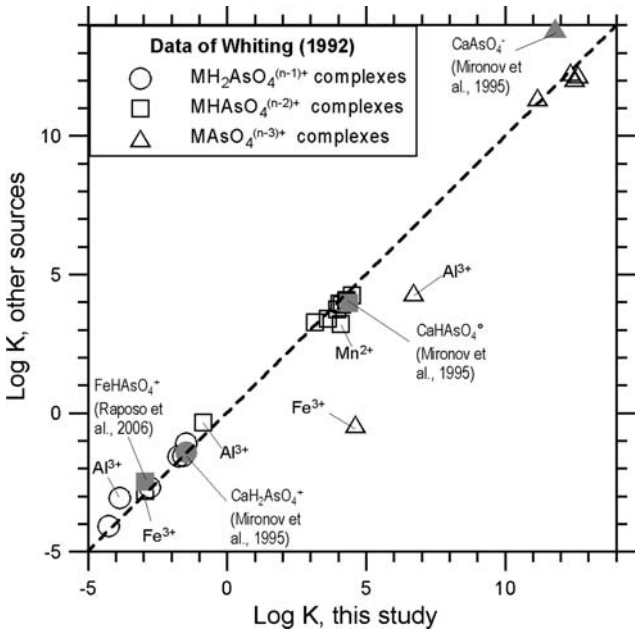

Fig. 7 Correlation plot between the logarithms of the thermodynamic constants of the destruction reactions of arsenate complexes obtained in this study (see Table 2) and the corresponding log *K* from other sources, namely: Whiting (1992, data at 25°C, 1 bar), Raposo et al. (2006, data at 25°C, 1 bar) and Mironov et al. (1995, data at 40°C, 1 bar)

The log *K* of –2.97, evaluated in this study for the dissociation of the $FeHAsO_4^+$ complex (written as reaction 51) at 25°C, 1 bar differs from the corresponding, experimental value determined by Raposo et al. (2006), –2.45, by 0.52 log-units.

Finally, it is instructive to compare our destruction constants for Ca–arsenate complexes with those experimentally determined by Mironov et al. (1995) at 40°C (Table 3). The agreement is very good for the Ca–dihydroarsenate complex, with a deviation comparable with the experimental error, satisfactory for the Ca–hydroarsenate complex, with a deviation of 0.37 log-units, and very poor for the Ca–arsenate complex, with a deviation of 2.11 log-units. The discrepancy between our log *K* and that measured by Mironov et al. (1995) for the $CaAsO_4^-$ complex might be due to the lack of the $NaAsO_4^{2-}$ complex in the speciation model elaborated by Mironov et al. (1995). As a matter of fact, based on the thermodynamic equilibrium constants estimated in this work, the $NaAsO_4^{2-}$ complex results to be more important than the $CaAsO_4^-$ complex above pH 11.2 in a solution containing 1 mmol of both calcium and arsenate and pH adjusted by adding NaOH as in the experiments by Mironov et al. (1995).

Summing up, the agreement between the thermodynamic constants estimated in this work and those experimentally measured by Raposo et al. (2006) and Mironov et al. (1995) is good to fair in three cases and poor in one case, but this single disagreement might be due to uncertainties in the measured value.

Table 3 Comparison between the logarithms of the destruction constants of Ca–arsenate complexes (see reactions 50–52) experimentally measured by Mironov et al. (1995) and evaluated in this work. Data refer to 40°C, 1 bar

Aqueous complex	Log *K*		
	Mironov et al. (1995)	This work	Deviation
$CaH_2AsO_4^+$	–1.39 ± 0.08	–1.4777	0.09
$CaHAsO_4^\circ$	3.99 ± 0.05	4.3661	0.37
$CaAsO_4^-$	13.90 ± 0.1	11.7924	2.11

Consequences of arsenic complexing in different aquatic environments

Seawater

The theoretical distribution of dissolved As species in seawater was computed for the average composition reported by Nordstrom et al. (1979, Table 3), which is part of the EQ3NR Test Case Library (EQ3/6-V7-EQ3NR-TST-R04). This aqueous solution has a total As concentration of 4 ppb. Several trace elements were taken into account in geochemical modeling, including all the metals potentially forming aqueous complexes with arsenate and arsenite anions (see above). Speciation calculations were carried out at 25°C, 1.013 bar, pH of 8.22 and Eh of 500 mV, under the hypothesis of redox equilibrium. Although concentrations of trivalent As in shallow oxygenated seawater were found to be higher than expected on the basis of the redox-equilibrium hypothesis, trivalent As contents are significantly lower than those of pentavalent As (e.g., Cutter 1992 and references therein). Therefore, the redox-equilibrium approach is justified for evaluating the speciation of arsenate rather than that of all dissolved As.

The main species of dissolved arsenate resulting from speciation calculations (Table 4) is the $NaAsO_4^{2-}$ aqueous complex, which accounts for 55% of total dissolved As(*V*). It is followed by the $HAsO_4^{2-}$ ion and the $MgAsO_4^-$ complex, both explaining 14% of total dissolved pentavalent As, approximately. Less important contributions are provided by the $MgHAsO_4^\circ$, $NaHAsO_4^-$, $CaAsO_4^-$, $CaHAsO_4^\circ$, and $KAsO_4^{2-}$ complexes. Excluding the $HAsO_4^{2-}$ ion, the other arsenate complexes listed above involve the major cations Na^+, Mg^{2+}, Ca^{2+} and K^+ (in decreasing order of importance)

and represent altogether 85.26 % of total dissolved As(*V*). In contrast, the role of trace elements in As complexing appears to be minor owing to their relatively low concentrations in seawater.

This predicted distribution is different from the expectations of Lowenthal et al. (1977), who suggested ion complexing of dissolved arsenate with Mg^{2+} and Ca^{2+} ions in seawater. Besides, results of these calculations are at variance with those carried out leaving the metal–arsenate aqueous complexes out of consideration, suggesting prevalence of $HAsO_4^{2-}$ ion (98.71% of total dissolved pentavalent As) accompanied by a minor amount of $H_2AsO_4^-$ ion (0.90 %).

High-temperature geothermal liquids

The speciation of dissolved As in the liquids hosted in deep, high-temperature geothermal reservoirs was evaluated referring to ''synthetic'' aqueous solutions, whose chemical composition was computed by means of the computer code EQ3NR hypothesizing equilibrium with albite, K-feldspar, clinozoisite, calcite, clinochlore, daphnite, muscovite, quartz, anhydrite, pyrite, and fluorite at 250°C, 39.7 bar (saturation pressure for pure water) and variable Cl concentration, from 0.003 to 3 mol/kg. Each of these pure mineral phases fixes the activity of compatible dissolved species, i.e., Na^+, K^+, Ca^{2+}, HCO_3^-, Mg^{2+}, Fe^{2+}, Al^{3+}, SiO_2, SO_4^{2-}, HS^-, and F^-, respectively [see Guidi et al. (1990) and Chiodini et al. (1991) for further details]. The coexistence of calcite and clinozoisite acts as a P_{CO_2} buffer, as recognised by Giggenbach (1984). Solution pH depends on salinity and temperature (Ellis 1970; Chiodini et al. 1991), but is expected to span a relatively limited range, which is satisfactorily reproduced in these calculations. In this geochemical model, redox conditions are fixed by the SO_4^{2-}/HS^- redox pair, i.e., by anhydrite/pyrite coexistence. This mineral pair determines conditions slightly more oxidising than the hydrothermal FeO–$FeO_{1.5}$ redox buffer of Giggenbach (1987), but these oxygen fugacities are often recorded in the geothermal systems explored through deep drilling (Giggenbach 1997).

Table 4 Main species of dissolved pentavalent arsenic in average seawater at 25°C, 1.013 bar based on EQ3NR modeling

Species	Molality	Percentage
$NaAsO_4^{2-}$	2.8730E-08	55.07
$HAsO_4^{2-}$	7.5064E-09	14.39
$MgAsO_4^-$	7.2734E-09	13.94
$MgHAsO_{4(aq)}$	4.8040E-09	9.21
$NaHAsO_4^-$	1.6971E-09	3.25
$CaAsO_4^-$	9.6277E-10	1.85
$CaHAsO_{4(aq)}$	5.7847E-10	1.11
$KAsO_4^{2-}$	4.3682E-10	8.373E-01
Total	5.2170E-08	99.65

Total arsenic concentration was taken equal to 3 ppm, representing a reasonable value for high-temperature geothermal liquids (Ellis 1977). Under the temperature, log f_{O_2} values of the geochemical model, trivalent As prevails over pentavalent As, and undissociated arsenious acid is by far the main dissolved As species in the considered pH range 5–6.8 (Fig. 8). Although these results are not surprising (as discussed in Introduction), geochemical modeling of the considered multicomponent system (comprising several metal–arsenate and metal–arsenite aqueous complexes) provides an evidence more robust than that based on Eh-pH plots (e.g., Fig. 1), which refer to the very simple system As-O_2–H_2O. It must be underscored that, upon boiling of high-temperature geothermal liquids, undissociated arsenious acid enters the separated geothermal vapors and may be transported towards the surface, as suggested by Pokrovski et al. (2002) and Aiuppa et al. (2006), together with minor amounts of several other neutral volatile As species (Planer-Friedrich et al. 2006).

Acid mine drainage

The Bunker Hill Mine/South Fork Coeur d'Alene River case history (Tonkin et al. 2002) was considered as an example of As speciation in acid mine drainage and in aqueous solutions deriving from mixing of acid mine waters and surface waters.

The mixing process was modeled by means of the EQ6 code at the constant temperature of 22.1°C. The P_{CO_2} of acid mine water was constrained at the average atmospheric value ($10^{-3.5}$ bar) whereas the P_{CO_2} of river water is equal to $10^{-2.51}$ bar. During the progressive addition of river water to mine water, P_{CO_2} experiences a gradual increase, attains the maximum of $10^{-1.54}$ bar for a fraction of river water in the mixture (x) of 0.825 (pH = 4.46) and decreases for $x > 0.825$. The pH of the mixture increases slightly from 2.5 to 3.2 for $x < 0.70$, whereas it exhibits a sharp increase for $x > 0.70$, up to the river water pH value of 7.4. The redox potential is fixed at very high values (0.9–0.7 V) throughout the simulation by the Fe^{3+}/Fe^{2+} redox couple. Consequently, pentavalent As prevails by far over trivalent As.

The geochemical models predicts precipitations of schwertmannite, barite, alunite, gibbsite and Fe(III)hydroxide, in satisfactory agreement with the PHREEQC simulation carried out by Tonkin et al. (2002).

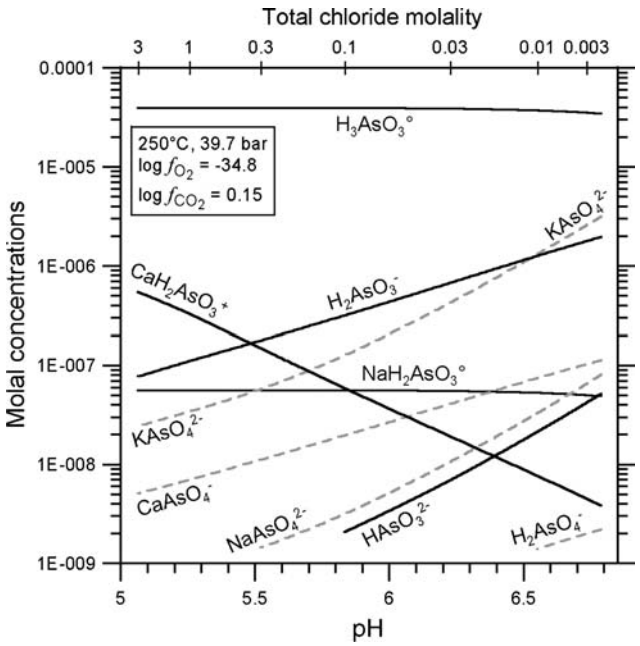

Fig. 8 Theoretical distribution of dissolved As species in full equilibrium geothermal liquids at 250°C, saturation pressure, and variable total chloride molality

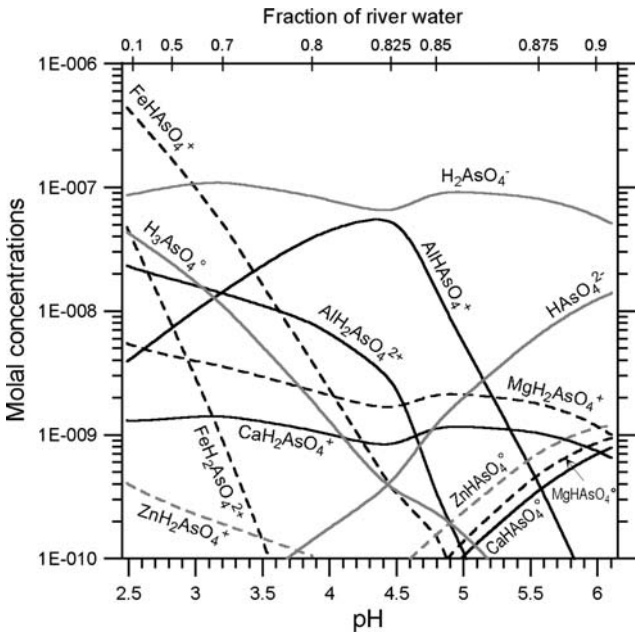

Fig. 9 Theoretical distribution of dissolved As species upon mixing of the acid rock drainage from the Bunker Hill Mine with the South Fork Coeur d'Alene River (analytical data from Tonkin et al. 2002)

The molal concentrations of metal–arsenate complexes, arsenic acid and the products of its progressive dissociation are plotted against both pH and x in Fig. 9. This plot suggests that the complexes $FeHAsO_4^+$ and $AlHAsO_4^+$ are very important below pH 3.5 and at pH values of 3.5–4.75, respectively. The dihydroarsenate complexes of Fe^{3+} and Al^{3+} are also important in acidic aqueous solutions. Of course, this theoretical distribution of dissolved As species pertains to this example and cannot be generalized. Nevertheless, cationic arsenate complexes are expected to be present in important amounts in acid mine drainage, together with $H_2AsO_4^-$ ion and/or $H_3AsO_4^\circ$, depending on pH, redox potential, chemistry of the aqueous phase, etc. In turn, these cationic arsenate species are expected to interact with mineral surfaces (like clays, metal oxides and hydrous oxides of Al, Fe and Mn) in a way completely different from anionic and/or neutral species, thus causing a different mobility of As in aquatic and soil systems.

Solubility product of solid arsenates

A detailed discussion on the role of Fe(III)–arsenate complexes in the evaluation of the solubility products of amorphous ferric arsenate and crystalline scorodite ($FeAsO_4 \cdot 2H_2O$) is found in Langmuir et al. (2006). Similarly, the thermodynamic properties of Ca–arsenate complexes are of fundamental importance to evaluate the solubility products of solid Ca arsenates. To estimate the thermodynamic stability of solid Ca arsenates at 23 ± 1 °C, Bothe and Brown (1999) took into account the aqueous complexes $CaH_2AsO_4^+$, $CaHAsO_4^\circ$, and $CaAsO_4^-$. They estimated log β values at 23 ± 1 °C of 1.30, 2.66, and 4.36, respectively, based on the log β values at 40°C reported by Mironov et al. (1995, see above). Since the log β of the $CaAsO_4^-$ complex is ~2 log-units lower than the corresponding value estimated in this study, it is interesting to underscore the effect of this discrepancy on the solubility products (log K_{sp}) of solid Ca arsenates. To this purpose, selected experimental data of Bothe and Brown (1999) were run by means of the EQ3NR code taking into account our thermodynamic constants of the $CaH_2AsO_4^+$, $CaHAsO_4^\circ$, and $CaAsO_4^-$ complexes. Measured pH, total Ca and total As(V) molal concentrations were treated as input data. The computed speciation of the aqueous solutions assumed to be in equilibrium with different solid Ca arsenates is given in Table 5, also reporting the log K_{sp} values derived on the basis of these speciation results. Interestingly, the deviation between our log K_{sp} values and those suggested by Bothe and Brown (1999) increases with pH owing to the increasing importance of the $CaAsO_4^-$ complex.

Therefore, the stability of relevant metal–arsenate complexes have to be known with sufficient precision to estimate the solubility products of solid arsenates.

Conclusions

The standard thermodynamic properties at 25°C, 1 bar (Gibbs free energy and enthalpy of formation, entropy, isobaric heat capacity, volume, and conventional Born coefficient) and the *P*–*T*-independent coefficients of the revised HKF equations of state (a_1, a_2, a_3, a_4, c_1, and c_2) were estimated for several metal–arsenate and metal–arsenite aqueous complexes, following the approach of Shock and Helgeson (1988) and Sverjensky et al. (1997) and substantiating these estimations with alternative approaches, whenever possible.

Starting from these data, the log *K* of the destruction reactions of these metal–arsenate and metal–arsenite aqueous complexes were computed by using the code SUPCRT92 at the *P*, *T* conditions required by the EQ3/6 software package, version 7.2b.

With the exceptions of the $AlAsO_4^o$ and $FeAsO_4^o$ complexes, the log *K* at 25°C, 1 bar estimated in this work are in fair agreement with those of Whiting (1992). Besides, the thermodymanic equilibrium constants estimated in this work are in good to fair agreement with those measured experimentally for the $CaH_2AsO_4^+$ and $CaHAsO_4^o$ complexes at 40°C (Mironov et al. 1995) and for $FeHAsO_4^+$ complex at 25°C (Raposo et al. 2006), whereas the disagreement with the experimental log *K* at 40°C for the $CaAsO_4^-$ complex (Mironov et al. 1995) might be due to uncertainties in this measured value.

The consequences of arsenate and arsenite complexing with dissolved metals were investigated for:

1. Seawater, where the main species of dissolved arsenate is the $NaAsO_4^{2-}$ aqueous complex (55% of total dissolved pentavalent As), followed by $HAsO_4^{2-}$ (14%), $MgAsO_4^-$ (14%), $MgHAsO_4^o$ (9%) with minor contributions of $NaHAsO_4^-$, $CaAsO_4^-$, $CaHAsO_4^o$, and $KAsO_4^{2-}$.
2. High-temperature geothermal liquids, in which undissociated arsenious acid is by far the prevailing dissolved species of arsenic, in line with the reducing conditions (log f_{O_2} of –34.8) and the comparatively low pH values (5–6.8) in the considered full-equilibrium geochemical model.
3. Acid mine drainage and aqueous solutions deriving from mixing of acid mine waters and surface waters, where the hydroarsenate and dihydroarsenate complexes of Fe^{3+} and Al^{3+} result to be important under acidic conditions. Although the theoretical As distribution cannot be generalized, acid mine drainage is expected to contain important quantities of cationic arsenate complexes, which interact with mineral surfaces differently from anionic and/or neutral species, thus determining a different fate of arsenic in aquatic and soil systems.

Table 5 Results of speciation calculations (this study) for aqueous solutions assumed to be in equilibrium with different solid Ca arsenates at 23°C, 1 bar

Solid Ca arsenate	$Ca_4(OH)_2(AsO_4)_2{\cdot}4\ H_2O$	$Ca_5(OH)(AsO_4)_3$	$Ca_3(AsO_4)_2{\cdot}2\ H_2O$	$Ca_3(AsO_4)_2{\cdot}H_2O$	$Ca_3(AsO_4)_2{\cdot}H_2O$	$CaHAsO_4{\cdot}H_2O$	$CaHAsO_4{\cdot}H_2O$
Total Ca molality	7.98E-03	4.80E-04	8.00E-04	7.98E-03	9.98E-03	2.37E-02	2.94E-02
Total As(*V*) molality	1.60E-06	2.60E-04	4.00E-05	6.54E-03	9.48E-03	2.74E-02	7.34E-02
pH	12.23	9.77	11.18	7.55	7.32	6.22	5.76
log *a* OH^-	–1.8321	–4.2919	–2.882	–6.512	–6.7421	–7.8422	–8.3026
log *a* Ca^{2+}	–2.3967	–3.5537	–3.2141	–2.4562	–2.4012	–2.128	–2.2099
log *a* $CaOH^+$	–3.0923	–6.709	–4.9594	–7.8316	–8.0067	–8.8336	–9.3759
log *a* $CaAsO_4^-$	–5.8571	–3.8257	–4.4281	–3.5097	–3.5685	–4.3986	–4.8335
log *a* $CaHAsO_{4(aq)}$	–9.8261	–5.3347	–7.3472	–2.7988	–2.6276	–2.3576	–2.3325
log *a* $CaH_2AsO_4^+$	–16.0765	–9.1252	–12.5476	–4.3692	–3.968	–2.5981	–2.1129
log *a* AsO_4^{3-}	–9.1012	–5.9129	–6.855	–6.6945	–6.8082	–7.9115	–8.2644
log *a* $HAsO_4^{2-}$	–9.7126	–4.0643	–6.4164	–2.6259	–2.5096	–2.5129	–2.4058
log *a* $H_2AsO_4^-$	–15.18	–7.0717	–10.8337	–3.4133	–3.067	–1.9703	–1.4032
log *a* $H_3AsO_{4(aq)}$	–25.153	–14.5847	–19.7567	–8.7062	–8.13	–5.9333	–4.9062
log *a* H_2O	–0.00018	0	–0.00002	–0.00008	–0.00011	–0.00029	–0.00061
log K_{sp} (this study)	–31.45	–39.80	–23.35	–20.76	–20.82	–4.64	–4.62
log K_{sp} (B.B. 1999)	–28.10	–38.30	–21.02	–21.15	–21.15	–4.74	–4.74
Δ log K_{sp}	–3.35	–1.50	–2.33	0.39	0.33	0.10	0.12

Input data are from Bothe and Brown (1999). Also given are both the log K_{sp} values derived on the basis of our speciation results and the corresponding log K_{sp} values proposed by Bothe and Brown (1999)

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