

# Speciation and Reduction Potentials of Metal Ions in Concentrated Chloride and Sulfate Solutions Relevant to Processing Base Metal Sulfides

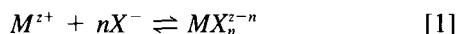
G. SENANAYAKE and D. M. MUIR

The speciation, Eh-pH and Eh-log  $a_{Cl^-}$  dependence of Fe(III), Fe(II), Cu(II), Cu(I), Ag(I), Pb(II), Zn(II), Ni(II), As(III), Sb(III), and Bi(III) ions in practical (high ionic strength) sulfate and chloride solutions are discussed. The emphasis is placed on those ions which form strong sulfato-, chloro-, and hydroxo-complex species. Measured potentials are compared with potentials calculated from reported association and stability constants to test the applicability of these constants in nonideal solutions and to characterize predominant species.

## I. INTRODUCTION

A knowledge of reduction potential (Eh) and speciation of a metal ion is essential in the understanding of hydro-metallurgical processes and in the equilibrium modeling of dump leach reactions.<sup>1-6</sup> Recently, species distribution diagrams for a number of base metal chloro-complexes have been reviewed<sup>1,7,8</sup> and Pourbaix diagrams have been extended to consider the Eh-pH and Eh-log  $a_{Cl^-}$  dependence and stability regions of a number of complexed and/or hydrolyzed metal ion species in chloride and sulfate media.<sup>2,4,5,9-11</sup> However, the reported association constants ( $K_n$ ) or stability constants ( $\beta_n$ ) used for the construction of these diagrams usually relate to ideal solutions with unit ionic activity coefficients ( $\gamma_i = 1$ ), or sometimes to solutions of particular ionic strength. Such values are questionable in solutions of high ionic strength where the ionic activities are far from ideality.<sup>1,2,6,7,12</sup> In a previous paper it was shown that ionic activities and reduction potentials can be reliably and rapidly estimated by emf measurements using appropriate cells and liquid-junction potential corrections ( $E_j$ ) for up to 6 M  $CaCl_2$  or  $MgCl_2$  solution or up to 4 M HCl.<sup>12</sup> Values of log  $\gamma_i$  for nonassociated ions rise rapidly in concentrated solutions according to the hydration number of the ion, due to a decrease in water activity ( $a_w$ ). Conversely, values of log  $\gamma_i$  for associated ions decrease rapidly according to the activity of the counter-ion and its association or stability constant.

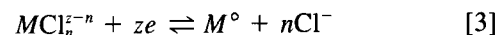
In general, the stability constant  $\beta_n$  for the formation of a complex ion  $MX_n^{z-n}$  (Eq. [1]) is related to the activity ratio of the species involved according to Eq. [2].



$$\beta_n(a) = \frac{a_{MX_n^{z-n}}}{a_{M^{z+}} \cdot a_{X^-}^n} \quad [2]$$

However, because activities are often not known, it is convenient to measure concentrations and report values of  $\beta_n(c)$  at a given ionic strength, or to extrapolate  $\beta_n(c)$  values to infinite dilution and report values of  $\beta_n^0$ , which is the true

thermodynamic stability constant. To allow for changes in activity in practical solutions, some authors have used  $\beta_n^0$  and calculated values of  $\gamma_i$  based upon the Debye-Hückel, Davies, Harned, or Pitzer empirical relationships,<sup>13,14</sup> but in concentrated solutions, no allowance has been made for the decrease in water activity  $a_w$ , and the hydration of the ions.<sup>15</sup> Except for the recently reported work by Majima and Awakura on water and solute activities of  $H_2SO_4$ - $Fe_2(SO_4)_3$ - $H_2O$  and  $HCl$ - $FeCl_3$ - $H_2O$  solution systems,<sup>16</sup> most researchers in fact ignore the hydration effects on the uncomplexed or complexed metal ions. Thus the accuracy of the calculated standard potential of the  $MCl_n^{z-n}/M^0$  couple according to Eqs. [3] and [4] is questionable.



$$E^0_h = E^0 - \frac{2.303 RT}{zF} (\log \beta_n^0 - n \log a_{Cl^-}) \quad [4]$$

where  $E^0$  represents the value in pure water.

This paper therefore compares the calculated and measured reduction potentials, in terms of the Eh-pH and Eh-log  $a_{Cl^-}$  relationships, in order to examine the nature of chloro- or sulfato-complex speciation, and the effect of changes in ionic activities on the validity of the stability or association constants used. The systems of interest in this work are the ions associated with the processing of base metal sulfides in concentrated chloride or sulfate solutions (*viz.*, Fe(III)/Fe(II), Cu(II)/Cu(I), Zn(II), Pb(II), Ni(II), Ag(I), As(III), Sb(III), and Bi(III)). In the case of As(III), Sb(III), and Bi(III), due regard is given to the formation of hydrolyzed species above pH 1.

## II. EXPERIMENTAL

Analytical grade reagents were used throughout. Stock solutions of Bi(III) and Sb(III) were prepared by the dissolution of  $Bi_2O_3$  and  $Sb_2O_3$  in dilute  $HClO_4$  and  $HCl$ , respectively, or by the dissolution of antimony potassium tartrate in dilute  $H_2SO_4$ . Unless otherwise stated, the test solutions were maintained at pH 0. Bismuth and antimony electrodes were freshly prepared by electroplating onto platinum foil in either acidic  $Bi(NO_3)_3$  or antimony potassium tartrate solutions.<sup>17</sup> The zinc and lead amalgam electrodes were prepared by stirring the cleaned metal with mercury under nitrogen atmosphere, until no unreacted

G. SENANAYAKE, formerly Postgraduate Student, Murdoch University, Perth, Western Australia, is Lecturer, University of Sri Jayewardenepura, Nugegoda, Sri Lanka. D. M. MUIR is Associate Professor in Mineral Chemistry, Murdoch University, Perth, Western Australia 6150. Manuscript submitted January 12, 1987.

metal remained; the metal surface was cleaned by immersion in dilute nitric acid and careful washing with distilled water. In sulfate solutions, a bismuth amalgam electrode was used which was prepared by dissolution of the pure bismuth in mercury or by electrolysis. Test solutions of Fe(III) and Fe(II) in 1 M Na<sub>2</sub>SO<sub>4</sub> were freshly prepared from their respective ammonium iron sulfate salts.

Emf and pH measurements were carried out on deoxygenated test solutions under argon using a Radiometer pHM 26 pH/mV meter and a saturated calomel reference electrode. Measurements were made at 298 ± 0.2 K, and were stable and reproducible to within 1 mV. They were corrected for liquid-junction potentials using the Henderson equation.<sup>12</sup> The value of *E<sub>j</sub>* at the sat. KCl:1 M Na<sub>2</sub>SO<sub>4</sub> junction was estimated as -5 mV, assuming no bisulfate ion formation.

### III. RESULTS AND DISCUSSION

#### A. Sulfate Solutions

Sulfate ion forms weak outer-sphere ion-pairs with most transition metals leading to a significant decrease in the activity of the metal ion in practical sulfate solutions, but relatively small changes in Eh (≅ 30 mV). Typically the association constant, log *K*, for divalent metals, like Cu<sup>2+</sup>, is about 0.6,<sup>18</sup> and the predominant species in solution are neutral M · SO<sub>4</sub> ion-pairs.<sup>19</sup> Sulfate association is particularly strong with the trivalent Fe<sup>3+</sup> ion and to a lesser extent with the proton (Table I), but is much weaker with monovalent ions like Ag<sup>+</sup> and Cu<sup>+</sup>. With many trivalent ions, hydrolysis competes with complexation. The hydrolysis of As(III), Sb(III), Bi(III), and Fe(III) leads to the formation of a range of hydroxo-complexes with varying stability (Table I). While the sulfate association of Fe(III) is much stronger than its water association, this is not the case with Sb(III) and Bi(III), which predominantly exist as hydrolyzed MO<sup>+</sup> species.

Table I also highlights the effect of an increase in ionic strength from *I* = 0 to *I* = 1. It can be seen that the stability constant of Fe(SO<sub>4</sub>)<sub>2</sub><sup>-</sup> exhibits a 1000-fold increase upon increasing the ionic strength, while the stability constants of FeSO<sub>4</sub><sup>+</sup> and FeSO<sub>4</sub><sup>0</sup> show a 100- and 10-fold decrease, respectively. These changes largely correspond to the variation in γ<sub>*i*</sub> of the three differently charged species. However, because of the limited solubility of background sulfate salts, it would not be expected that sulfate solutions would exhibit significant changes in ionic activities caused by changes in water activity and hydration effects. This study therefore focuses on the predicted and measured potentials of the Fe(III)/Fe(II), Sb(III)/Sb(0), and Bi(III)/Bi(0) couples in sulfate media to examine the predominant speciation.

#### (a) Fe(III)-Fe(II)-SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O

Figure 1 shows the distribution diagram for 0.1 M Fe(III) and Fe(II) species in 1 M total sulfate solution calculated from recent literature values of association and hydrolysis constants [Table I]. Previously published distribution diagrams<sup>19</sup> and Pourbaix diagrams<sup>2,4</sup> considered lower total sulfate concentrations and less reliable constants. These diagrams underestimate the formation of Fe(SO<sub>4</sub>)<sub>2</sub><sup>-</sup> and FeHSO<sub>4</sub><sup>+</sup> species which appear to predominate at pH 2 and pH < 0, respectively, in more concentrated sulfate solution. As shown by Figure 1, the predicted speciation is sensitive to pH, but, of course, is dependent on the ratio of SO<sub>4</sub><sup>2-</sup>:Fe and the accuracy of the constants used.

If Fe(SO<sub>4</sub>)<sub>2</sub><sup>-</sup> and FeSO<sub>4</sub> are the predominant species between pH 0.5 and 2.5 (Figure 1), then the predicted Eh of the Fe(III)/Fe(II) couple can be related to the concentration of SO<sub>4</sub><sup>2-</sup> in solution by Eq. [5], and hence to pH through Eq. [6].

$$Eh = E^{\circ} - \frac{2.303 RT}{F} \left( \log \frac{\beta_2(c)}{K_1(c)} - \log[\text{SO}_4^{2-}] \right) \quad [5]$$

Table I. Equilibrium Constants for the Sulfate Association and Hydrolysis of H<sup>+</sup>, Fe(III), Bi(III), Sb(III), and As(III) at 25 °C<sup>a</sup>

Equilibrium	log <i>K</i> ( <i>I</i> = 0)	log <i>K</i> ( <i>I</i> = 1)
H <sup>+</sup> + SO <sub>4</sub> <sup>2-</sup> ⇌ HSO <sub>4</sub> <sup>-</sup>	1.99	1.07
Ag <sup>+</sup> + SO <sub>4</sub> <sup>2-</sup> ⇌ AgSO <sub>4</sub> <sup>-</sup>	—	0.23 <sup>b</sup>
Fe <sup>3+</sup> + SO <sub>4</sub> <sup>2-</sup> ⇌ FeSO <sub>4</sub> <sup>+</sup>	4.04	2.33 <sup>c</sup>
Fe <sup>3+</sup> + 2SO <sub>4</sub> <sup>2-</sup> ⇌ Fe(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	1.34	4.23 <sup>c</sup>
Fe <sup>3+</sup> + HSO <sub>4</sub> <sup>-</sup> ⇌ FeHSO <sub>4</sub> <sup>2+</sup>	—	0.78 <sup>c</sup>
Fe <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup> ⇌ FeSO <sub>4</sub> <sup>0</sup>	2.3	1.00 <sup>d</sup>
Fe <sup>3+</sup> + H <sub>2</sub> O ⇌ FeOH <sup>2+</sup> + H <sup>+</sup>	—	-2.69
Fe <sup>3+</sup> + 2H <sub>2</sub> O ⇌ Fe(OH) <sub>2</sub> <sup>+</sup> + 2H <sup>+</sup>	—	-5.67
2Fe <sup>3+</sup> + 2H <sub>2</sub> O ⇌ Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup> + 2H <sup>+</sup>	—	-2.72
Bi <sup>3+</sup> + H <sub>2</sub> O ⇌ BiOH <sup>2+</sup> + H <sup>+</sup>	-1.09 <sup>e</sup>	-1.55 <sup>f</sup>
Bi <sup>3+</sup> + 2H <sub>2</sub> O ⇌ Bi(OH) <sub>2</sub> <sup>+</sup> + 2H <sup>+</sup>	-4.00 <sup>e</sup>	-4.37 <sup>f</sup>
SbO <sup>+</sup> + H <sub>2</sub> O ⇌ HSbO <sub>2</sub> + H <sup>+</sup>	-0.87 <sup>g</sup>	—
AsO <sup>+</sup> + H <sub>2</sub> O ⇌ HAsO <sub>2</sub> + H <sup>+</sup>	-0.34 <sup>g</sup>	—

(a) Reference 18(a) unless stated otherwise

(b) *I* = 3

(c) *I* = 1.2

(d) Reference [18(b)]

(e) Reference [20]

(f) Reference [21]

(g) Pourbaix Atlas (1963)

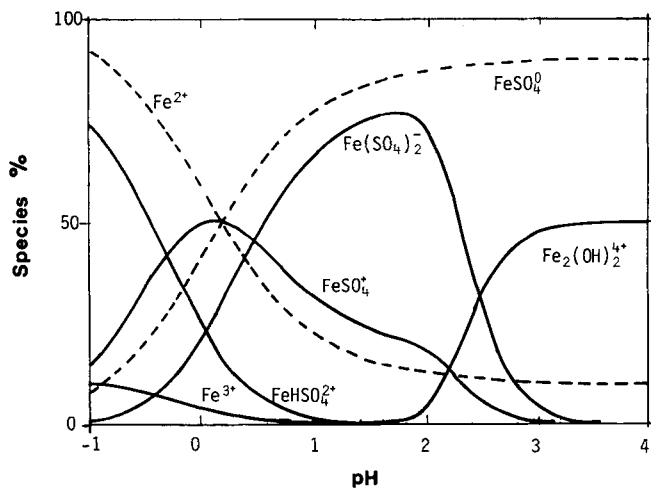


Fig. 1—Effect of pH on species distribution of Fe(III) and Fe(II) in sulfate solution at 25 °C. Conditions: total  $\text{SO}_4^{2-} = 1 \text{ M}$ ;  $\text{Fe(III)} = \text{Fe(II)} = 0.1 \text{ M}$ ; constants from Table I.

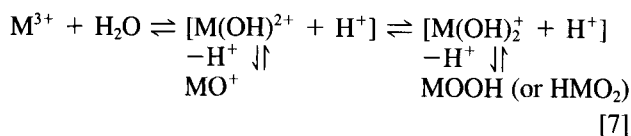
$$\log \frac{(x - [\text{SO}_4^{2-}])}{[\text{SO}_4^{2-}]} = pK_a - \text{pH} \quad [6]$$

where  $\beta_2(c)$  and  $K_1(c)$  are the stability and association constants for  $\text{Fe}(\text{SO}_4)_2^-$  and  $\text{FeSO}_4$  formation,  $pK_a$  is the acidity constant for  $\text{HSO}_4^-$ , and  $x$  is the total sulfate + bisulfate concentration in solution.

Figure 2 compares the calculated and measured Eh-pH relationship for the Fe(III)/Fe(II) couple between pH 0 and 3 at equimolar 0.01 M and 0.1 M ionic concentrations in 1 M  $\text{Na}_2\text{SO}_4$  solution. Superimposed on the abscissa is the corresponding change in  $[\text{SO}_4^{2-}]$  with pH (Eq. [6]). Clearly the measured potentials are far from ideality ( $E^\circ h = 770 \text{ mV}$ ), but in fact agree quite closely with those predicted assuming the predominance of  $\text{Fe}(\text{SO}_4)_2^-$ , and the complete dissociation of the  $\text{Na}_2\text{SO}_4$  background electrolyte. The measured Eh decreases with pH with a slope of 21 mV/pH which corresponds to a Nernstian slope of 59 mV/ $\log [\text{SO}_4^{2-}]$  at 298 K when the variation of  $[\text{SO}_4^{2-}]$  with pH is considered. The deviation of 10 to 20 mV between the predicted and measured values, shown in Figure 2, is believed to arise from the partial association of  $\text{Na}_2\text{SO}_4$  and lower activity of  $\text{SO}_4^{2-}$  in real solutions. Thus the potential measurements are in accord with the speciation presented in Figure 1 and changes in the activity of  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  in 1 M  $\text{Na}_2\text{SO}_4$  solution due to ionic strength are small relative to changes due to ion-pairing or association.

#### (b) As(III)-Sb(III)-Bi(III)- $\text{SO}_4^{2-}$ - $\text{H}_2\text{O}$

Hydrolysis of these ions in water leads to a range of species according to the pH (Eq. [7]). For comparison with later figures, the ideal species distribution, based on the hydrolysis constants in Table I, is depicted in Figure 3.



The ease of hydrolysis of M(III), and hence the predominance of  $\text{HMO}_2$  species, follows the order  $\text{As(III)} >$

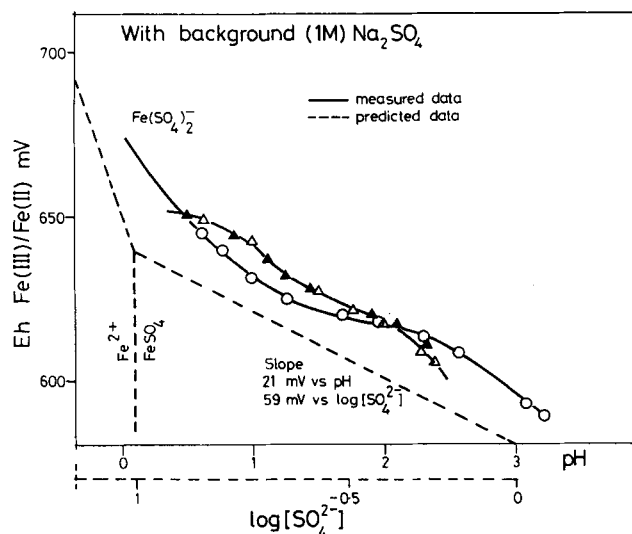


Fig. 2—Eh-pH relationship of Fe(III)-Fe(II)- $\text{SO}_4^{2-}$  system at 25 °C. Comparison of measured and predicted values. Key: broken lines: predicted; full lines: measured.  $\circ$  Fe(III) = Fe(II) = 0.01 M;  $\triangle$  Fe(III) = Fe(II) = 0.1 M.

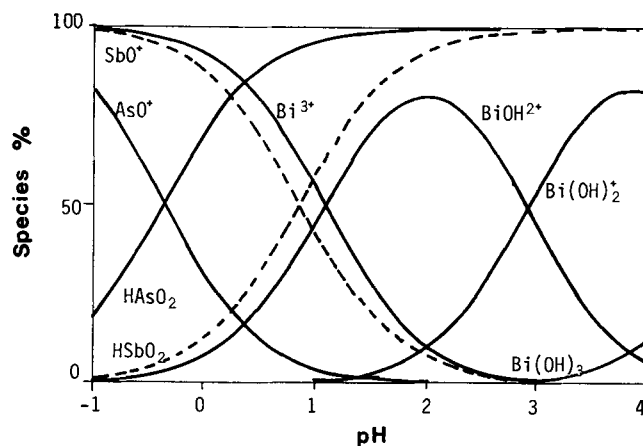


Fig. 3—Effect of pH on species distribution of As(III), Sb(III) and Bi(III) in water at 25 °C. Conditions:  $\text{As(III)} = \text{Sb(III)} = \text{Bi(III)} = 10^{-4} \text{ M}$  using noncomplexing perchlorate media and hydrolysis constants in Table I.

$\text{Sb(III)} > \text{Bi(III)}$ .<sup>23</sup> Conversely, the pH required to produce the unhydrolyzed  $\text{M}^{3+}$  ion is lowest for As(III) and highest for Bi(III). The Eh vs pH dependence of these systems is predicted to be 20 mV/pH, 39 mV/pH, or 59 mV/pH, according to whether the  $\text{M}(\text{OH})^{2+}$ ,  $\text{MO}^+$ , or  $\text{HMO}_2$  species predominate (Eqs. [8] through [10]) and assuming no ion-pairing or complexation.

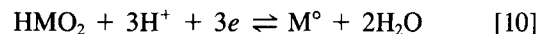
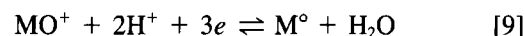
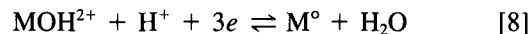


Figure 4 shows the calculated Eh-pH relationships and regions of predominance of these species. However, in practical sulfate solutions of moderate ionic strength and  $0 < \text{pH} < 3$ , it is difficult to predict the species precisely, due to possible sulfate association or changes in the activity of  $\text{M}^{3+}$  or  $\text{SO}_4^{2-}$ .

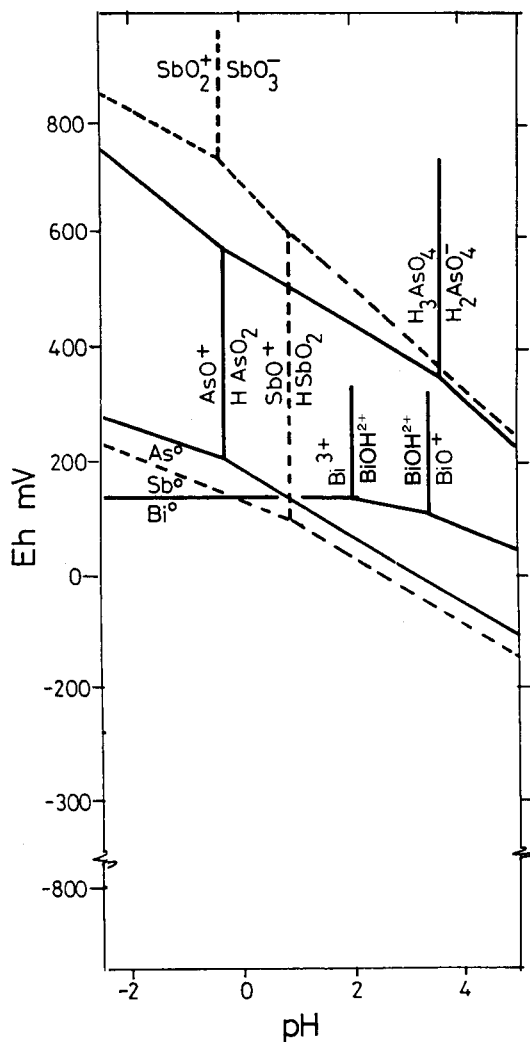


Fig. 4—Calculated Eh-pH relationships for As(III)-Sb(III)-Bi(III) in non-complexing perchlorate media at 25 °C (unit activity species).

The measured Eh-pH relationships for the reduction of Sb(III) and Bi(III) in  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  solutions between pH 0 and 4 are shown in Figures 5 and 6. Superimposed on the figures are the predicted Eh values of Sb(III) and Bi(III) in the presence of 1 M  $\text{NaClO}_4$  as background salt. The Eh-pH dependence clearly indicates that for most hydrometallurgical solutions in this pH range, the predominant M(III) species are  $\text{Bi}(\text{OH})_2^+$  and  $\text{HSbO}_2$  (or  $\text{SbOOH}$ ). Although no potential measurements were made on the As(III)/As(0) system, it can be predicted that  $\text{HAsO}_2$  is the predominant species in the range pH 0 to 4.<sup>4,23</sup> Accordingly, except for Bi(III) in the presence of  $\text{NaCl}$ , it makes little difference to the Eh whether the background salt is sulfate, perchlorate, or chloride.

The independence of the reduction potential of Bi(III) with pH in the presence of  $\text{NaCl}$ , reflects the strong complexation with  $\text{Cl}^-$  and the predominance of the  $\text{BiCl}_5^{3-}$  species, as discussed below. Much higher concentrations of  $\text{Cl}^-$  are required for the  $\text{SbCl}_4^-$  species to predominate in this pH range.

## B. Chloride Solutions

Moderate or strong chloro-complexation is exhibited by the precious metals, Group IB and IIB metals, and certain transition and other metals in the Periodic Table. Of significance to the processing of base metal sulfides, are the strong complexes formed by Cu(I), Ag(I), Zn(II), Pb(II), Fe(III), Sb(III), and Bi(III), and the weak, or lack of, complexation exhibited by Cu(II), Fe(II), and Ni(II) (Table II). Because of the high solubility of many chloride salts, not only is complexation more prevalent, but the activity of water may drop significantly, leading to large increases in the activity of the proton and divalent metal ions in particular.

### (a) As(III)-Sb(III)-Bi(III)- $\text{Cl}^-$ - $\text{H}_2\text{O}$

In concentrated chloride solutions at pH < 1, both Sb(III) and Bi(III) predominate as chloro-complexes, but As(III) is still extensively hydrolyzed and forms basic chlorides of the type  $\text{As}(\text{OH})_x\text{Cl}_y$  with low association constants (Table II). Figure 7 shows the predicted species distribution of Sb(III) and Bi(III), which indicates the predominance of  $\text{SbCl}_5^{2-}$ ,  $\text{SbCl}_6^{3-}$ , and  $\text{BiCl}_6^{3-}$  in chloride solutions of hydrometallurgical interest. The  $E^\circ h$ -log  $a_{\text{Cl}^-}$  and Eh-pH relationships for the As(III) and Bi(III)- $\text{Cl}^-$ - $\text{H}_2\text{O}$  systems based on the published values of  $\beta_n$  (Table II) are shown in Figure 8. Unlike Bi(III), the chloro-complexation of As(III) is favorable only at low pH and high  $a_{\text{Cl}^-}$ .

The problem lies in predicting or identifying the exact chloro-complex species and  $E^\circ h$  in concentrated chloride solutions, such as used for processing complex sulfides. The exact  $E^\circ h$  may be critical in electrolyte purification steps involving cementation onto copper.<sup>4</sup>

Measured values of  $E^\circ h$  Sb(III) and Bi(III) in practical  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$  solutions ranging in concentration from 0.1 to 10 M  $\text{Cl}^-$  are presented in Figure 9. While there is reasonable agreement between the predicted and measured potentials for Sb(III), there appears to be a systematic discrepancy of almost 100 mV with the Bi(III) data. However, the dependence of  $E^\circ h$  on log  $a_{\text{Cl}^-}$  indicates that in these practical solutions, the predominant species are  $\text{SbCl}_4^-$  and  $\text{BiCl}_5^{2-}$  rather than  $\text{SbCl}_5^{2-}$ ,  $\text{SbCl}_6^{3-}$ , and  $\text{BiCl}_6^{3-}$  indicated by the species distribution diagrams (Figure 7). The indicated speciation of As(III) shown in Figure 8 is supported by the measured solubility of  $\text{As}_2\text{O}_3$  in water. The solubility of  $\text{As}_2\text{O}_3$  as the  $\text{HAsO}_2$  species is unaffected by  $\text{HCl}$  up to 4 M, but increases rapidly beyond 4 M  $\text{HCl}$  (pH -1),<sup>22</sup> due to chloro-hydroxo-complexation, as indicated in Figure 8(b).

### (b) Fe(III)/Fe(II), Cu(II), Cu(I), Ag(I), Pb(II), Zn(II), and Ni(II) in $\text{Cl}^-$ - $\text{H}_2\text{O}$

The predicted  $E^\circ h$ -log  $a_{\text{Cl}^-}$  relationships and speciation of the above transition-metal ions (derived from reported  $\beta_n^\circ$  values in Table II) are compared in Figures 10 and 11 with measured values of  $E^\circ h$  made in various practical solutions of  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$  containing up to 10 M  $\text{Cl}^-$ , at pH 0. In these acidic solutions, hydrolyzed species of Fe(III) such as  $\text{FeOH}^{2+}$  are neglected, as well as polynuclear copper complexes such as  $\text{Cu}_2\text{Cl}_4^{2-}$  which have been reported to exist only in very small proportions.<sup>8,29,30</sup>

In general, there is good agreement with the predicted and measured Eh of the Fe(III)/Fe(II), Cu(II)/Cu(0), Pb(II)/Pb(0), Zn(II)/Zn(0), and Ni(II)/Ni(0) couples in

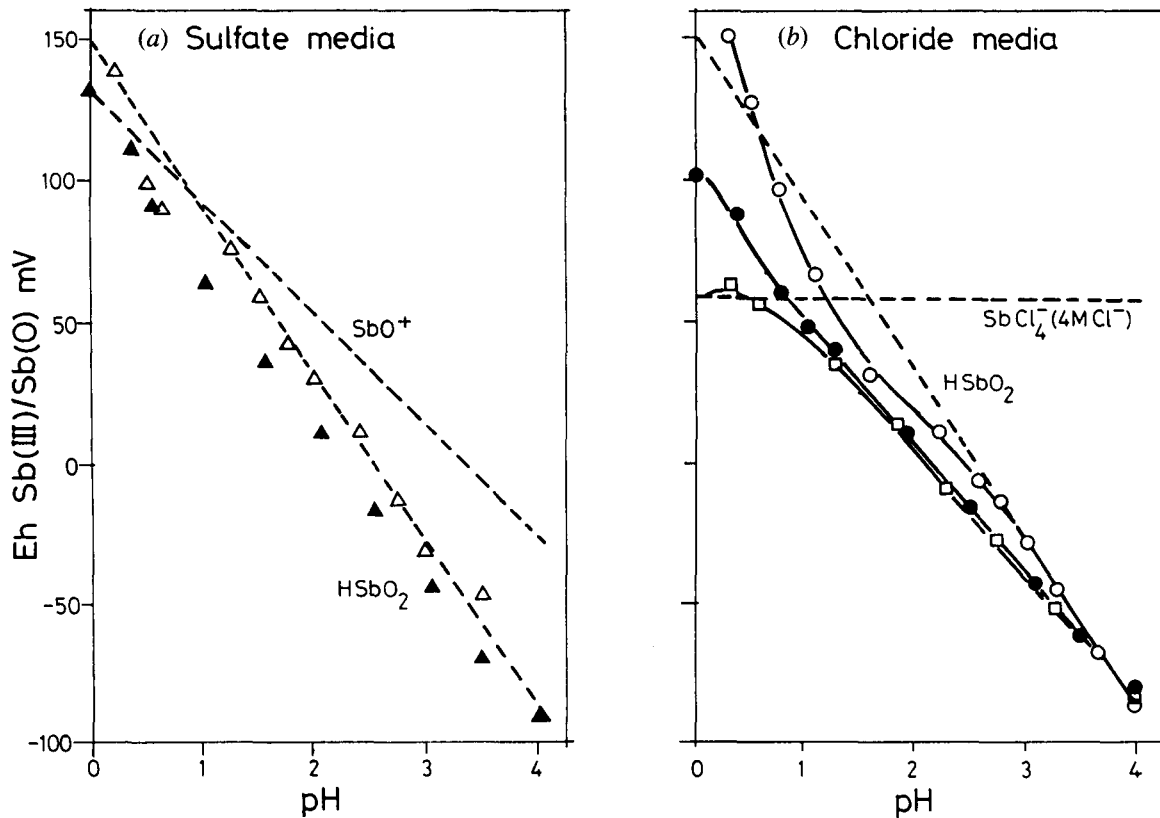


Fig. 5—Eh-pH relationships of Sb(III) in chloride and sulfate media at 25°C. Conditions: Sb(III) = 10<sup>-4</sup> M; broken lines: calculated values using Nernst equation and assuming unit activity of species in noncomplexing (perchlorate) media. Key:  $\Delta$  0.1 M Na<sub>2</sub>SO<sub>4</sub>;  $\blacktriangle$  1 M Na<sub>2</sub>SO<sub>4</sub>;  $\circ$  0.1 M NaCl;  $\bullet$  1 M NaCl;  $\square$  4 M NaCl.

solutions containing up to 3 M Cl<sup>-</sup>, but significant differences (> 50 mV) are observed in more concentrated chloride solutions. There are particular discrepancies with the values of Cu(II)/Cu(I), Cu(I)/Cu(0), and Ag(I)/Ag(0) couples in all the solutions tested. These differences relate to the hydration effects and the nonideal behavior of complex species, since the ideal values of  $\gamma_i = 1$  are assumed in Eq. [4].

As recently discussed by Skou *et al.*,<sup>15</sup> the stability constants of chloro-complexes in high ionic strength solutions are better represented by Eq. [12], which makes allowance for the hydration effects on all the ions involved in the complexation equilibrium (Eq. [11]). By combining Eq. [12] with Bjerrum's hydration treatment,<sup>12,31</sup> the changes in  $E^\circ$  from its ideal value in pure water ( $\Delta E^\circ$ ) may be represented by Eqs. [13] and [14].

Table II. Stability Constants of Chloro-Complexes at Zero Ionic Strength (25 °C)

Equilibrium	log $\beta_n^\circ$				Reference
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	
$\text{Fe}^{3+} + n\text{Cl}^- \rightleftharpoons \text{FeCl}_n^{3-n}$	1.48	2.13	-0.01		18
$\text{Fe}^{2+} + n\text{Cl}^- \rightleftharpoons \text{FeCl}_n^{2-n}$	0.35	0.40			24 <sup>a</sup>
$\text{Cu}^{2+} + n\text{Cl}^- \rightleftharpoons \text{CuCl}_n^{2-n}$	0.21	-0.40			25
$\text{Cu}^+ + n\text{Cl}^- \rightleftharpoons \text{CuCl}_n^{1-n}$	3.50	5.48	4.80	10.30 <sup>d</sup>	26
$\text{Ag}^+ + n\text{Cl}^- \rightleftharpoons \text{AgCl}_n^{1-n}$	3.22	5.04	5.04	5.30	27
$\text{Pb}^{2+} + n\text{Cl}^- \rightleftharpoons \text{PbCl}_n^{2-n}$	1.60	1.78	1.68	1.38	28
$\text{Zn}^{2+} + n\text{Cl}^- \rightleftharpoons \text{ZnCl}_n^{2-n}$	0.43	0.61	0.53	0.20	18
$\text{Bi}^{3+} + n\text{Cl}^- \rightleftharpoons \text{BiCl}_n^{3-n}$	2.09	3.90	5.40	6.87	18 <sup>b</sup>
$\text{Sb}^{3+} + n\text{Cl}^- \rightleftharpoons \text{SbCl}_n^{3-n}$	2.26	3.49	4.18	4.72	18 <sup>c</sup>
$\text{As}(\text{OH})_3 + n\text{H}^+ + n\text{Cl}^- \rightleftharpoons \text{As}(\text{OH})_{3-n}\text{Cl}_n + \text{H}_2\text{O}$	-1.07	-4.54	-8.74		18

(a)  $I = 2$  (c)  $I = 4.5$ ; log  $\beta_5 = 4.72$ , log  $\beta_6 = 4.11$   
(b)  $I = 2.5$ ; log  $\beta_5 = 7.68$ , log  $\beta_6 = 8.04$  (d) for  $\text{Cu}_2\text{Cl}_4^{2-}$

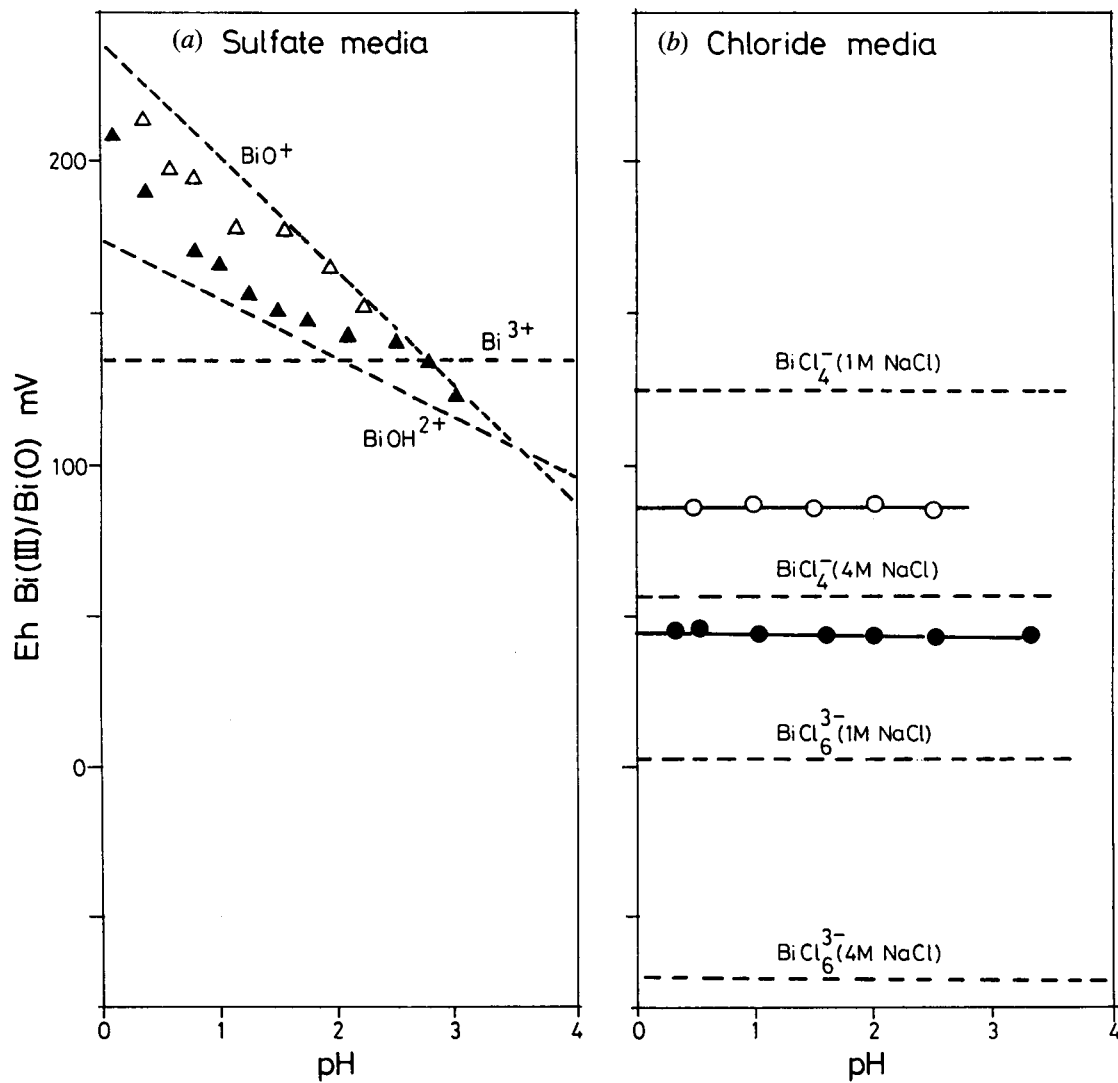


Fig. 6—Eh-pH relationships of Bi(III) in chloride and sulfate media at 25 °C (conditions and key as Fig. 5).

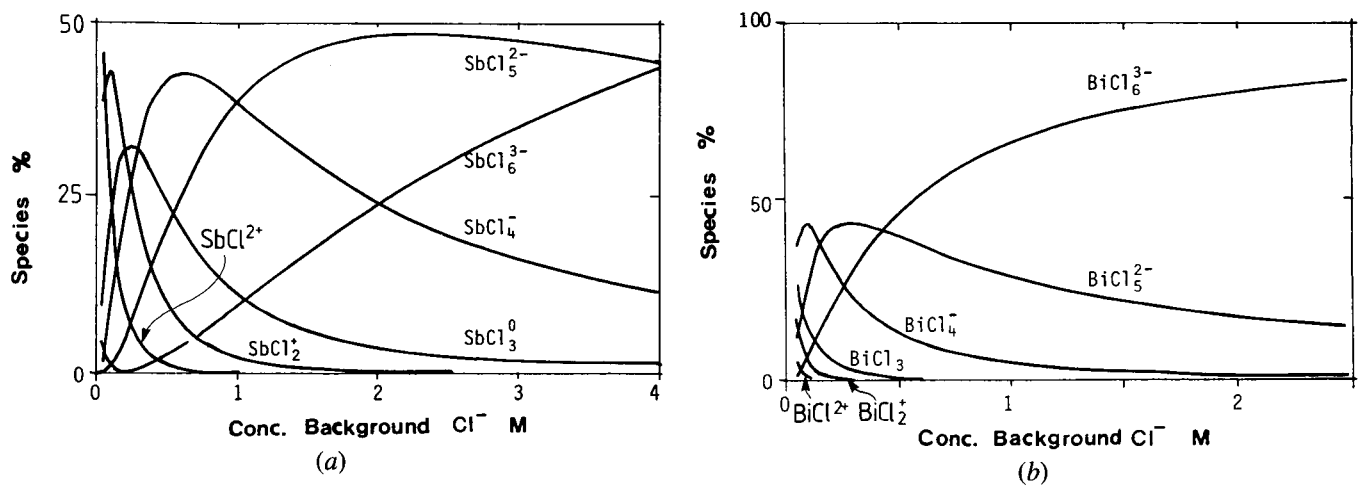


Fig. 7—Species distribution of Sb(III) and Bi(III) in chloride media at 25 °C. Conditions: (a)  $\text{Sb(III)} = 10^{-4}$  M;  $I = 4$  M ( $\text{NaClO}_4$ ); pH = 0 (b)  $\text{Bi(III)} = 10^{-4}$  M;  $I = 2.5$  M ( $\text{NaClO}_4$ ); pH = 0.

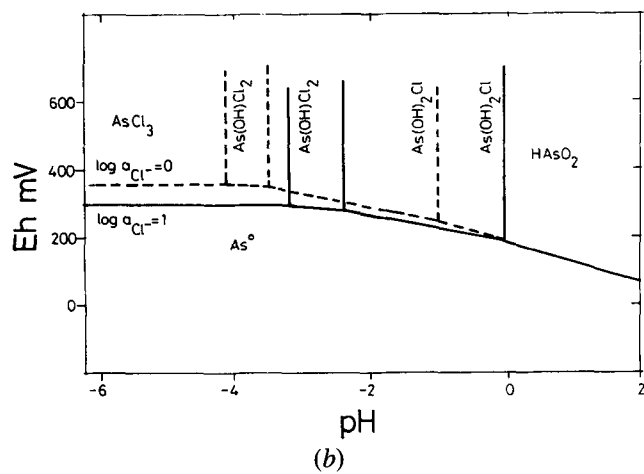
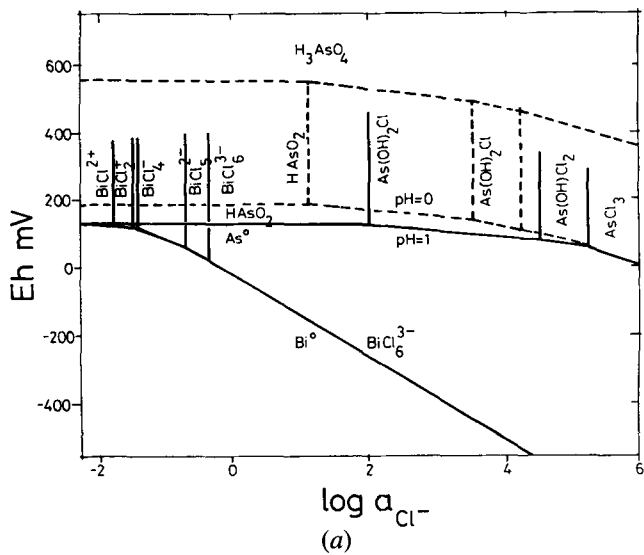
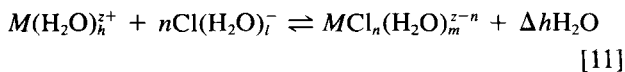


Fig. 8—Calculated Eh-log  $a_{Cl^-}$  and Eh-pH relationships for As(III), and Eh-log  $a_{Cl^-}$  relationships for Bi(III) in chloride media at 25 °C. Conditions: As(III) =  $10^{-3}$  M; Bi(III) =  $10^{-4}$  M either at pH 0 and 1 or log  $a_{Cl^-}$  = 0 and 1.



$$\beta_n(a) = \frac{a_{MCl_n(H_2O)_m^{z-n}} \cdot (a_w)^{\Delta h}}{a_{M(H_2O)_h^{z^+}} \cdot (a_{Cl(H_2O)_i^-})^n} \quad [12]$$

$$\Delta E^\circ \cdot \frac{zF}{2.303 RT} = \log \gamma_{M^{z^+}} \quad [13]$$

$$= \log \gamma_{MCl_n(H_2O)_m^{z-n}} \cdot \frac{1}{(a_w)^m} \cdot \frac{1}{\beta_n(a) \cdot (a_{Cl^-})^n} \quad [14]$$

$$= \log \gamma_i(\text{elect}) \cdot \gamma_i(\text{hydr}) \cdot \gamma_i(\text{complex}) \quad [15]$$

These equations can be used to calculate and rationalize the variation of overall activity coefficient  $\gamma_{M^{z^+}}$ , resulting from the composite of electrostatic (Debye-Hückel), hydration, and complexation effects (Eq. [15]).

Figure 12 summarizes the overall change in  $\gamma_{M^{z^+}}$  and  $\gamma_{M^+}$  according to the total chloride concentration of the solution. Values of  $\gamma_{M^{z^+}}$  differ by  $10^6$  in 1 M  $Cl^-$  solution and by  $10^{12}$

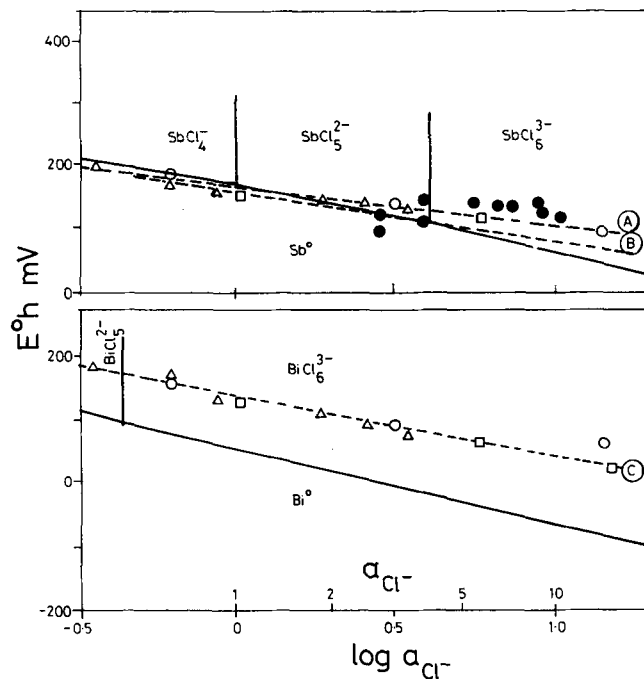


Fig. 9—Measured variation of  $E^0h$  of Sb(III) and Bi(III) with log  $a_{Cl^-}$ . Conditions: temp. = 25 °C; pH  $\leq$  0.2; Sb(III) = Bi(III) =  $10^{-4}$  M ( $E^0h$  corresponds to Eh corrected to 1 M electroactive species). Key:  $\Delta$  NaCl;  $\square$  CaCl<sub>2</sub>;  $\circ$  MgCl<sub>2</sub>;  $\bullet$  HCl. Solid lines: predicted from data in Table II; dashed lines: best fitting lines. A assuming only SbCl<sub>3</sub> species, B assuming only SbCl<sub>4</sub><sup>-</sup> species, and C assuming only BiCl<sub>5</sub><sup>2-</sup> species.

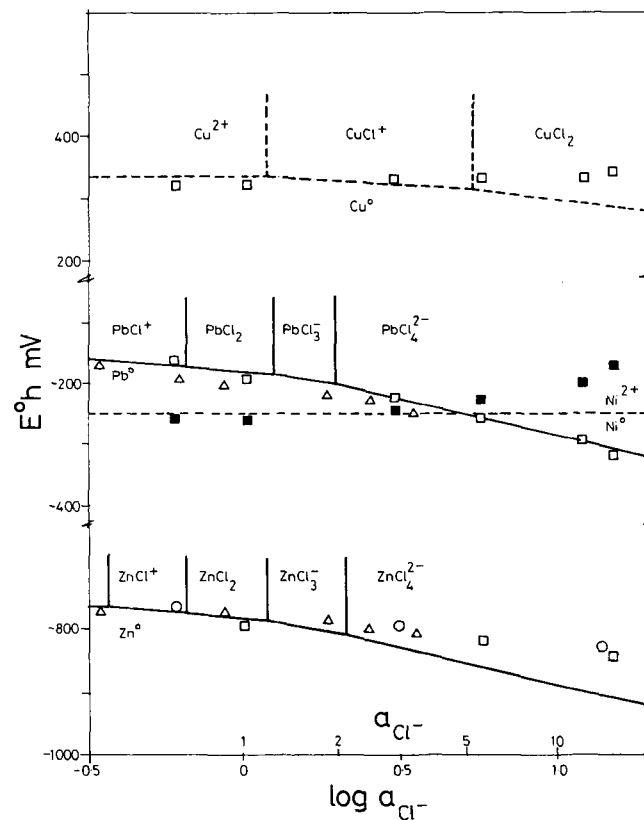


Fig. 10— $E^0h$ -log  $a_{Cl^-}$  relationships for the Cu-Pb-Zn-Ni-Cl-H<sub>2</sub>O system at 25 °C. Key: Solid lines predicted from  $\beta_n^*$  (Table II).  $\Delta$  NaCl;  $\square$  CaCl<sub>2</sub>;  $\circ$  MgCl<sub>2</sub>;  $\blacksquare$  CaCl<sub>2</sub><sup>.2</sup>

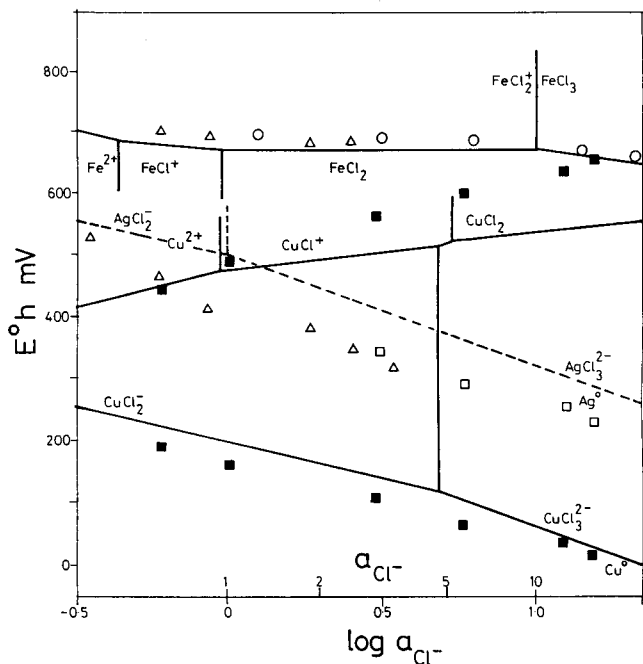


Fig. 11— $E^{\circ}h$ - $\log a_{Cl^-}$  relationships for the Fe(III)/Fe(II)-Cu(II)/Cu(I)-Ag(I)-Cu(I)-Cl<sup>-</sup>-H<sub>2</sub>O system at 25 °C. Key: solid lines predicted from  $\beta_n^0$  (Table II).  $\Delta$  NaCl;  $\circ$  MgCl<sub>2</sub>;  $\blacksquare$  CaCl<sub>2</sub>.

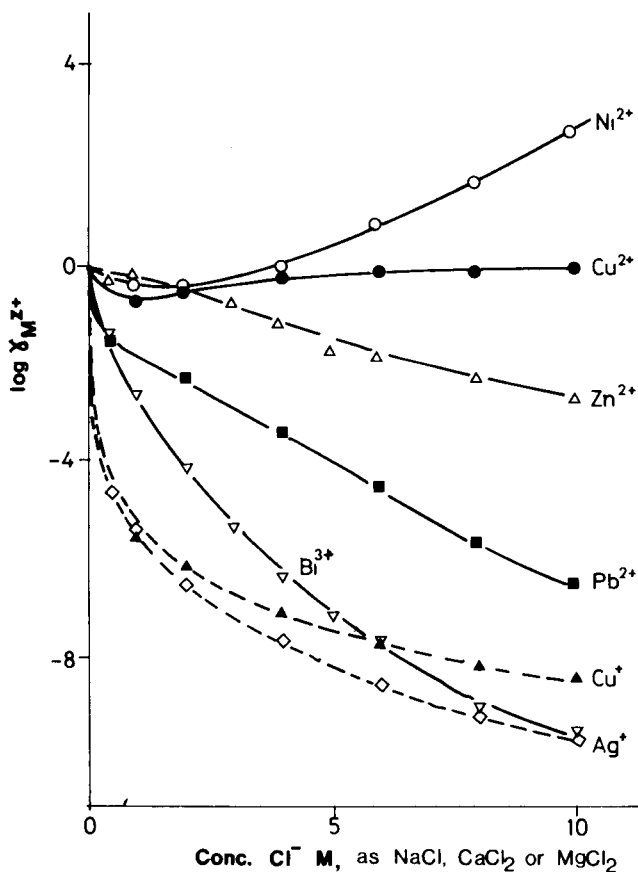


Fig. 12—Effect of background chloride salts on transition-metal ion activity coefficients in water at 25 °C (data calculated from  $E^{\circ}h$ ; Figs. 7 to 9).

in 10 M Cl<sup>-</sup> solution according to the metal ion considered. In high ionic strength solutions,  $\gamma_i(\text{elect})$  is small compared to the other terms and can be neglected. Clearly the  $\gamma_i(\text{complex})$  term predominates for those metal ions which form strong chloro-complexes (e.g., Ag<sup>+</sup>) but the  $\gamma_i(\text{hydr})$  term is important for nonassociating ions like Ni<sup>2+</sup>. According to the hydration theory,<sup>32</sup> the activity of nonassociated cations rises sharply in high ionic strength solutions due to the decrease in water activity. As recently reported,<sup>12</sup> plots of Eh or log  $\gamma_i$  vs -log  $a_w$ , for  $i = H^+, Na^+, Ni^{2+}, Ca^{2+}$ , and Mg<sup>2+</sup> in concentrated chloride solutions, are linear with slopes corresponding to the hydration number of the cation. For the metal ions considered in this work, the hydration numbers are reported to be about  $12 \pm 2$  for Zn<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>,<sup>33</sup> and about 2 for Pb<sup>2+</sup><sup>34</sup> and Ag<sup>+</sup>.<sup>35</sup> Only limited data exist on the hydration numbers ( $m$ ) of complex species. Skou *et al.*<sup>15</sup> have determined that for ZnCl<sup>+</sup>, ZnCl<sub>3</sub><sup>-</sup>, and ZnCl<sub>4</sub><sup>2-</sup>,  $m = 12, 4,$  and  $0$ , respectively. Thus it is unreasonable to assume an activity coefficient of 1 for all similar complexes.

The observed discrepancy in  $E^{\circ}h$  for all the M<sup>2+</sup> ions is, therefore, directly attributed to the increase in  $\gamma_{M^{2+}}(\text{hydr})$ . For ions which form only weak chloro-complexes like Cu<sup>2+</sup> and Zn<sup>2+</sup>, a decrease in activity resulting from complexation is compensated by an increase in activity resulting from the lower water activity in concentrated solutions. Thus the observed Eh changes are less than predicted on the basis of Eq. [1].

The effect of ionic strength on the activity of complex ions like CuCl<sub>2</sub><sup>-</sup> and AgCl<sub>3</sub><sup>2-</sup> is more difficult to measure or predict. If it is assumed that  $m = 0$ , and that the difference between the measured and predicted values of  $E^{\circ}h$  for the Cu(I)/Cu(0) and Ag(I)/Ag(0) couples (Figure 10) reflect the true activity of the CuCl<sub>2</sub><sup>-</sup> and AgCl<sub>3</sub><sup>2-</sup> species, then the calculated values of  $\gamma_{CuCl_2^-}$  and  $\gamma_{AgCl_3^{2-}}$  in 0.5 to 5 M CaCl<sub>2</sub> solution remain constant around 0.55 and 0.08, respectively, seemingly unaffected by water activity. These calculated values compare favorably with values of  $\gamma_{Cl^-}^2/\gamma_{CuCl_2^-}$  recently reported by Fritz<sup>14a</sup> which were estimated from the saturated solubility of CuCl in chloride solutions. These values, together with reported values of  $\gamma_{Cl^-}$  and calculated values of  $\gamma_{CuCl_n^{1-n}}$ , are summarized in Table III.

Thus the neglect of activity terms in the prediction of  $E^{\circ}h$ - $\log a_{Cl^-}$  diagrams can lead to significant discrepancies with measured  $E^{\circ}h$  values in solutions of high ionic strength. With further knowledge of ionic activities, particularly of complex ions, it should be possible to refine the accuracy of Pourbaix diagrams for practical solutions. But for most applications it seems reasonable to construct such

Table III. Activity Coefficients of Cl<sup>-</sup>, CuCl<sub>2</sub><sup>-</sup>, and CuCl<sub>3</sub><sup>2-</sup> in Aqueous Chloride Solutions at 25 °C

Solution	$\gamma_{Cl^-}$	$\gamma_{Cl^-}^2/\gamma_{CuCl_2^-}$	$\gamma_{Cl^-}^3/\gamma_{CuCl_3^{2-}}$	$\gamma_{CuCl_2^-}$	$\gamma_{CuCl_3^{2-}}$
2 M HCl	0.41 <sup>a</sup>	0.86 <sup>b</sup>	3.28 <sup>b</sup>	0.20 <sup>c</sup>	0.02 <sup>c</sup>
5 M NaCl	0.69 <sup>a</sup>	0.675 <sup>b</sup>	2.49 <sup>b</sup>	0.70 <sup>c</sup>	0.13 <sup>c</sup>

(a) Reference 12; (b) Reference 14a; (c) calculated



diagrams from available  $\beta_n^\circ$  values and assume ideality without serious errors.

## ACKNOWLEDGMENTS

The award of a Colombo Plan Scholarship to G. Senanayake by the Australian Development Assistance Bureau is gratefully acknowledged. We also thank Dr. Brian Clare for his computational assistance with the distribution diagrams.

## REFERENCES

1. D. M. Muir: Warren Spring Laboratory Report L.R. 425 (ME), Stevenage, U.K., 1984.
2. D. M. Muir and G. Senanayake: (1985) *Extraction Metallurgy '85*, M. J. Jones, ed., IMM London, pp. 65-91.
3. (a) K. C. Liddell and R. G. Bautista: *Metall. Trans. B*, 1981, vol. 12B, pp. 627-37. (b) K. C. Liddell and R. G. Bautista: *Metall. Trans. B*, 1983, vol. 14B, pp. 5-15.
4. D. M. Muir and G. Senanayake: *Hydrometallurgy*, 1985, vol. 14, pp. 279-93.
5. D. M. Muir, M. D. Benari, B. W. Clare, P. Mangano, and A. J. Parker: *Hydrometallurgy*, 1983, vol. 9, pp. 257-75.
6. G. Senanayake: Ph.D. Thesis, Murdoch University, Perth, W. Australia, 1987.
7. J. J. C. Jansz: "Thermodynamics of aqueous chloride solutions: Calculations of ionic activities and distribution data for chloro-complexes", paper presented to AIME Conference, Los Angeles, CA, Feb. 1984.
8. R. T. Kimura, P. A. Haunschild, and K. C. Liddell: *Metall. Trans. B*, 1984, vol. 15B, pp. 213-19.
9. E. Peters: *Metall. Trans. B*, 1976, vol. 7B, pp. 505-17.
10. A. Moreau, J. P. Frayret, F. Del Rey, and R. Pointeau: *Electrochim. Acta*, 1982, vol. 27, pp. 1281-91.
11. C. I. House and G. H. Kelsall: *Electrochim. Acta*, 1984, vol. 29, pp. 1459-64.
12. G. Senanayake and D. M. Muir: *Electrochim. Acta*, 1987, in press.
13. S. Aditya and R. C. Das: *J. Scient. Ind. Res.*, 1977, vol. 36, pp. 206-13.
14. J. J. Fritz: *J. Phys. Chem.*, (a) 1984, vol. 88, pp. 4358-61; (b) 1980, vol. 84, pp. 2241-46; (c) 1981, vol. 85, pp. 890-94.
15. E. Skou, T. Jacobsen, W. Van der Hoeven, and S. Atlung: *Electrochim. Acta*, 1977, vol. 22, pp. 169-74.
16. (a) H. Majima and Y. Awakura: *Metall. Trans. B*, 1985, vol. 16B, pp. 433-39; (b) H. Majima and Y. Awakura: *Metall. Trans. B*, 1986, vol. 17B, pp. 621-27.
17. *Encyclopedia of Electrochemistry of the Elements*, A. J. Bard, ed., Marcel Dekker, New York, NY, 1975, vol. 4.
18. (a) L. G. Sillen and A. E. Martell: "Stability constants of metal ion complexes", Chemical Society Special Publication No. 17, London, 1964; (b) L. G. Sillen and A. E. Martell: "Stability constants supplement No. 25", Chemical Society Special Publication No. 26, London, 1971.
19. B. W. Clare, P. Singh, P. Mangano, A. J. Parker, and D. M. Muir: *Aust. J. Chem.*, 1983, vol. 36, pp. 1687-94.
20. D. W. Barnum: *Inorg. Chem.*, 1983, vol. 22, pp. 2297-2305.
21. V. P. Antonovich, E. M. Nevskaya, E. I. Shelikhina, and V. A. Nazarenko: *Zhur. Neog. Khim.*, 1975, vol. 20, pp. 2968-74.
22. W. F. Linke and A. Seidell: "Solubility of Inorganic and Metal Organic Compounds", Amer. Chem. Soc., New York, NY, 1965, pp. 234-35.
23. R. E. Mesmer and C. F. Baes: "The hydrolysis of cations", Wiley-Interscience, London, 1976.
24. J. N. Butler: "Ionic Equilibria: A Mathematical Approach", Addison-Wesley, New York, NY, 1964, p. 468.
25. J. Bjerrum and L. H. Skibsted: *Acta Chem. Scand.*, 1977, vol. A31, pp. 673-77.
26. R. M. Smith and A. E. Martell: *Critical stability constants*, vol. 4: *Inorganic complexes*, Plenum Press, New York, NY, 1976, pp. 105-06.
27. S. Ahrlund and J. Rawsthorne: *Acta Chem. Scand.*, 1970, vol. 24, pp. 157-72.
28. H. C. Helgeson: *Amer. J. Sci.*, 1969, vol. 267, pp. 729-804.
29. G. W. McDonald, T. J. Udovic, J. A. Dumesic, and S. H. Langer: *Hydrometallurgy*, 1984, vol. 13, pp. 125-35.
30. V. P. Vasilev, V. I. Shorokhova, O. G. Raskova, and L. I. Klepikova: *Zhur. Fiz. Khim.*, 1984, vol. 58, pp. 2700-05.
31. N. Bjerrum: *Z. Anorg. Chem.*, 1920, vol. 109, pp. 275-79.
32. R. G. Bates, B. R. Staples, and R. A. Robinson: *Anal. Chem.*, 1970, vol. 42, pp. 867-71.
33. J. Burgess: "Metal ions in solution", John Wiley, London, 1978.
34. L. Leifer and E. Hogfeldt: *Proc. 1st Australian Electrochemistry Conference*, Sydney, 1963, pp. 107-14.
35. H. Sadek: *J. Electroanal. Chem.*, 1983, vol. 144, pp. 11-32.