

THE STABILITIES OF ARSENIC (V) AND ARSENIC (III)

COMPOUNDS IN AQUEOUS METAL EXTRACTION SYSTEMS

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The stabilities of a number of metal arsenates and metal arsenites are calculated from critically selected free energy or equilibrium constant data and some experimental data, and presented in the form of log activity versus pH diagrams. Carbon dioxide in the atmosphere is shown to have an effect in reducing the stability of a number of the metal arsenates and most of the metal arsenites considered. The relevance to disposal of arsenic from mineral processing wastes is emphasised.

Introduction

Stability diagrams for arsenic compounds are of importance for predicting the solubility of these compounds in relation to a variety of hydro-metallurgical processes, and in considering waste disposal problems. Monhemius (1) has published "precipitation diagrams" for a number of metal arsenates but these are incomplete and misleading since the possible equilibria for the complete system have not been considered.

The current practice for the disposal of arsenic wastes from mineral processing operations is to stabilise the arsenic in the form of either metal arsenates or arsenites and to contain this material in residues dumps, tailings ponds, and underground storage areas. A previous paper (2) indicates that the widely held opinion that ferric arsenate, calcium arsenate and magnesium arsenate are extremely insoluble, is incorrect. Stability diagrams were presented to show a relatively high solubility for these compounds which, in the case of both calcium and magnesium arsenates, is enhanced by the presence of carbon dioxide, even at levels of its normal concentration in air.

The solubility of other metal arsenates and arsenites has now been examined by thermodynamic calculation with presentation in the form of log activity versus pH stability diagrams ("solubility diagrams").

Stability Diagrams for Metal-Arsenic-Water Systems

The previous paper (2) outlines briefly the derivation of log activity vs pH diagrams from free energy data. The various equilibria considered for ferric arsenate, calcium arsenate, and magnesium arsenate solubilities are detailed and the pH-concentration equations which lead to the plotting of the stability diagrams are shown. Some experimental data from Nishimura and Tozawa (3) are used to substantiate the validity of the diagrams.

In this work stability diagrams are presented for the arsenates of copper (11), cobalt (11), nickel (11), lead (11), zinc (11), manganese (11), strontium (11), barium (11), cadmium (11), iron (11), aluminium (11), chromium (11), silver (1) and mercury (1) in the presence of carbon dioxide in the atmosphere ($p_{CO_2} = 10^{-3.47}$ atmos.). Diagrams for calcium arsenate and magnesium arsenate are revised here to take into account the dissolved carbonate complexes of calcium and magnesium. The free energy data which was used to calculate the diagrams were critically selected and are considered to be reliable.

Diagrams are also presented for the arsenites of calcium (11), magnesium (11), barium (11), iron (11), copper (11), zinc (11) and lead (11) in the presence of carbon dioxide in the atmosphere. The data from which these arsenic (11) systems have been calculated are less reliable, having been obtained from an interpretation of some experiments reported by Chuklansev (4) and also some of the author's own experiments; hence some approximate standard free energies of formation for the metal arsenite compounds are included separately in Table I.

For brevity, the equilibria considered and the pH-concentration equations are not reported here since they may be easily deduced from the diagrams. The diagrams are drawn for equal activity of both the metal ion and the arsenic (V) ion along the solution/solid interface of the metal-arsenic compound, and for convenience all of the intersections are

shown as straight line intersections rather than curved boundaries to agree with the theoretical consideration of constant total activity of dissolved species.

Results and Discussion

Figures 1 to 16 present stability diagrams for Metal-Arsenic (V)-Water systems at 298.15K and a carbon dioxide partial pressure of $10^{-3.47}$ atmospheres (which is equivalent to the concentration of carbon dioxide in atmospheric air).

The effect of atmospheric carbon dioxide in some of the systems such as calcium is shown to be very significant and certainly must be considered in relation to long term disposal of processing waste. The concentration of carbon dioxide in the atmosphere has increased from about 315 p.p.m. in 1958 to 338 p.p.m. in 1980 (5) and it is this latest figure which is used for the calculation of the diagrams in this work.

If the solubility of particular metal arsenates is in fact the stabilising influence in a disposal situation, then it seems that those arsenates which are usually chosen (calcium, magnesium and ferric iron) for stability may not be appropriate. Figure 17 which shows the stability regions for a number of metal arsenates under the influence of atmospheric carbon dioxide ($p_{CO_2} = 10^{-3.47}$ atmospheres) would indicate that copper, zinc, lead, barium and mercury may be the actual stabilising influence in many disposal situations. Barium arsenate appears in this figure to be an extremely insoluble compound and mercurous arsenate has a similar low solubility. Both of these compounds may have application to the stabilisation of arsenic (V) and may in fact be responsible for the stability of some residues and the low levels of arsenic in particular effluents.

Stability diagrams can be drawn for many of the additional components in complex systems that relate more closely to the real disposal environment, and will be found to be an invaluable guide to predicting the inter-related chemical equilibria. Sulphate in particular is important where insoluble sulphates are formed as is the case with barium, and since barium arsenate must be given serious consideration as a likely compound for stabilising arsenic, the barium-arsenic (V)-sulphate system is shown in Figure 18 at a sulphate level equivalent to the solubility of $BaSO_4$ (barite). A comparison of Figures 8 and 18 indicates the relatively better stability of barium arsenate in a sulphate system.

The diagrams for the arsenic (11) systems are shown in Figures 19 to 28. Most of these systems show the limiting effect of carbon dioxide in the atmosphere and a generally higher solubility of arsenite compared to arsenate which leads to the conclusion that none of the metal arsenites is suitably stable to be considered for disposal purposes. Calcium-arsenic (11) in particular is shown in Figure 19 to have considerable solubility under conditions influenced by carbon dioxide in the atmosphere.

Since calcium hydroxide is commonly used to precipitate arsenic (11) as the "basic calcium arsenite" it is appropriate to consider this system in the absence of carbon dioxide. Figure 20, which has been calculated from some experimental work by Robins and Nishimura (6), shows the existence of two calcium arsenites $Ca(AsO_2)_2$ and $Ca(AsO_2)_2 \cdot Ca(OH)_2$. The dibasic arsenite $Ca(AsO_2)_2 \cdot 2Ca(OH)_2$ which has been reported in the

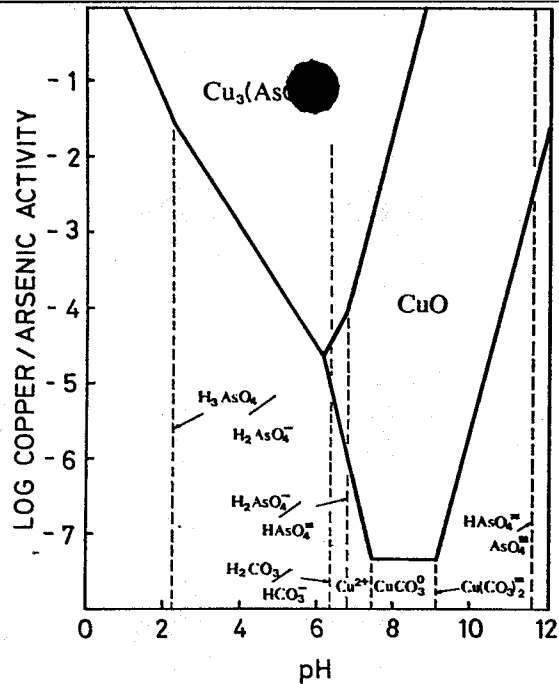


FIGURE 1 THE COPPER (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF COPPER AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

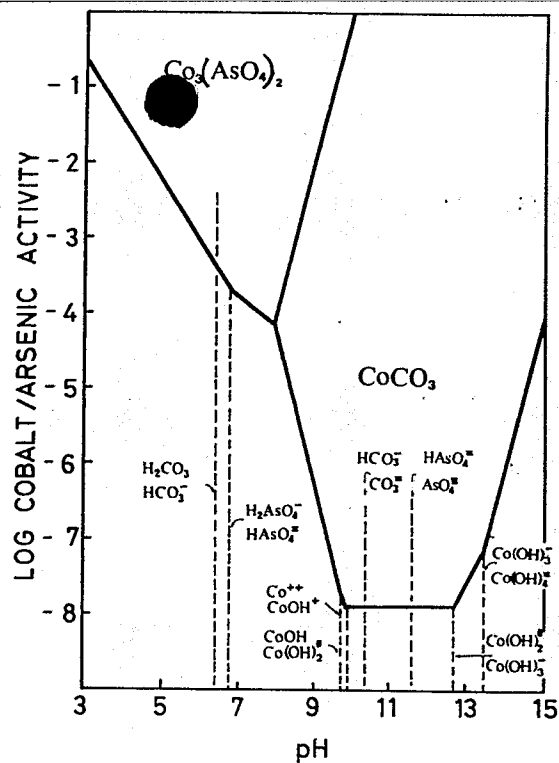


FIGURE 2 THE COBALT (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF COBALT AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

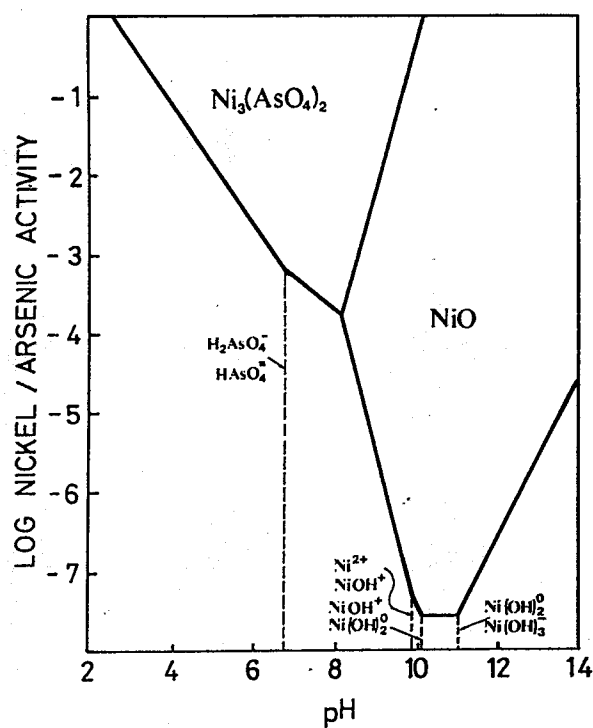


FIGURE 3 THE NICKEL (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF NICKEL AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

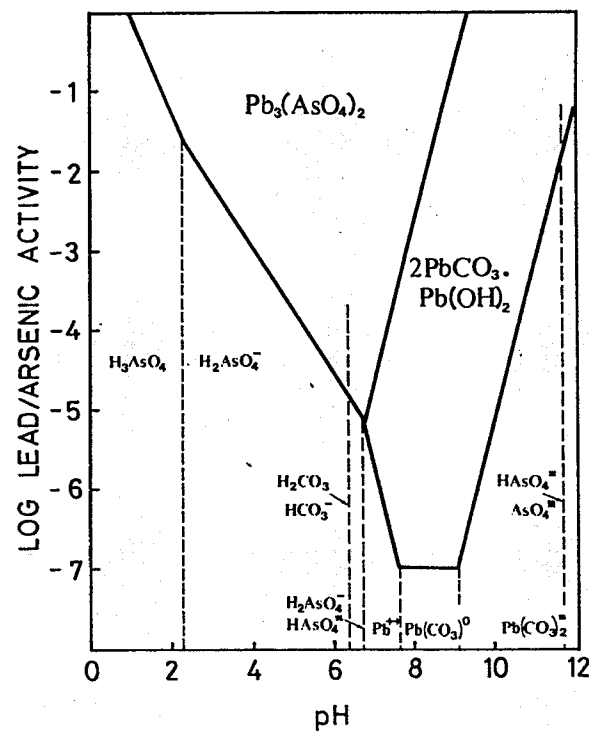


FIGURE 4 THE LEAD (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF LEAD AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

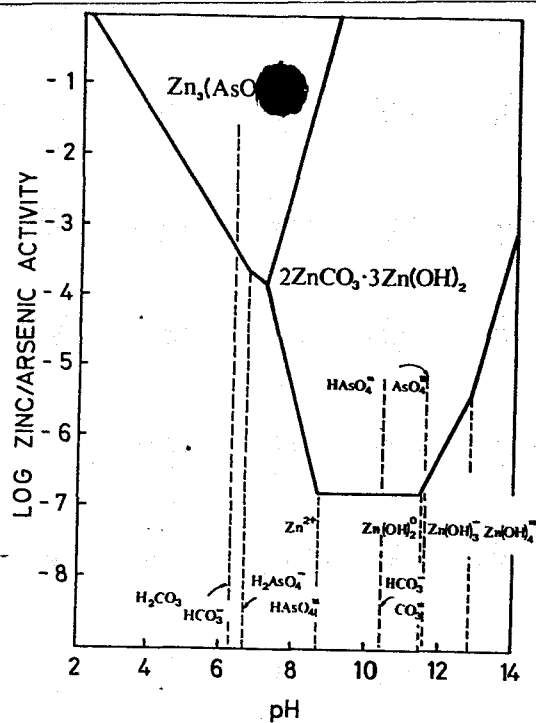


FIGURE 5 THE ZINC (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF ZINC AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

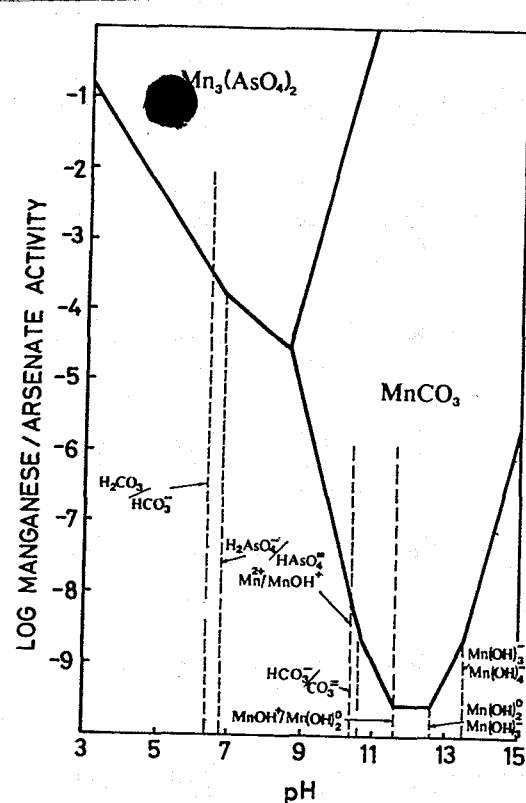


FIGURE 6 THE MANGANESE (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF MANGANESE AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

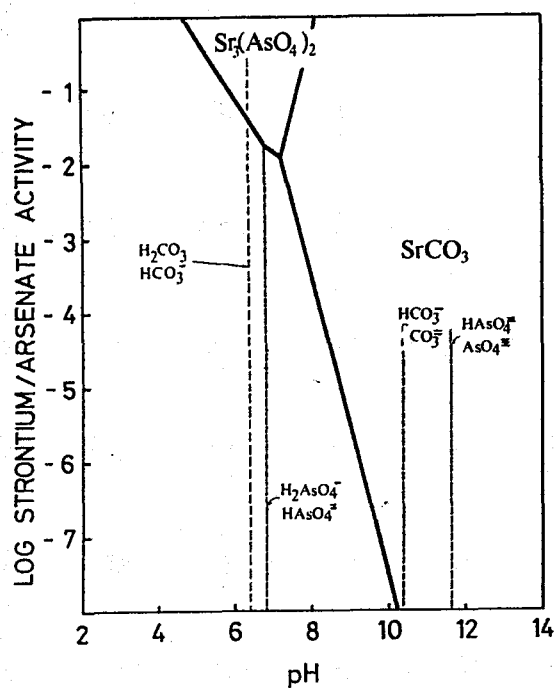


FIGURE 7 THE STRONTIUM (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF STRONTIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

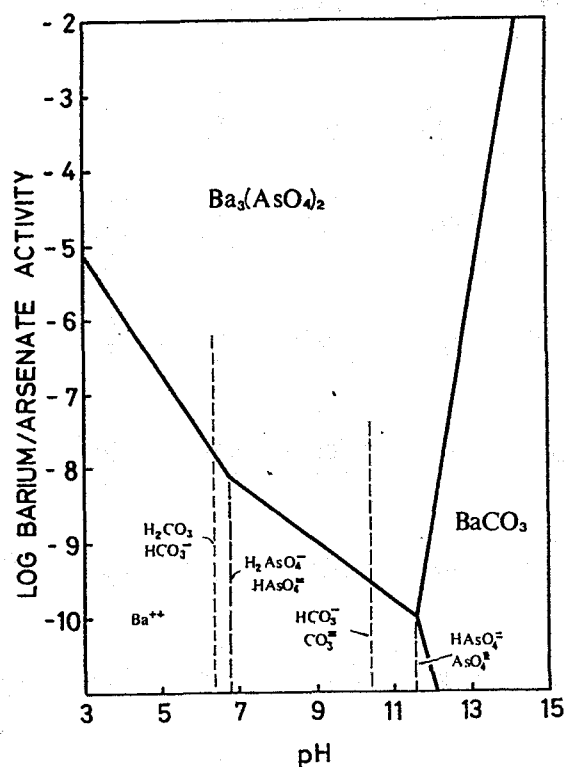


FIGURE 8 THE BARIUM (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF BARIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

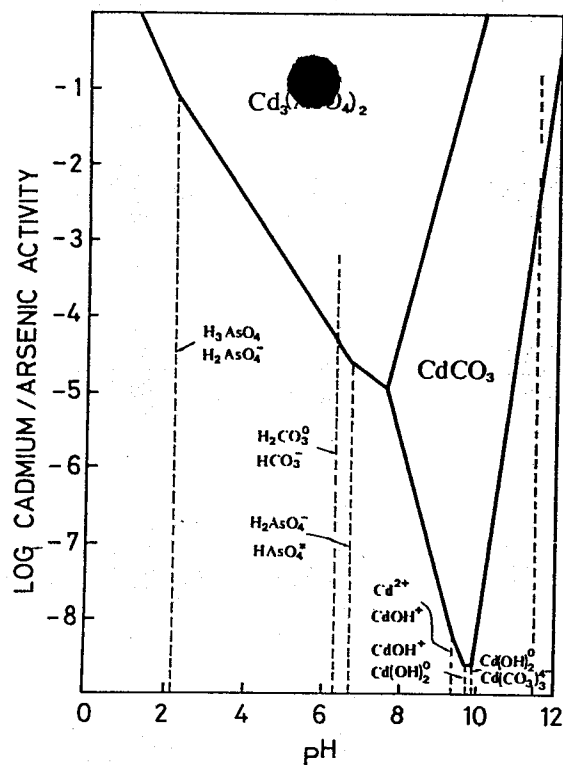


FIGURE 9 THE CADMIUM (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF CADMIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

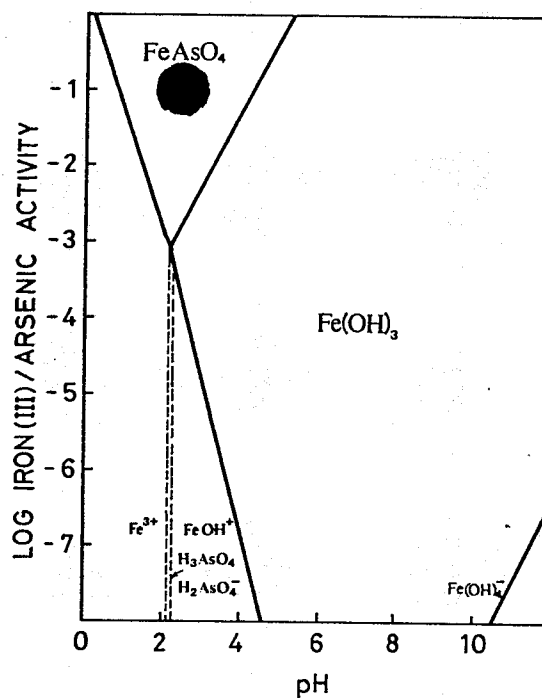


FIGURE 10 THE IRON (III) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF IRON AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

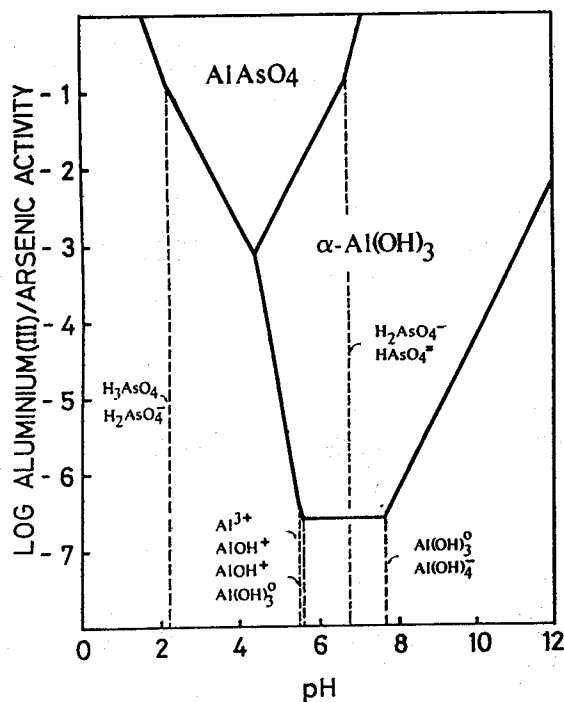


FIGURE 11 THE ALUMINIUM (III) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF ALUMINIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

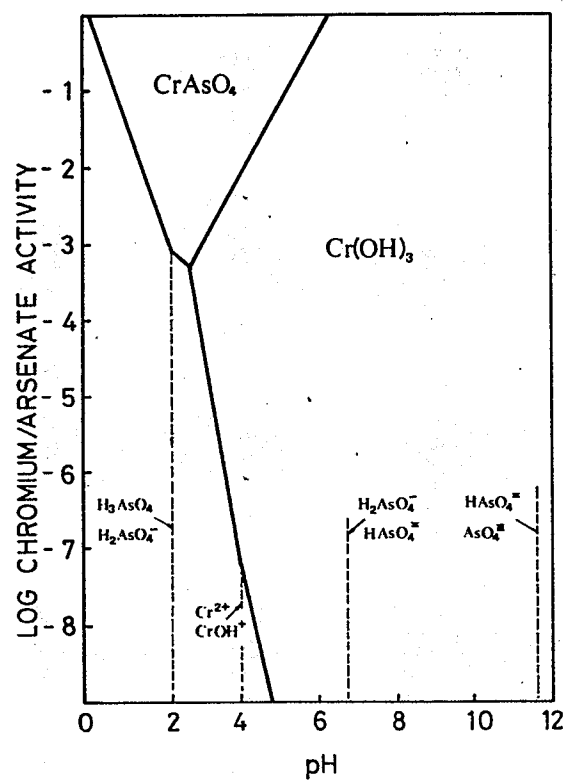


FIGURE 12 THE CHROMIUM (III) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF CHROMIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

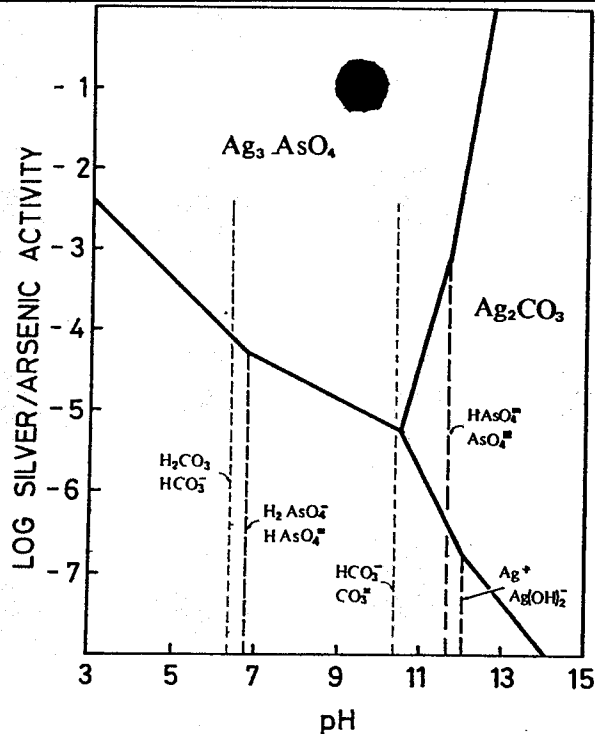


FIGURE 13 THE SILVER (I) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF SILVER AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

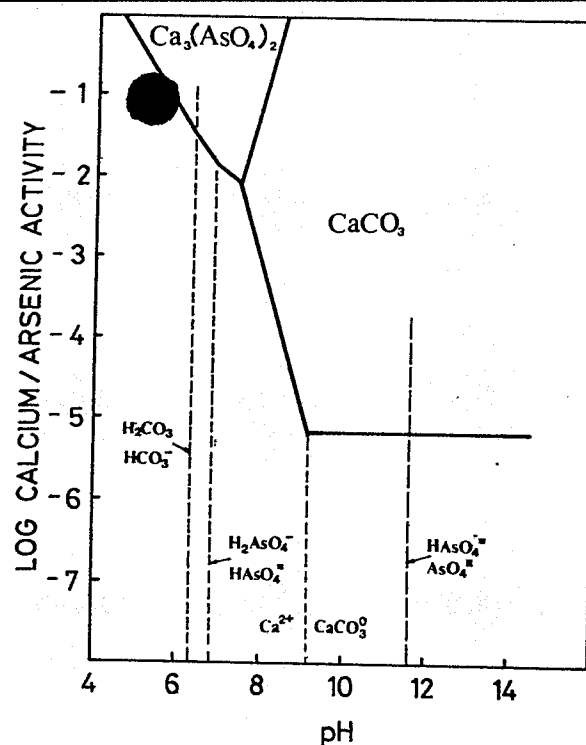


FIGURE 14 THE CALCIUM (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF CALCIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

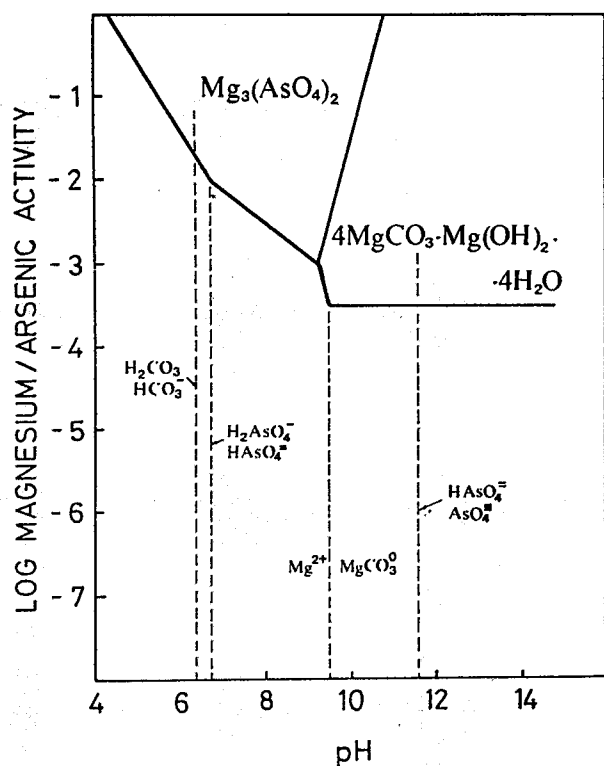


FIGURE 15 THE MAGNESIUM (II) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF MAGNESIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

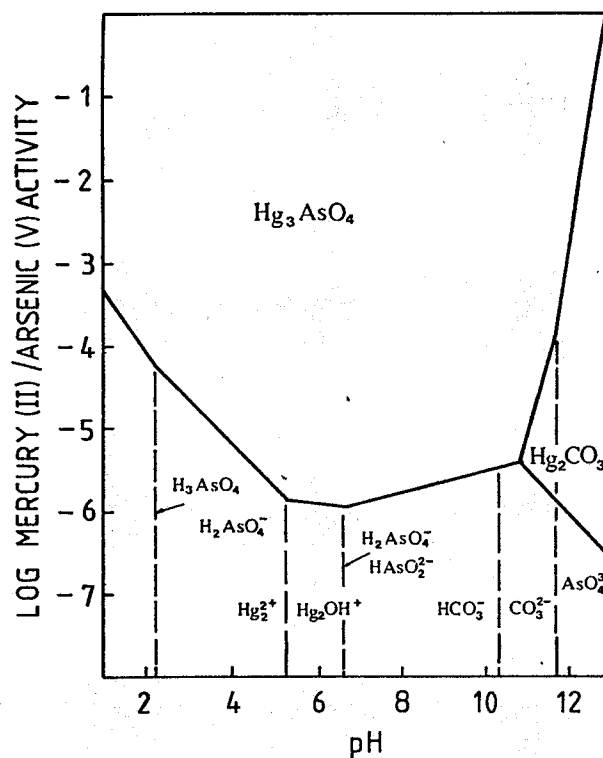


FIGURE 16 THE MERCURY (I) - ARSENIC (V) - WATER SYSTEM FOR EQUAL ACTIVITIES OF MERCURY AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

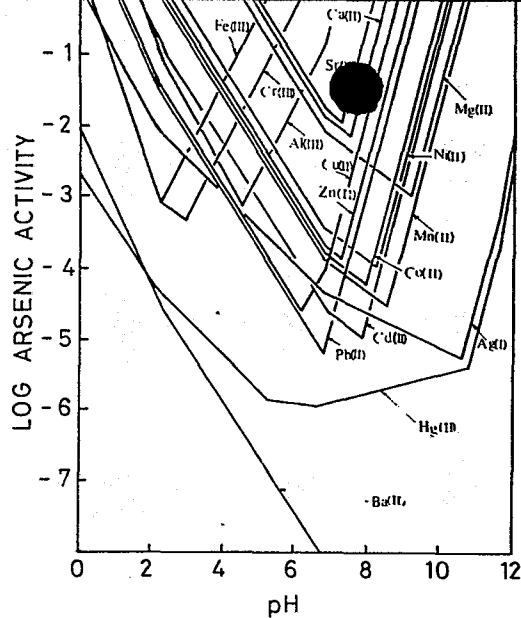


FIGURE 17 THE STABILITY REGIONS FOR THE VARIOUS METAL ARSENATES AT EQUAL ACTIVITIES OF METAL ION AND ARSENIC (V) AND FOR $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

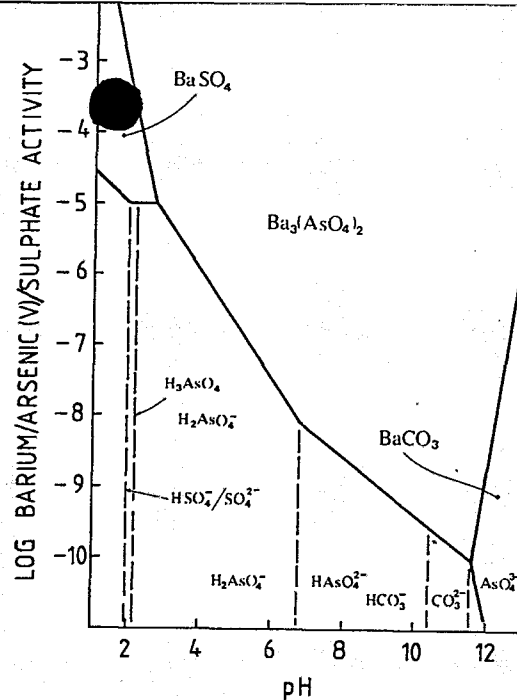


FIGURE 18 THE BARIUM (II) - ARSENIC (V) - SULFATE - WATER SYSTEM FOR EQUAL ACTIVITIES OF BARIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES AND SULPHATE ACTIVITY EQUAL TO THE SOLUBILITY OF BARIUM SULPHATE

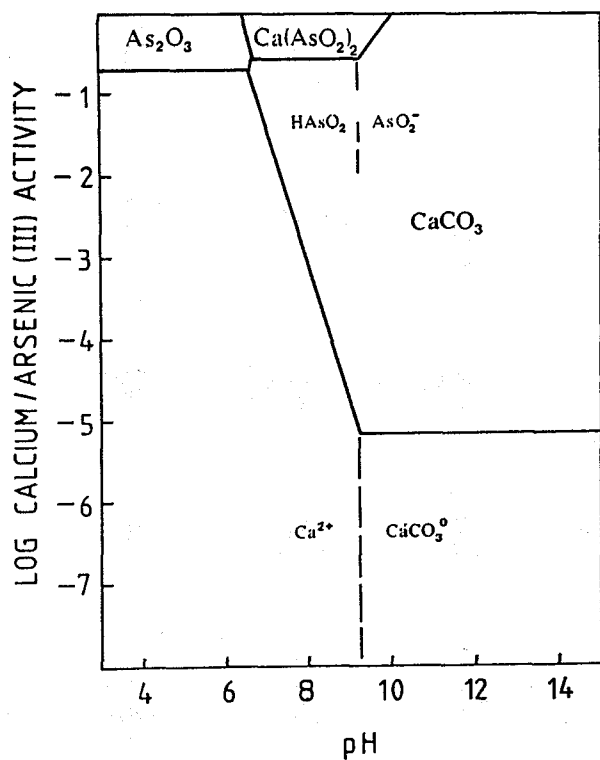


FIGURE 19 THE CALCIUM (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF CALCIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

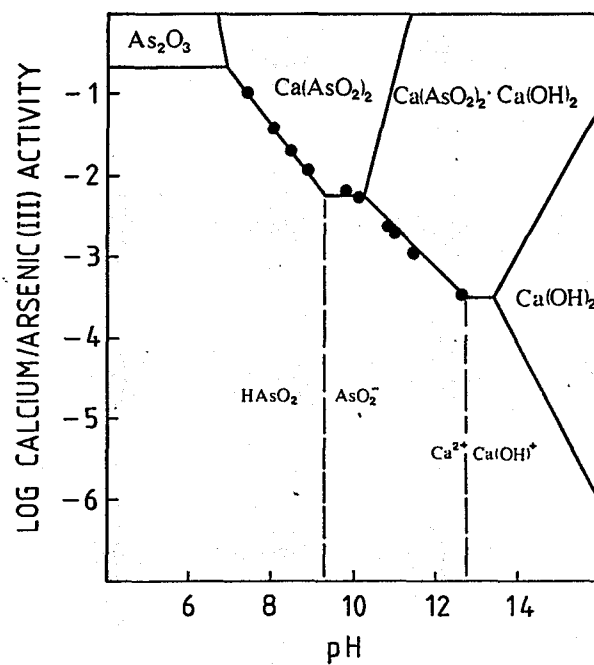


FIGURE 20 THE CALCIUM (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF CALCIUM AND ARSENIC AND IN THE ABSENCE OF CARBON DIOXIDE. EXPERIMENTAL POINTS FROM ROBINS AND NISHIMURA (6)

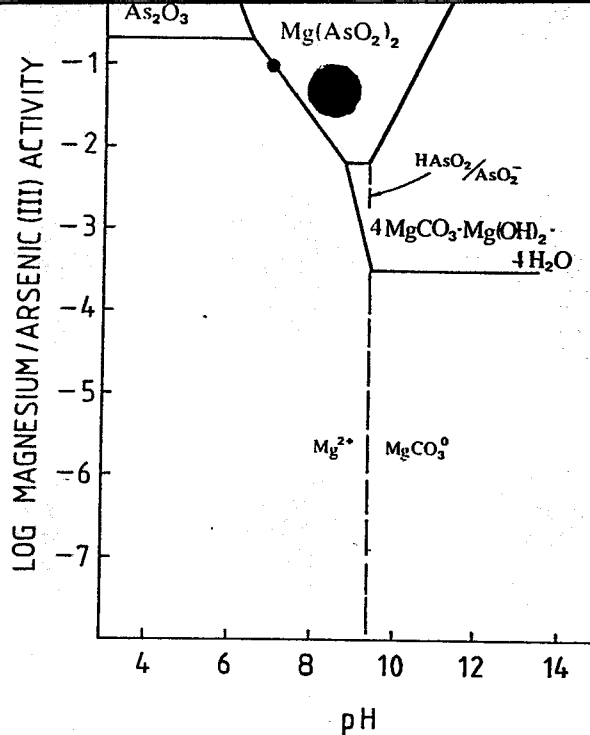


FIGURE 21 THE MAGNESIUM (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF MAGNESIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES. EXPERIMENTAL POINT FROM ROBINS AND NISHIMURA (6)

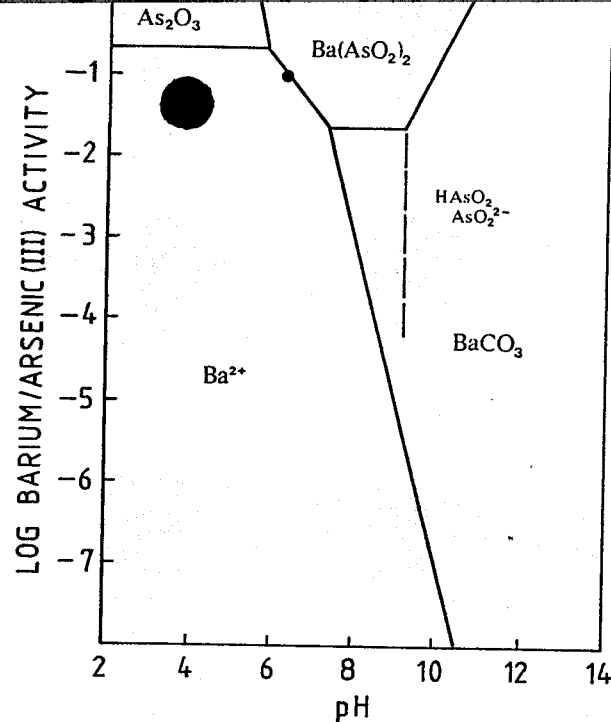


FIGURE 22 THE BARIUM (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF BARIUM AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES. EXPERIMENTAL POINT FROM ROBINS AND NISHIMURA (6)

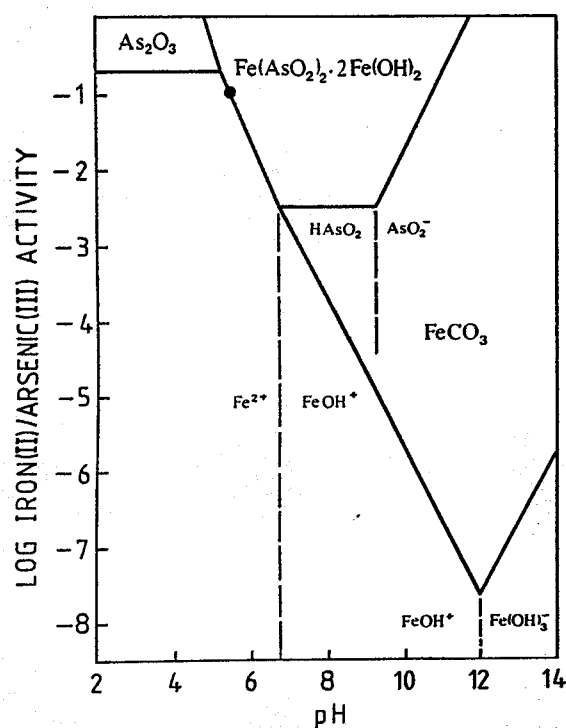


FIGURE 23 THE IRON (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF IRON AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES. EXPERIMENTAL POINT FROM ROBINS AND NISHIMURA (6)

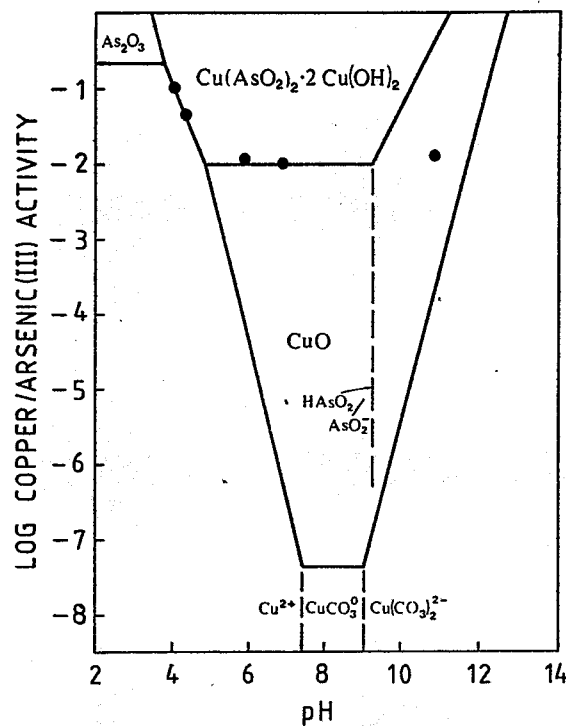


FIGURE 24 THE COPPER (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF COPPER AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES. EXPERIMENTAL POINTS FROM ROBINS AND NISHIMURA (6)

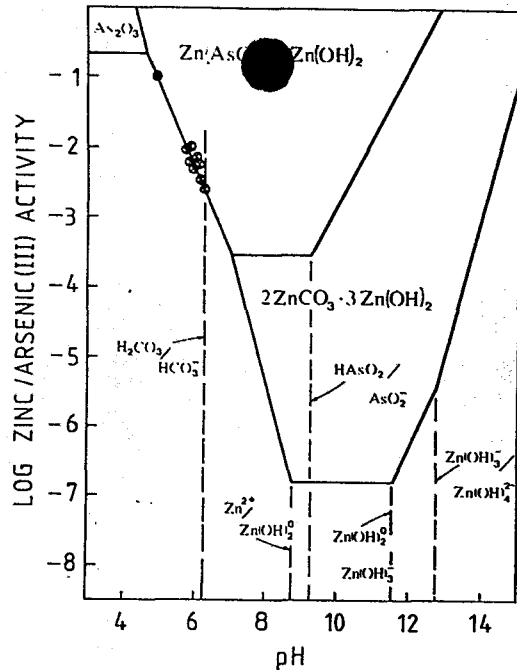


FIGURE 25 THE NICKEL (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF NICKEL AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES. EXPERIMENTAL POINTS FROM ROBINS AND NISHIMURA (6) AND CHUKHLANSEV (3)

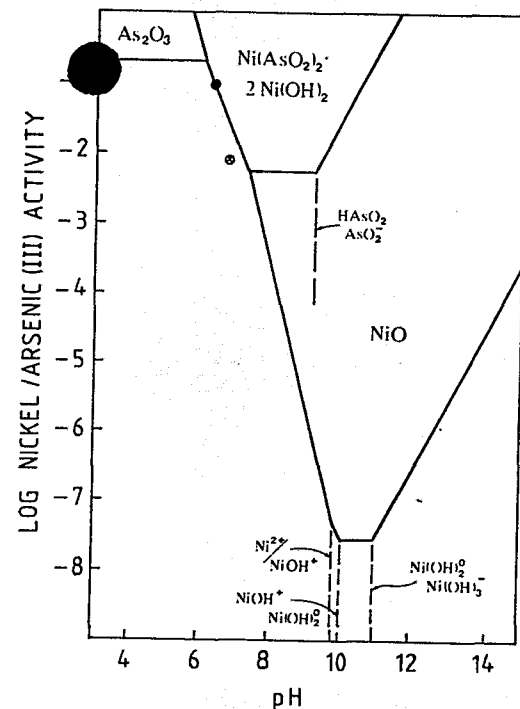


FIGURE 26 THE ZINC (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF ZINC AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES. EXPERIMENTAL POINTS FROM ROBINS AND NISHIMURA (6) AND CHUKHLANSEV (3)

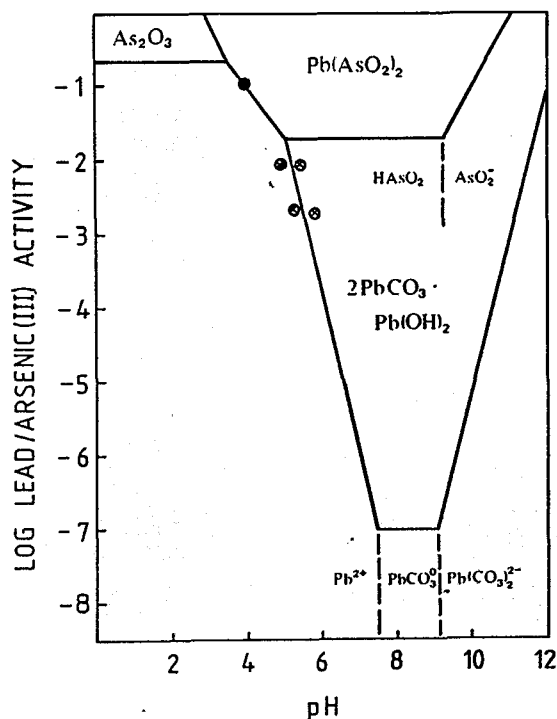


FIGURE 27 THE LEAD (II) - ARSENIC (III) - WATER SYSTEM FOR EQUAL ACTIVITIES OF LEAD AND ARSENIC AND $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES. EXPERIMENTAL POINTS FROM ROBINS AND NISHIMURA (6) AND CHUKHLANSEV (3)

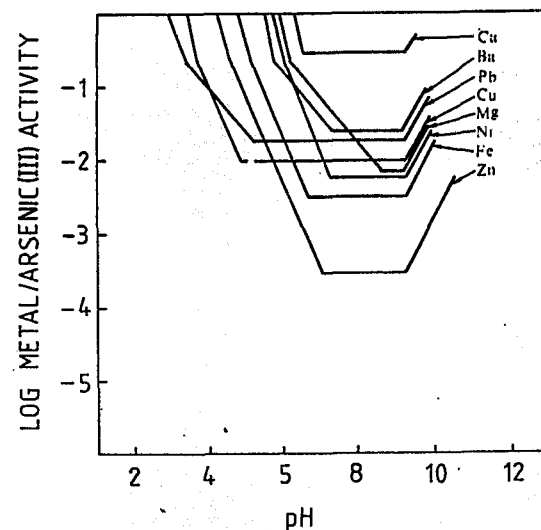


FIGURE 28 THE STABILITY REGIONS FOR THE VARIOUS METAL ARSENITES AT EQUAL ACTIVITIES OF METAL ION AND ARSENIC (III) AND FOR $P_{CO_2} = 10^{-3.47}$ ATMOSPHERES

literature probably does not exist. This diagram shows that at a pH of about 12 the solubility of the basic arsenate is > 20 mg/l.

Conclusions

The problem of stabilising arsenic is one which needs a great deal of further investigation at the fundamental level of determining solubilities of both arsenates and arsenites and also investigating the likely existence of complex arsenic compounds which may have good stability.

The diagrams which are presented in this paper can only be regarded as tentative, and apply only to the simple system represented without the complex chemical physical and biological factors which influence the behaviour of arsenic in the natural environment.

Acknowledgement

This work has received the cooperation and financial support of Mount Isa Mines Limited, Queensland, Australia, and Australian Mineral Industries Research Association Limited.

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