The Solubility of Metal Arsenates

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It has often been considered that certain metal arsenates because of their low solubility provide a convenient form for the disposal of arsenic residues. In this paper stability diagrams for $FeAsO_4$, $Ca_3(AsO_4)_2$ and $Mg_3(AsO_4)_2$ are derived which show comparatively high solubility of these compounds. The presence of CO_2 in the air has a pronounced effect in greatly increasing the solubility of $Ca_3(AsO_4)_2$ and significantly affecting that of $Mg_3(AsO_4)_2$.

THE residues from nonferrous mining and processing operations often contain appreciable quantities of arsenic compounds which are in many cases considered to be stable. Arsenic is often "stabilized" as ferric arsenate, calcium arsenate, magnesium arsenate and other metal arsenic (v) compounds and disposed of in slag, tailings and residues dumps.

The solubility of the metal arsenic (v) compounds is generally considered to be extremely low. Seidell[1] gives solubility data for a number of metal arsenates but the original source of the data is often very old and, for reasons given later, probably most unreliable.

In 1956 Chukhlansev[2,3] published work on the solubility of a number of metal arsenates, the results of which have been used in several compilations of thermodynamic data both in the form of solubility products[4] and free energies of formations.[5] Chukhlansev's experiments were performed in aqueous solutions using NaOH, H_2SO_4, HNO_3 or HCl to adust pH. The solubilities show a general linear relationship between log solubility and pH and this has been used by other workers for extrapolating to conditions of higher pH and as the basis of the opinion that metal arsenates under specific conditions of pH are extremely insoluble. Direct extrapolation of solubility products without considering the particular equlibria involved can also lead to large errors when assessing solubilities at various pH values.

Recently, Tozawa Umetsu and Nishimura[6] and Nishimura and Tozawa[7] reported a variation to Chukhlansev's linear relationship between log solubility and pH for ferric, calcium and magnesium arsenates which indicated that extrapolation of Chukhlansev's results to higher pH could lead to solubilities which are two low by up to two orders of magnitude. Nishimura and Tozawa explained their results as being due to the decomposition of the particular arsenate to the hydroxide at higher pH, liberating the appropriate arsenic (v) oxyanion.

The solubilities of ferric, calcium and magnesium arsenates at various pH values can be fairly accurately predicted using available free energy data for the various substances in each system.

THERMODYNAMIC STABILITY DIAGRAMS

A convenient approach to this problem of metal arsenate solubility is to consider all of the known equilibria in the particular system and to construct the appropriate stability diagram. A general equation for all hydrolitic equilibria can be written:

$$aA + x\mathrm{H}^+ = bB + c\mathrm{H_2O}$$

and the standard reaction isotherm

$$\Delta G^o = -RT \ln K$$

expanded by taking $T = 298.15$ K, $\mathrm{pH} = -\log a_{\mathrm{H}^+}$ and $a_{\mathrm{H_2O}} = 1$, to obtain the equation

$$x\mathrm{pH} = \frac{-\Delta G^o_{298.15\,\mathrm{K}}(\mathrm{kJ})}{5.708} = -\log \frac{a_B^b}{a_A^a}$$

This equation applied to each of the known or deduced equilibria in a particular system results in a straight line on a plot of log activity of the dissolved ion *vs* pH (approximately log solubility *vs* pH).

A number of metal arsenate-water systems are considered here in this way and appropriate "solubility"/pH diagrams drawn.

THE IRON (111) ARSENATE-WATER SYSTEM

Free energy data for the various substances considered here were taken mostly from NBS Technical Note 270,[5] Parts 3 and 4 are given in Table I.

The equilibria which have been considered in this system are set out as follows together with the calculated free energy change and the pH-concentration equation.

$$\mathrm{FeOH^{2+} + H^+ = Fe^{3+} = H_2O}$$

$$\Delta G^o = -12.38\ \mathrm{kJ}$$

$$\mathrm{pH} = 2.17 - \log^{\mathrm{Fe^{3+}}}/\mathrm{FeOH^{2+}} \qquad [1]$$

$$\mathrm{Fe(OH)_2^+ + H^+ = FeOH^{2+} + H_2O}$$

$$\Delta G^o = -28.53\ \mathrm{kJ}$$

$$\mathrm{pH} = 5.00 - \log \mathrm{FeOH^{2+}/Fe(OH)_2^+} \qquad [2]$$

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Manuscript submitted May 8, 1980.

ISSN 0360-2141/81/0311-0103$00.75/0

Table I. Free Energy Data for Species Considered in the Iron (III) Arsenate-Water System

Formula	$\Delta G^o_{f,298.15\,K}$ kJ
H_2O (liq)	−237.18
Fe^{3+} (m = 1)	− 4.60
$FeOH^{2+}$ (m = 1)	−229.41
$Fe(OH)_2^+$ (m = 1)	−438.06
$Fe(OH)_3$ (c)	−696.64
H_3AsO_4 (m = 1)	−766.09
$H_2AsO_4^-$ (m = 1)	−753.29
$HAsO_4^{2-}$ (m = 1)	−714.71
AsO_4^{3-} (m = 1)	−648.52
$FeAsO_4$ (c)	−768.64* −776.42†

*Calculated from Ref. 4 and used in calculating the stability diagrams.

†Calculated from Ref. 7.

$$H_2AsO_4^- + H^+ = H_3AsO_4$$
$$\Delta G^o = -12.80\ \text{kJ}$$
$$pH = 2.24 - \log \frac{H_3AsO_4}{H_2AsO_4^-} \qquad [3]$$

$$HAsO_4^{2-} + H^+ = H_2AsO_4^-$$
$$\Delta G^o = -38.58\ \text{kJ}$$
$$pH = 6.76 - \log \frac{H_2AsO_4^-}{HAsO_4^{2-}} \qquad [4]$$

$$AsO_4^{3-} + H^+ = HAsO_4^{2-}$$
$$\Delta G^o = -66.19\ \text{kJ}$$
$$pH = 11.60 - \log \frac{HAsO_4^{2-}}{AsO_4^{3-}} \qquad [5]$$

$$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$$
$$\Delta G^o = -19.50\ \text{kJ}$$
$$pH = 1.14 - 1/3 \log Fe^{3+} \qquad [6]$$

$$Fe(OH)_3 + 2H^+ = FeOH^{2+} + 2H_2O$$
$$\Delta G^o = -7.15\ \text{kJ}$$
$$pH = 0.63 - 1/2 \log FeOH^{2+} \qquad [7]$$

$$FeAsO_4 + 3H^+ = H_3AsO_4 + Fe^{3+}$$
$$\Delta G^o = -2.05\ \text{kJ}$$
$$\begin{aligned} pH = {} & 0.12 - 1/3 \log H_3AsO_4 \\ & - 1/3 \log Fe^{3+} \end{aligned} \qquad [8]$$

$$FeAsO_4 + H_2O + 2H^+ = H_3AsO_4 + FeOH^{2+}$$
$$\Delta G^o = 10.33\ \text{kJ}$$
$$\begin{aligned} pH = {} & -0.90 - 1/2 \log H_3AsO_4 \\ & - 1/2 \log FeOH^{2+} \end{aligned} \qquad [9]$$

$$FeAsO_4 + H_2O + H^+ = H_2AsO_4^- + FeOH^{2+}$$
$$\Delta G^o = 23.14\ \text{kJ}$$
$$\begin{aligned} pH = {} & -4.05 - \log H_2AsO_4^- \\ & - \log FeOH^{2+} \end{aligned} \qquad [10]$$

$$FeAsO_4 + 3H_2O = Fe(OH)_3 + H_2AsO_4^- + H^+$$
$$\Delta G^o = 30.25\ \text{kJ}$$
$$pH = 5.30 + \log H_2AsO_4^- \qquad [11]$$

Taking the case of equal concentrations of the particular arsenic and iron ions which are obtained by the solution of $FeAsO_4$ Fig. 1 can be derived. It can readily be seen from this diagram that the minimum solubility of ferric arsenate lies at about pH = 2.2 and under the conditions of equal dissolved iron and arsenic this concentration is equal to approximately 10^{-3} m As (or 75 mg/l).

Also shown on Fig. 1 are the experimental solubility points of Tozawa and coworkers.[6,7] Reasonably good agreement is revealed except for the points to the middle right of the diagram. In this region ferric arsenate has decomposed to ferric hydroxide which has probably not allowed equilibrium to be attained due to its coating of the original ferric arsenate particles. Tozawa's experiments allowed only 24 h for equilibration.

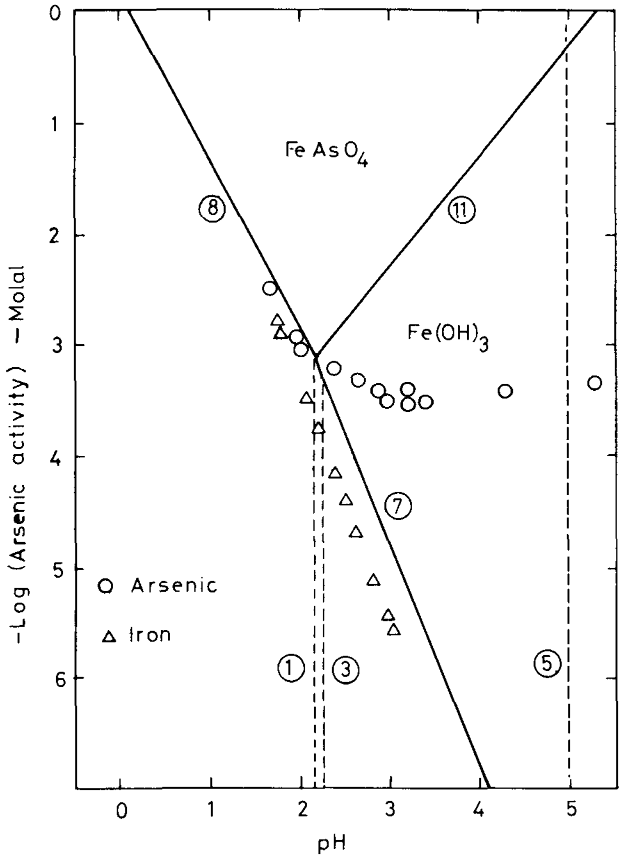

Fig.1—The ferric arsenate-water system showing also some of the experimental analyses for both iron and arsenic from Ref. 6.

THE CALCIUM-ARSENATE-WATER SYSTEM

Free energy data were taken from NBS Technical Note 270[5] Parts 3 and 6 and these data for calcium ions and compounds are given in Table II.

The equilibria which have been considered in this system are set out as follows together with the calculated free energy changes and the pH-concentration equations.

$$CaOH^+ + H^+ = Ca^{2+} + H_2O$$
$$\Delta G^o = -72.34 \text{ kJ}$$
$$pH = 12.68 - \log \frac{Ca^{++}}{CaOH^+} \qquad [12]$$

$$Ca(OH)_2^o + H^+ = CaOH^+ + H_2O$$
$$\Delta G^o = -87.45 \text{ kJ}$$
$$pH = 15.32 - \log \frac{CaOH^+}{Ca(OH)_2^o} \qquad [13]$$

$$Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$$
$$\Delta G^o = -129.37 \text{ kJ}$$
$$pH = 11.33 - 1/2 \log Ca^{2+} \qquad [14]$$

$$Ca(OH)_2 + H^+ = CaOH^+ + H_2O$$
$$\Delta G^o = -57.02 \text{ kJ}$$
$$pH = 10.0 - \log CaOH^+ \qquad [15]$$

$$Ca(OH)_2 = Ca(OH)_2^o$$
$$\Delta G^o = 30.42 \text{ kJ}$$
$$\log Ca(OH)_2^o = -5.33 \qquad [16]$$

$$Ca_3(AsO_4)_2 + 4H^+ = 2H_2AsO_4^- + 3Ca^{2+}$$
$$\Delta G^o = -104.10 \text{ kJ}$$
$$pH = 4.56 - 1/2 \log H_2AsO_4^- - 3/4 \log Ca^{2+} \qquad [17]$$

$$Ca_3(AsO_4)_2 + 2H^+ = 2HAsO_4^{2-} + 3Ca^{2+}$$
$$\Delta G^o = -26.94 \text{ kJ}$$
$$pH = 2.36 - \log HAsO_4^{2-} - 3/2 \log Ca^{2+} \qquad [18]$$

Table II. Free Energy Data for the Species Considered in the Calcium Arsenate-Water System

Formula	$\Delta G^o_{f,\ 298.15\ K}$ kJ
Ca^{2+} ($m = 1$)	−553.54
$CaOH^+$ ($m = 1$)	−718.39
$Ca(OH)_2^o$ ($m = 1$)	−868.14
$Ca(OH)_2$ (c)	−898.56
$Ca_3(AsO_4)_2$ (c)	−306.31

$$Ca_3(AsO_4)_2 = 2AsO_4^{3-} + 3Ca^{2+}$$
$$\Delta G^o = 105.44 \text{ kJ}$$
$$\log AsO_4^{3-} = -9.24 - 3/2 \log Ca^{2+} \qquad [19]$$

$$Ca_3(AsO_4)_2 + 3H_2O = 2AsO_4^{3-} + 3CaOH^+ + 3H^+$$
$$\Delta G^o = 322.42 \text{ kJ}$$
$$pH = 18.83 + 2/3 \log AsO_4^{3-} + \log CaOH^+ \qquad [20]$$

$$Ca_3(AsO_4)_2 + 6H_2O = 2AsO_4^{3-} + 3Ca(OH)_2 + 6H^+$$
$$\Delta G^o = 493.46 \text{ kJ}$$
$$pH = 14.41 + 1/3 \log AsO_4^{3-} \qquad [21]$$

Figure 2 has been derived for equal concentrations of the appropriate calcium and arsenic ions (very little difference is obtained if the ratio of the calcium ion to the arsenic ion is taken as 3/2 which is the solution product ratio).

When Tozawa's results for the solubility of calcium arsenate are compared to this diagram the agreement deviates by the "splitting" of the experimental values of arsenic and calcium in solution with the ion equivalent of arsenic about sixteen times the ion equivalent of calcium. This is certainly due to the formation of another solid compound which is very likely to be a carbonate formed due to the presence of CO_2 in the atmosphere.

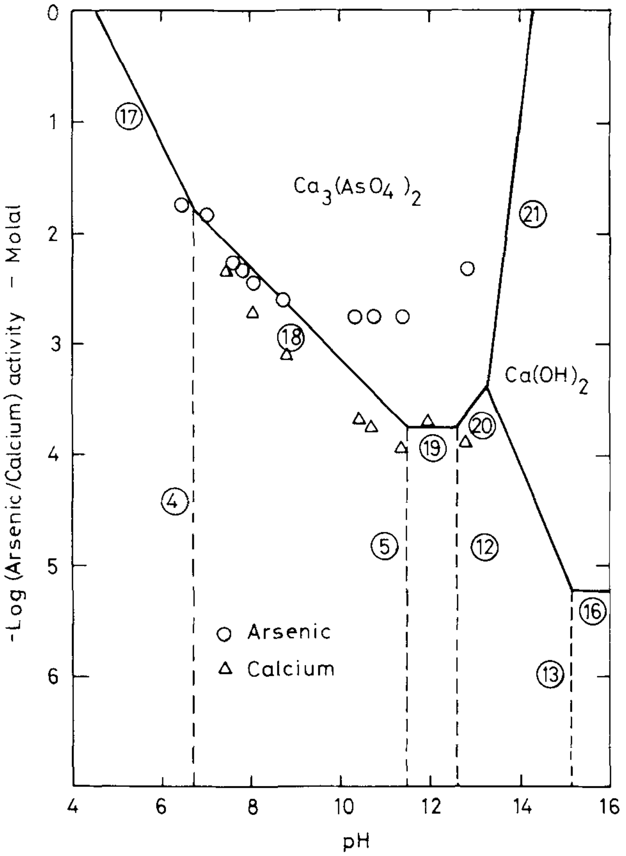

Fig.2—The calcium arsenate-water system. Experimental points are taken from Ref. 6.

THE CALCIUM ARSENATE-CARBONATE-WATER SYSTEM

Stability diagrams for this system were drawn up using the additional free energy data from NBS Technical Note[5] Parts 3 and 6 and given in Table III and the equilibria set out below.

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$
$$\Delta G^o = -12.80\ \text{kJ}$$
$$pH = 2.24 - \log Ca^{2+} - \log HCO_3^- \qquad [22]$$

$$CaCO_3 = Ca^{2+} + CO_3^{2-}$$
$$\Delta G^o = 46.15\ \text{kJ}$$
$$\log Ca^{2+} = -8.08 - \log CO_3^{2-} \qquad [23]$$

$$CaCO_3 + H_2O = CaOH^+ + \log CO_3^{2-} + H^+$$
$$\Delta G^o = 119.75\ \text{kJ}$$
$$pH = 20.98 + \log CaOH^+ + \log CO_3^{2-} \qquad [24]$$

$$Ca_3(Aso_4)_2 + 3HCO_3^- = 3CaCO_3 + 2HAsO_4^{2-} + H^+$$
$$\Delta G^o = 7.70\ \text{kJ}$$
$$pH = 1.35 + 2\log HAsO_4^{2-} - 3\log HCO_3^- \qquad [25]$$

$$Ca_3(AsO_4)_2 + 3CO_3^{2-} + 2H^+ = 3CaCO_3 + 2HAsO_4^{2-}$$
$$\Delta G^o = -169.16\ \text{kJ}$$
$$pH = 14.80 - \log HAsO_4^{2-} + 3/2\log CO_3^{2-} \qquad [26]$$

$$Ca_3(AsO_4)_2 + 3CO_3^{2-} = 3CaCO_3 + 2AsO_4^{3-}$$
$$\Delta G^o = -36.78\ \text{kJ}$$
$$\log AsO_4^{3-} = 3.22 + 3/2\log CO_3^{2-} \qquad [27]$$

$$Ca(OH)_2 + CO_3^{2-} + 2H^+ = CaCO_3 + 2H_2O$$
$$\Delta G^o = -176.77\ \text{kJ}$$
$$pH = 15.49 + 1/2\log CO_3^{2-} \qquad [28]$$

Figure 3 was drawn up for a carbonate or bicarbonate activity of 10^{-4} molal which is an appropriate value for a closed system which has initially been in contact with the atmosphere at pH below 7. This would have been a likely condition for Tozawa's experiments which were carried out over a 24 h period and not equilibrated with the atmosphere where $p_{CO_2} = 10^{-3.52}$ atmospheres.

Figure 4 was calculated for the system in equilibrium with CO_2 in the atmosphere where:

(a) $\log[H_2CO_3^o] = -4.97$

(b) $\log[HCO_3^-] = pH - 11.35$

(c) $\log[CO_3^{2-}] = 2pH - 21.68$

This diagram shows that under these conditions the minimum solubility of $Ca_3(AsO_4)_2$ is at a pH of 7.8 and is equivalent to an arsenic concentration of approximately 0.5 g/l.

THE MAGNESIUM ARSENATE-CARBONATE-WATER SYSTEM

Free energy data were taken from NBS Technical Note 270[5] Parts 3 and 6 and those data for magnesium ions and compounds are given in Table IV.

$$MgOH^+ + H^+ = Mg^{2+} + H_2O$$
$$\Delta G^o = -65.23\ \text{kJ}$$
$$pH = 11.43 - \log\frac{Mg^{2+}}{MgOH^+} \qquad [29]$$

$$Mg(OH)_2^o + H^+ = MgOH^+ + H_2O$$
$$\Delta G^o = -94.52\ \text{kJ}$$
$$pH = 16.56 - \log\frac{MgOH^+}{Mg(OH)_2^o} \qquad [30]$$

$$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O$$
$$\Delta G^o = -95.60\ \text{kJ}$$
$$pH = 8.37 - 1/2\log Mg^{2+} \qquad [31]$$

Table III. Free Energy Data for the Additional Species Considered in the Calcium Arsenate-Carbonate-Water System

Formula	$\Delta G^o_{f,\ 298.15\ K}$ kJ
$H_2CO_3^o$ ($m = 1$)	− 623.16
HCO_3^- ($m = 1$)	− 586.85
CO_3^{2-} ($m = 1$)	− 527.90
$CaCO_3$ (*c*) calcite	−1128.84

Table IV. Free Energy Data for the Species Considered in the Magnesium Arsenate-Water System

Formula	$\Delta G^o_{f,\ 298.15\ K}$ kJ
Mg^{2+} ($m = 1$)	− 454.80
$MgOH^+$ ($m = 1$)	− 626.76
$Mg(OH)_2^o$ ($m = 1$)	− 769.44
$Mg(OH)_2$ (*c*)	− 833.58
$Mg_3(AsO_4)_2$ (*c*)	−2773.78*
$MgCO_3$ (*c*)	−1012.11
$MgCO_3 \cdot 3H_2O$ (*c*)	−1726.32
$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (*c*)	−5864.17‡
$Mg(OH)_2 \cdot MgCO_3 \cdot 3H_2O$	−2568.35
$MgHCO_3^o$ ($m = 1$)	−1049.68†
$MgCO_3^o$ ($m = 1$)	−1003.53†

*Calculated from Ref. 4.
†Reference 8.
‡Reference 9.

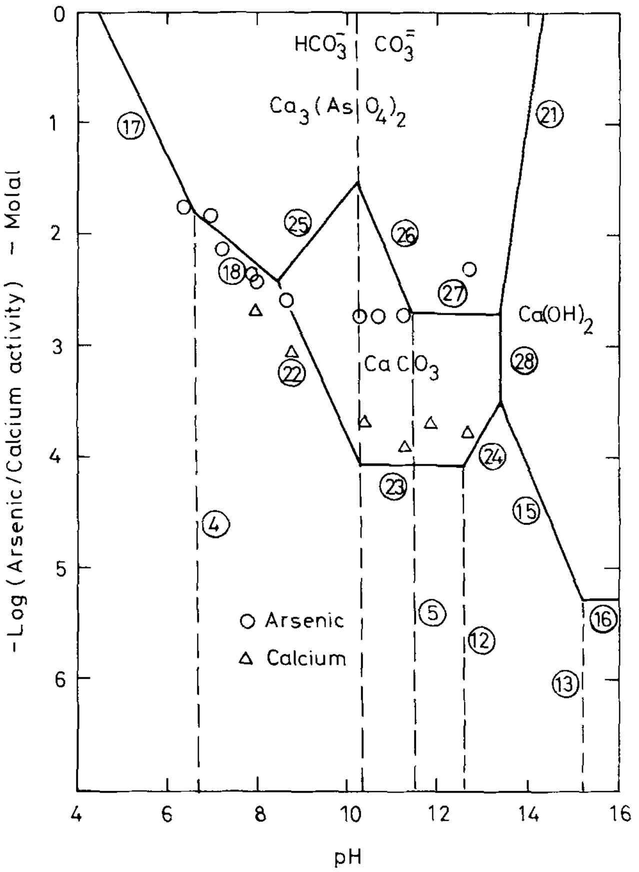

Fig.3—The calcium arsenate-carbonate-water system at a carbonate/bicarbonate activity of 10^{-4}. Experimental points are taken from Ref. 6.

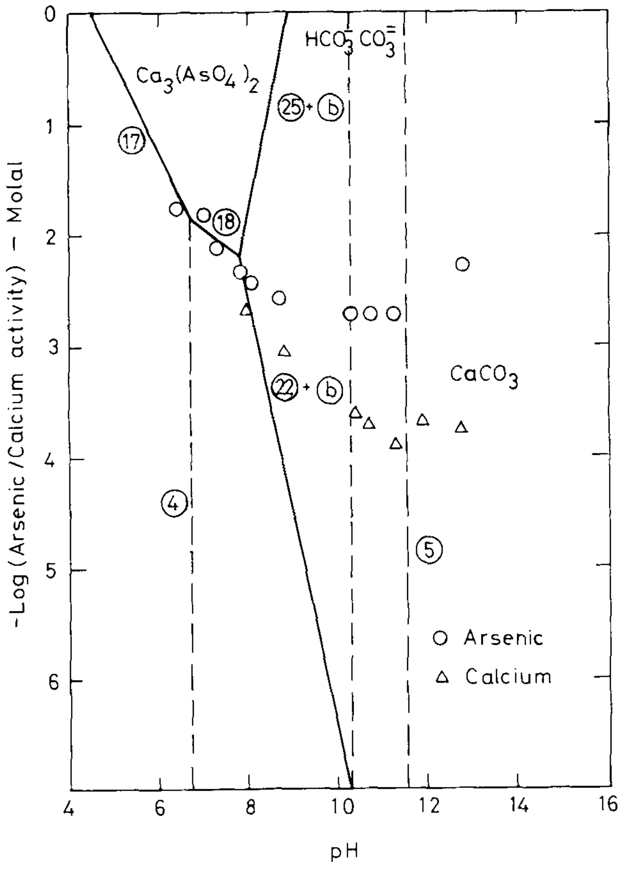

Fig.4—The calcium arsenate-carbonate-water system at a carbonate/bicarbonate activity in equilibrium with atmospheric carbon dioxide (p_{CO_2} = $10^{-3.52}$ ats.) Experimental points are taken from Ref. 6.

$$Mg(OH)_2 + H^+ = MgOH^+ + H_2O$$
$$\Delta G^o = -30.38 \text{ kJ}$$
$$pH = 5.32 - \log MgOH^+ \qquad [32]$$

$$Mg(OH)_2 = Mg(OH)_2^o$$
$$\Delta G^o = 64.14 \text{ kJ}$$
$$\log Mg(OH)_2^o = -11.24 \qquad [33]$$

$$Mg_3(AsO_4)_2 + 4H^+ = 2H_2AsO_4^- + 3Mg^{2+}$$
$$\Delta G^o = -97.19 \text{ kJ}$$
$$pH = 4.26 - 1/2 \log H_2AsO_4^- - 3/4 \log Mg^{2+} \qquad [34]$$

$$Mg_3(AsO_4)_2 + 2H^+ = 2HAsO_4^{2-} + 3Mg^{2+}$$
$$\Delta G^o = -20.04 \text{ kJ}$$
$$pH = 1.76 - \log HAsO_4^{2-} - 3/2 \log Mg^{2+} \qquad [35]$$

$$Mg_3(AsO_4)_2 + 6H_2O = 3Mg(OH)_2 + 2H\,AsO_4^{2-} + 4H^+$$
$$\Delta G^o = 266.73 \text{ kJ}$$
$$pH = 11.6\ 8 + 1/2 \log HAsO_4^{2-} \qquad [36]$$

$$Mg(OH)_2 \cdot MgCO_3 \cdot 3H_2O + 3H^+ = 2Mg^{2+} + HCO_3^- + 5H_2O$$
$$\Delta G^o = -114.01 \text{ kJ}$$
$$pH = 6.66 - 2/3 \log Mg^{2+} - 1/3 \log HCO_3^- \qquad [37]$$

$$Mg(OH)_2 \cdot MgCO_3 \cdot 3H_2O = 2\,Mg(OH)_2 + CO_3^{2-} + H_2O + 2H^+$$
$$\Delta G^o = 136.11 \text{ kJ}$$
$$pH = 11.92 + 1/2 \log CO_3^{2-} \qquad [38]$$

$$2Mg_3(AsO_4)_2 + 3HCO_3^- + 15H_2O = 3[Mg(OH)_2 \cdot MgCO_3 \cdot 3H_2O] + 4HAsO_4^{2-} + 5H^+$$
$$\Delta G^o = 301.96 \text{ kJ}$$
$$pH = 10.58 - 3/5 \log HCO_3^- + 4/5 \log HAsO_4^{2-} \qquad [39]$$

$$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O + 6H^+ = 5Mg^{2+} + 4HCO_3^- + 6H_2O$$

$$\Delta G^o = -180.33 \text{ kJ}$$

$$pH = 5.27 - 2/3 \log HCO_3^- - 5/6 \log Mg^{2+} \qquad [40]$$

$$5Mg_3(AsO_4)_2 + 12HCO_3^- + 18H_2O = 3[4MgCo_3 \cdot Mg(OH)_2 \cdot 4H_2O] + 10HAsO_4^{2-} + 8H^+$$

$$\Delta G^o = 440.74 \text{ kJ}$$

$$pH = 9.65 + 5/4 \log HAsO_4^{2-} - 3/2 \log HCO_3^- \qquad [41]$$

$$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O + 2H^+ = 5Mg^{2+} + 4CO_3^{2-} + 6H_2O$$

$$\Delta G^o = 55.48 \text{ kJ}$$

$$pH = -4.86 - 2 \log Co_3^{2-} - 5/2 \log Mg^{2+} \qquad [42]$$

$$5Mg_3(AsO_4)_2 + 12CO_3^{2-} + 18H_2O + 4H^+ = 3[4MgCo_3 \cdot Mg(OH)_2 \cdot 4H_2O] + 10HAsO_4^{2-}$$

$$\Delta G^o = -266.69 \text{ kJ}$$

$$pH = 11.68 - 5/2 \log HAsO_4^{2-} + 3 \log CO_3^{2-} \qquad [43]$$

Figure 5 is a stability diagram for the magnesium arsenate-carbonate-water system at a carbonate (or bicarbonate) activity of 10^{-3} molal. This activity of carbonate was chosen to approximate a closed system which had initially been in equilibrium with the CO_2 in air ($10^{-3.52}$ atmospheres) at a pH less than neutral, so that Tozawa's results could be explained. Under these conditions the basic carbonate which is stable at pH greater than 9.3 is the compound $Mg(OH)_2 . MgCO_3 \cdot 3H_2O$ (antinite). Tozawa's results fit well into the stability region of this compound. A carbonate activity of 10^{-4} molal would result in a decrease in this stability region to the point of disappearance.

Figure 6 is a stability diagram for the same system but under conditions where equilbrium exists with the carbon dioxide in the atmosphere ($p_{CO_2} = 10^{-3.52}$ atmospheres). Under these conditions it can be shown that the basic carbonate which is stable is the compound $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (hydromagnesite), over a very wide range of pH. Minimum solubility of $Mg_3(AsO_4)_2$ is at pH = 9.3 equivalent to an arsenic concentration of approximately 75 mg/l.

CONCLUSIONS

Stability diagrams for iron (111) arsenate, calcium arsenate, and magnesium arsenate, which have been calculated using reliable free energy data, reveal that the solubility of these compounds is significantly higher in the region of minimum solubility than has been

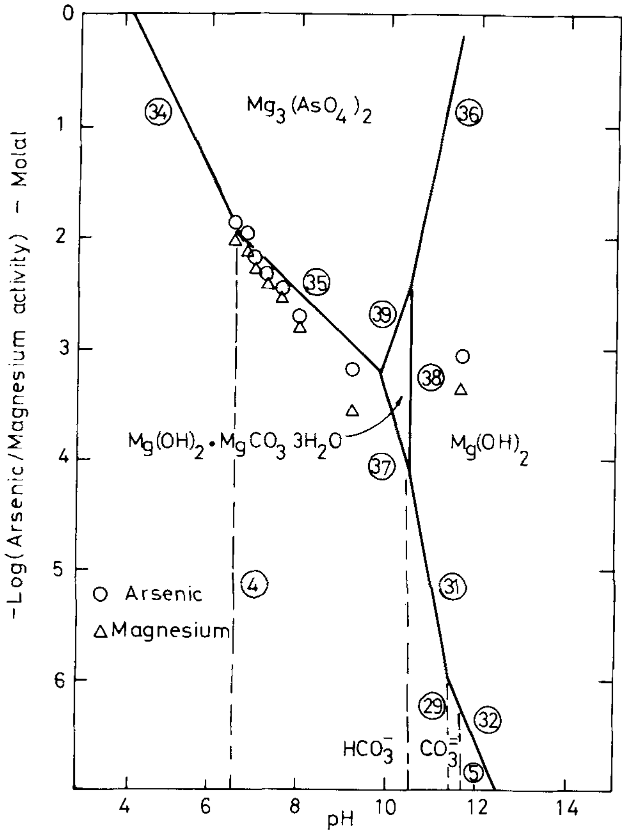

Fig. 5—The magnesium arsenate-carbonate-water system at a carbonate/bicarbonate activity of 10^{-3}. Experimental points are taken from Ref. 6.

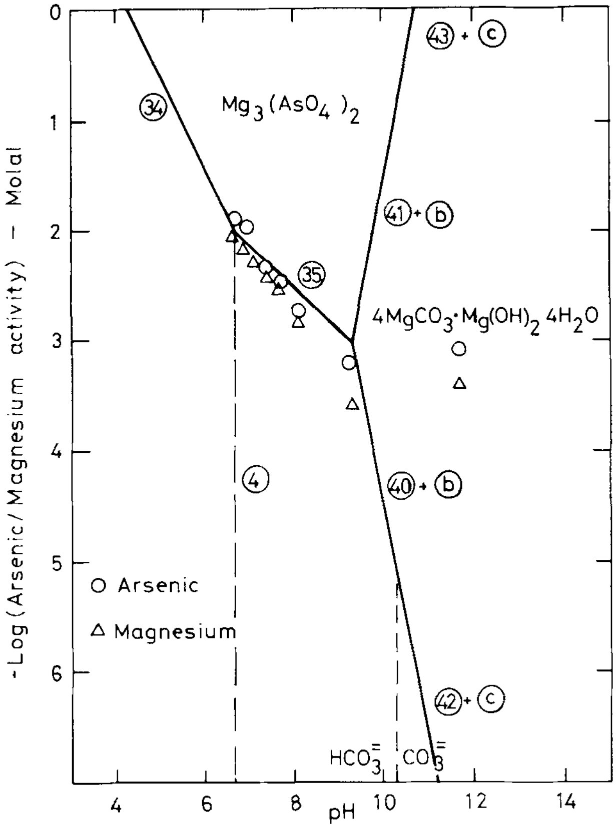

Fig. 6—The magesium arsenate-carbonate-water system at a carbonate/bicarbonate activity in equilibrium with atmospheric carbon dioxide ($p_{CO_2} = 10^{-3.52}$ ats.) Experimental points are taken from Ref. 6.

widely assumed. The presence of carbonate at very low concentration has a large affect in greatly increasing the minimum solubility of calcium arsenate by approximately two orders of magnitude, and also significantly affecting the solubility of magnesium arsenate.

The experimental results which have been published by Tozawa and coworkers[6,7] show fairly close agreement with the calculated diagrams but an accurate equilibrium study of the systems involved would be appropriate.

The significance of the higher than recognized solubilities of metal arsenates leads to important considerations in relation to the disposal of arsenic containing residues from metal extraction processes. The misuse of published solubility products has led to the widely accepted conclusion that metal arsenates (under specific conditions of pH) are extremely insoluble. In this work an attempt has been made to take into account all of the reactions which could influence the solubility of each of the three arsenates considered. Some of the equilibria which are presented in the equations above do not appear as lines on the stability diagrams but are important in attaining the end result . Other equilibria for which equations are not presented were also considered.

The equilibrium considerations reported here relate to a simple system consisting of pure components. In relation to the mobility of arsenic in ground waters associated with residues from metal extraction processes this chemical model is too simple by far and should be considered together with all of the possible heterogeneous interactions in the natural aquatic environment including adsorption and organic complexing. Holm *et al* and Gulens *et al* have discussed various aspects of the occurrence and mobility of arsenic in gound waters.[10] Chemical modelling in such systems is a field which is evolving rapidly and one in which the hydrometallurgist must become more active.

ACKNOWLEDGMENT

This work was carried out at the U.S. Bureau of Mines Research Center, Salt Lake City, Utah, in September 1979, while the author was visiting that laboratory under a U.S./Australia Agreement for Scientific and Technical Co-operation.

REFERENCES

1. A. Seidell: *Solubilities of Inorganic and Metal Organic Compounds*, vols. I & II, Van Nostrand, New York, 1958, 1965.
2. V. G. Chukhlansev: *Zh. Neorg. Khim.*, 1956, vol. 1, pp. 1975–82.
3. V. G. Chukhlansev: *Zh. Anal. Khim.*, 1956, vol. 11, pp. 529–35.
4. L. G. Sillen and A. E. Martell: *Stability Constants of Metal-Ion Complexes*, The Chemical Society Special Publication No. 17, 1964.
5. D. D. Wagman *et al*: *Selected Values of Chemical Thermodynamic Properties*, U.S. National Bureau of Standards, Technical Note 270 Parts 3, 4 and 6, 1968, 1969, 1971.
6. K. Tozawa, Y. Umetsu, and T. Nishimura: Research Institute of Mineral Dressing & Metallurgy, Tohuku University, Sendai, Japan. Preprint of paper presented at A.I.M.E. 107th Annual Meeting, Denver, Colorado, U.S.A. Feb. 27 to Mar. 2, 1978, unpublished research.
7. T. Nishimura and K. Tozawa: 1978, *Bulletin of the Research Institute of Mineral Dressing and Metallurgy*, vol. 34, no. 1, pp. 19–26, Tohuku University, Sendai, Japan.
8. R. M. Garrels and C. L. Christ: *Solutions Minerals and Equilibria*, p. 416, Harper & Row, 1965.
9. R. A. Robie, B. S. Hemingway, and J. R. Fisher: *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressure and at Higher Temperatures*, p. 25, U.S. Geological Survey Bulletin 1452, U.S. Govt. Printing Office, 1978.
10. T. R. Holme, M. A. Anderson, D. G. Iverson, and R. S. Stanforth: Paper 31, and J. Gulens, D. R. Champ, and R. E. Jackson: Paper 4, *Chemical Modeling in Aqueous Systems*, E. A. Jenne, ed., A.C.S. Symposium Series No. 93, A.C.S., Washington, 1979.