Thermodynamic Modeling Of Aqueous FE-CU-AS-SB-BI-H2SO4 Solutions And Its Application For Redox Potential Determination In Copper Electrorefining From 25°C TO 70°C

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THERMODYNAMIC MODELING OF AQUEOUS FE-CU-AS-SB-BI-H$_2$SO$_4$ SOLUTIONS
AND ITS APPLICATION FOR REDOX POTENTIAL DETERMINATION IN COPPER
ELECTROREFINING FROM 25°C TO 70°C

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AND ITS APPLICATION FOR REDOX POTENTIAL DETERMINATION IN COPPER
ELECTROREFINING FROM 25°C TO 70°C

by

YONGTENG DONG, B.S.

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Abstract

Impurity elements in copper electrorefining (ER) electrolyte have been becoming a crucial issue on purity of copper cathode. The objective of this doctoral research is to develop a speciation model to understand impurity behavior in aqueous ER solutions.

A thermodynamic model of Fe(II)-Fe(III)-Cu(II)-H₂SO₄-H₂O system is developed and shown to reliably simulate the species distribution in industrial copper electrorefining electrolyte from 25°C to 70°C. The previously developed model of Fe(II)-Fe(III)-H₂SO₄-H₂O system under leaching conditions was first evaluated. It has proved that its applicability can be extended to much higher acid concentration (185 g/L) and high amount of copper (40-50 g/L). Cu(II) species were then identified from literature, and their thermodynamic data were collected and assessed for modeling calculation. Results reveal that after addition of high amount of copper, Fe(II) still distributes as free Fe²⁺, FeHSO₄⁺ and FeSO₄⁰; Fe(III) distributes as free Fe³⁺, FeSO₄⁺, FeHSO₄²⁺ and Fe(SO₄)_2⁻. Cu(II) dissolves as Cu²⁺, CuSO₄⁰ and CuHSO₄⁺. The proposed model was validated by reliable and accurate prediction of measured oxidation and reduction potential (ORP) throughout all solution conditions. Analysis indicates that Fe(II)-Fe(III)-H₂SO₄-H₂O solutions with a high H₂SO₄ and Cu(II) concentration can still be solely determined by Fe³⁺/Fe²⁺ couple. The results also prove the suitability of B-dot equation at high solution ionic strength up to 3M and a previously developed expression for ORP prediction.

The extension of above Fe(II)-Fe(III)-Cu(II)-H₂SO₄-H₂O model was made in solutions, containing additional As(III), As(V), Sb(III), Sb(V) and Bi(III) impurity elements with concentrations based on industrial condition. Identified species including aqueous H₃AsO₃⁰, AsO⁺, H₂AsO₄⁻, H₃AsO₄⁰, SbO⁺, H₃SbO₃⁰, Sb(OH)₅⁻, HSb(OH)₆⁰, BiO⁺ and Bi³⁺ were collected after critical review from literature as well as their thermodynamic data. Experimental ORP
measurements were also performed for validation of the proposed model. The distribution percentage of each species was quantitatively illustrated in detail from 25°C to 70°C. The results show that redox couple of free Fe³⁺/Fe²⁺ from Fe(III)/Fe(II) plays a predominant role on ORP determination after addition of As(III, V) and Sb(III, V). Furthermore, it has been verified that the previously developed expression with only two variables (nominal Fe³⁺/Fe²⁺ ratio and temperature) is capable of predicting ORPs in acidic sulfate solutions with high accuracy.

The findings of this work can provide a deeper understanding on speciation in copper electrorefining solutions and further facilitate the industrial process improvement.
Table of Contents

Acknowledgements........................................................................................................ iv
Abstract .......................................................................................................................... v
Table of Contents ........................................................................................................... vii
List of Tables ................................................................................................................ x
List of Figures ............................................................................................................... xi

Chapter 1: Introduction and literature review .............................................................. 1
  1.1 General information on copper electrorefining....................................................... 1
  1.2 Options for impurities removal ............................................................................. 6
    1.2.1 In-situ impurity control .................................................................................. 6
    1.2.2 Solvent extraction and ion exchange ............................................................. 6
    1.2.3 Adsorption of impurities onto activated carbon .......................................... 7
    1.2.4 Co-precipitation of impurities ..................................................................... 8
  1.3 Summary ............................................................................................................... 9
  1.4 Thermodynamic modeling and speciation studies based on hydrometallurgy ......10
    1.4.1 Speciation in Fe(II)-Fe(III)-H2SO4-H2O system up to 150°C ....................... 10
    1.4.2 Speciation in aqueous Cu-As-H2SO4 solutions ........................................... 14
    1.4.3 Speciation and reduction potentials of metal ions in concentrated chloride
        and sulfate solutions ....................................................................................... 15
    1.4.4 Thermodynamic modeling and electrodialysis in CuSO4-H2SO4-As-Sb-H2O
        at 25°C ........................................................................................................... 18
    1.4.5 Solubility study in Sb(III)-Sb(V)-H2SO4-H2O at 25°C ............................... 19
  1.5 Scope of the present work ..................................................................................... 20

Chapter 2: Thermodynamic data identification, collection, and evaluation ............... 22
  2.1 Introduction .......................................................................................................... 22
  2.2 Species and thermodynamic data in Fe(II, III)-Cu(II)-H2SO4-H2O solutions ....... 22
    2.2.1 Species and thermodynamic data in Fe(II, III)-H2SO4-H2O solutions .......... 23
    2.2.2 Species and thermodynamic data in Cu(II)-H2SO4-H2O solutions .............. 23
  2.3 Species and thermodynamic data in As(III, V)-Sb(III, V)-Bi(III)-H2SO4-H2O
      solutions ........................................................................................................... 27
    2.3.1 Ion interactions among As, Sb and Bi in copper electrorefining ................. 27
2.3.2 Species and thermodynamic data in As(III, V)-H_2SO_4-H_2O system .................28
2.3.3 Species and thermodynamic data in Sb(III, V)-H_2SO_4-H_2O system ...............31
2.3.4 Species and thermodynamic data in Bi(III)-H_2SO_4-H_2O system ..................35
2.4 Precipitates among As, Sb and Bi during copper electrorefining .......................37

Chapter 3: Model development and calculation .......................................................39
3.1 Introduction ........................................................................................................39
3.2 Construction of thermodynamic model .............................................................39
    3.2.1 Chemical equilibrium equations ...............................................................40
    3.2.2 Mass and charge balance ........................................................................41
    3.2.3 Ionic strength ...........................................................................................42
3.3 B-dot equation for activity coefficient ...............................................................42
3.4 Model calculation from 25°C to 70°C ...............................................................44
3.5 ORP calculation and validation for speciation from 25°C to 70°C ....................47

Chapter 4: Materials and methods .........................................................................49
4.1 Electrode preparation .......................................................................................49
4.2 Electrolyte preparation ....................................................................................49
    4.2.1 Electrolyte preparation for Fe(II, III)-Cu(II)-H_2SO_4-H_2O system ...........49
    4.2.2 Electrolyte preparation for aqueous system containing Fe(II, III), As(III, V),
        Sb(III, V), Bi(III), Cu(II) and H_2SO_4 .......................................................51
4.3 Electrochemical measurements from 25°C to 70°C .........................................53

Chapter 5: Thermodynamic modeling in Fe(II, III)-Cu(II)-H_2SO_4-H_2O solution and its
application to redox potential calculation up to 70°C .............................................55
5.1 Introduction ...................................................................................................55
5.2 Calculated species distribution in Fe(II, III)-H_2SO_4-H_2O system from 25°C to 70°C ...56
5.3 Calculated species distribution in Fe(II, III)-Cu(II)-H_2SO_4-H_2O system from 25°C
to 70°C ...........................................................................................................60
5.4 Comparison of redox potential between calculated results and experimental
measurements from 25°C to 70°C ....................................................................64
5.5 Applicability of the developed expression by comparison with experimental results
from 25°C to 70°C ...........................................................................................66
5.6 Effect of high acid and copper concentration on redox potential .......................68
5.7 Discussion on the effect of nominal Fe^{3+}/Fe^{2+} ratio and T on redox potential .......72
5.8 Effect of total concentration of Cu(II) and Fe on ORP measurement .................74
List of Tables

Table 2.1: Thermodynamic data and equilibrium formation constants at 25°C for the main aqueous species in Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions................................................................. 26
Table 2.2: Thermodynamic data and equilibrium formation constants at 25°C for the main species in aqueous As(III, V)-Sb(III, V)-Bi(III)-H₂SO₄-H₂O solutions........................................... 37
Table 3.1: Debye-Hückel parameters ($A_\gamma$ and $B_\gamma$) and $\tilde{B}$ values as a function of temperature. .... 44
Table 3.2: Standard and calculated equilibrium constants for the main species in aqueous Fe(II, III)-Cu(II)-As(III, V)-Sb(III, V)-Bi(III)-H₂SO₄-H₂O solutions from 25°C to 70°C by Criss-Cobble method .............................................................. 47
Table 4.1: Compositions of synthetic Fe(II, III)-H₂SO₄-H₂O and Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions, g/L.......................................................... 50
Table 4.2: Compositions of synthetic aqueous solutions containing Fe(II, III), As(III, V), Sb(III, V), Bi(III), Cu(II) and H₂SO₄, g/L...................................................................................... 52
Table 6.1: Compositions of synthetic Fe-As-Sb-Bi-Cu-H₂SO₄-H₂O solutions, g/L ............... 85
List of Figures

Figure 1.1: Main pyro-processes for extracting copper from sulfide ores [1]................................. 2
Figure 1.2: Schematic illustration of copper electrowinning with electrolytic cell. ......................... 3
Figure 1.3: Industrial production of copper cathode plate. ...................................................... 4
Figure 1.4: Effect of pH on species distribution of Fe(III) and Fe(II) in sulfate solution at 25°C. Conditions: total SO$_4^{2-}$ = 1M; Fe(III) = Fe(II) = 0.1M [38]. ......................................................... 16
Figure 1.5: Effect of pH on species distribution of As(III), Sb(III) and Bi(III) in water at 25°C [38]................................................................................................................................. 17
Figure 1.6: Transport direction of main species in As-Sb-CuSO$_4$-H$_2$O system. AM = anion membrane; CM = cation membrane; A = anolyte; C = catholyte; CC = concentrate compartment; WS = working solution [39]. .......................................................... 18
Figure 2.1: The effect of pH on distribution of various arsenic (III) species [76]. ....................... 29
Figure 2.2: Eh-pH equilibrium diagram for the system arsenic-water at 25°C and at unit activity of all species [77]. .......................................................... 29
Figure 2.3: The effect of pH on distribution of various arsenic (V) species [76] ....................... 31
Figure 4.1: Schematic illustration of experimental ORP(OCP) measurements by potentiostat in aqueous solutions containing Fe(II, III), As(III, V), Sb(III, V), Bi(III), Cu(II) and H$_2$SO$_4$. .............................. 53
Figure 5.1: Calculated species distribution diagram in aqueous Fe(II, III)-H$_2$SO$_4$-H$_2$O solution from 25°C to 70°C for samples #1 to #7 in Table 4.1 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios of 0.05 to 50 (a) at 25°C; (b) at 40°C; (c) at 50°C; (d) at 60°C; (e) at 65°C, and (f) at 70°C. The sum of the percentage values of Fe(II) species is 100%, which is also the case for the Fe(III) species. ............................. 58
Figure 5.2: Calculated species distribution diagram in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solution from 25°C to 70°C for samples #8 to #14 in Table 4.1 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios of 0.05 to 50 (a) at 25°C; (b) at 40°C; (c) at 50°C; (d) at 60°C; (e) at 65°C, and (f) at 70°C. The sum of the percentage values of Fe(II) species is 100%, which is also the case for the Fe(III) species and Cu(II) species. .................................................................................................................. 61
Figure 5.3: Comparison of the potentials predicted by thermodynamic modeling and measured by experiments vs SHE at 25°C (a) in various Fe(II, III)-H$_2$SO$_4$-H$_2$O solutions for tests #1 to #7, and (b) in Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions for tests #8 to #14 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C. ...................................................... 65
Figure 5.4: Comparison of the potentials calculated by Equation 5.1 and measured by experiments vs SHE at 25°C (a) in various Fe(II, III)-H$_2$SO$_4$-H$_2$O solutions for tests #1 to #7, and (b) in various Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions for tests #8 to #14 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C. ...................................................... 67
Figure 5.5: Calculated real Fe$^{3+}$/Fe$^{2+}$ ratios for test #1 to #7 in various Fe(II, III)-H$_2$SO$_4$-H$_2$O solutions, and test #8 to #14 in various Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions with nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C. ...................................................... 69
Figure 5.6: Comparison of the potentials predicted by modeling with Equation 3.10, measured by experiments and calculated by Equation 5.1 vs SHE at 25°C for (a) #9 and #15, (b) #10 and #16 respectively from 25°C to 70°C in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions. ...................................................... 75
Figure 5.7: Comparison of the potentials predicted by modeling with Equation 3.10, measured by experiments, and calculated by Equation 5.1 vs SHE at 25°C for (a) #11 and #17, (b) #12 and #18 respectively from 25°C to 70°C in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions. ...................................................... 77
Figure 5.8: Calculated pH (a) in aqueous Fe(II, III)-H₂SO₄-H₂O system for samples #1 to #7; (b) in aqueous Fe(II, III)-Cu(II)-H₂SO₄-H₂O system for samples #8 to #14 with nominal Fe³⁺/Fe²⁺ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C. ................................................................. 79

Figure 5.9: Calculated real ionic strength (a) in aqueous Fe(II, III)-H₂SO₄-H₂O system for samples #1 to #7; (b) in aqueous Fe(II, III)-Cu(II)-H₂SO₄-H₂O system for samples #8 to #14 with nominal Fe³⁺/Fe²⁺ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C. ................................................................. 80

Figure 6.1: Calculated species distribution in aqueous Fe(II, III)-Cu(II)-H₂SO₄ solutions from 25°C to 70°C for test #1~3 in Table 6.1 with nominal Fe³⁺/Fe²⁺ ratios of 0.1 to 10 (a) at 25°C; (b) at 40°C; (c) at 50°C; (d) at 60°C; (e) at 65°C, and (f) at 70°C. The sum of the percentage of Fe(II), Fe(III) and Cu(II) species is 100% respectively. ............................................................................. 87

Figure 6.2: Calculated species distribution diagram in aqueous Fe(II, III)-As(III, V)-Cu(II)-H₂SO₄ solutions from 25°C to 70°C for test #4~6 in Table 6.1 with nominal Fe³⁺/Fe²⁺ ratios of 0.1 to 10 for Fe(II), Fe(III), Cu(II), As(III) and As(V) species (a) and (a') at 25°C; (b) and (b') at 40°C; (c) and (c') at 50°C; (d) and (d') at 60°C; (e) and (e') at 65°C; (f) and (f') at 70°C. The sum of the percentage of Fe(II), Fe(III), Cu(II), As(III) and As(V) species is 100% respectively. ............................................................................. 91

Figure 6.3: Calculated species distribution diagram in aqueous Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H₂SO₄ solution from 25°C to 70°C for test #7~12 with nominal Fe³⁺/Fe²⁺ ratios of 0.1 to 10, As⁵⁺/As³⁺ ratio of 7:3 to 3:7, and Sb⁵⁺/Sb³⁺ ratio of 1 for Fe(II), Fe(III), Cu(II), As(III), As(V), Sb(III), Sb(V) and Bi(III) species (a) and (a') at 25°C; (b) and (b') at 40°C; (c) and (c') at 50°C; (d) and (d') at 60°C; (e) and (e') at 65°C; (d) and (d') at 70°C. The sum of the percentage of Fe(II), Fe(III), Cu(II), As(III), As(V), Sb(III), Sb(V) and Bi(III) species is 100% respectively. ............................................................................. 95

Figure 6.4: Comparison of the experimental ORPs for tests #1, 4 and 7 under nominal Fe³⁺/Fe²⁺ ratio 0.1:1, tests #2, 5 and 8 under nominal Fe³⁺/Fe²⁺ ratio 1:1, and tests #3, 6 and 9 under nominal Fe³⁺/Fe²⁺ ratio 10:1 in various solutions from 25°C to 70°C. Please refer to Table 6.1 that tests #1~3 are for aqueous Fe(II, III)-Cu(II)-H₂SO₄ solutions, tests #4~6 for Fe(II, III)-As(III, V)-Cu(II)-H₂SO₄ solutions, and tests #7~9 for Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H₂SO₄ solutions. ............................................................................. 98

Figure 6.5: Comparison of the potentials predicted by thermodynamic modeling and measured by experiments vs SHE at 25°C (a) in aqueous Fe(II, III)-Cu(II)-H₂SO₄ solutions for tests #1~3, (b) in Fe(II, III)-As(III, V)-Cu(II)-H₂SO₄ solutions for tests #4~6, and (c) in Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H₂SO₄ solutions for tests #7~9 with relative nominal Fe³⁺/Fe²⁺ ratios from 0.1 to 10, 1 As⁵⁺/As³⁺ ratio 3:7 to 7:3 and Sb⁵⁺/Sb³⁺ ratio 1 from 25°C to 70°C. .......... 101

Figure 6.6: Calculated activity Fe³⁺/Fe²⁺ ratios by thermodynamic modeling for relative tests #1~9 in Table 6.1 under nominal Fe³⁺/Fe²⁺ ratio from 0.1 to 10 in various solutions from 25°C to 70°C. Please note tests #1, 4 and 7 are under nominal Fe³⁺/Fe²⁺ ratio 0.1, tests #2, 5 and 8 under nominal Fe³⁺/Fe²⁺ ratio 1, and tests #3, 6 and 9 under nominal Fe³⁺/Fe²⁺ ratio 10. ......................... 103

Figure 6.7: Comparison of the potentials calculated by Equation 6.2 and measured by experiments vs SHE at 25°C (a) in aqueous Fe(II, III)-Cu(II)-H₂SO₄ solutions for tests #1~3, (b) in Fe(II, III)-As(III, V)-Cu(II)-H₂SO₄ solutions for tests #4~6, and (c) in Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H₂SO₄ solutions for tests #7~9 with nominal Fe³⁺/Fe²⁺ ratios from 0.1 to 10, As⁵⁺/As³⁺ ratio 3:7 to 7:3 and Sb⁵⁺/Sb³⁺ ratio 1 in the temperature range of 25°C to 70°C. ............................................................................. 105
Figure 6.8: Calculated (a) pH and (b) effective ionic strength in various solutions for tests #1~9 in Table 6.1 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.1 to 10 in the temperature range of 25°C to 70°C. ........................................................................................................................................................................................................................................................................107
Chapter 1: Introduction and literature review

1.1 General information on copper electrorefining

Copper pyrometallurgy accounts for nearly 80% copper production in the world including the processes mainly as flotation, smelting, converting, and electrorefining. The other 20% is produced hydrometallurgically with the processes of leaching, solvent extraction and electrowinning [1]. Copper most commonly exists in the earth’s crust as copper-iron-sulfide and copper sulfide minerals, for example chalcopyrite (CuFeS$_2$) and chalcocite (Cu$_2$S). The Cu concentration in an underground ore body is very low typically around 0.5~2% Cu. As shown Figure 1.1, pyrometallurgically produced copper is a complicated process that begins with mining of ore (less than 1% Cu) and ends up with pure copper sheets (99.99% pure Cu) called cathodes. Copper electrorefining is the final pyrometallurgical process to electrochemically dissolve casted copper anode (99.5% Cu) and electroplate pure copper onto copper or stainless-steel cathode (99.99% Cu) in high-copper and high-sulfate aqueous electrolyte. A large demand of pure commercial cathodic copper has arisen for the worldwide industrialization and infrastructure, especially for electrical vehicles due to its high thermal conductivity and corrosion resistance in many heat transfer applications. As the grade of Cu ore continues to decrease in worldwide mines, investigations of today’s copper electrorefining have been mainly focused on the increasing concentration of impurity elements in electrorefining electrolyte.
Figure 1.1: Main pyro-processes for extracting copper from sulfide ores [1].
In copper electrorefining process, an electrical potential is applied between a copper anode and a metal cathode (thin copper starter sheet) in an electrolyte containing CuSO$_4$ and H$_2$SO$_4$ as displayed in Figure 1.2.

![Figure 1.2: Schematic illustration of copper electrorefining with electrolytic cell.](image)

Copper anode is electrochemically dissolved into the electrolyte, producing copper cations and electron in the following reaction:

$$\text{Cu}^0_{\text{anode}} \rightarrow \text{Cu}^{2+} + 2e^- \quad E^o = -0.34\text{V} \quad (1.1)$$

Then the electrons are conducted toward the cathode through the external circuit and power supply. Cu cations migrate to the cathode by convection and diffusion in the electrolyte. Cu$^{2+}$ ions and electrons eventually recombine at the cathode surface to form copper metal without the anode impurities:

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0_{\text{cathode}} \quad E^o = +0.34\text{V} \quad (1.2)$$
These principal final cathodic copper plates are of high purity of 99.99% with less than 250 ppm oxygen and 20 ppm unwanted impurities.

In copper electrorefining electrolyte, some additives as grain refining agents are added in order to improve the morphology of cathode deposits in the electrorefining of copper. Thiourea, glue and chloride ions are commonly used in various refineries. Using these additives with proper amount will result in smooth and noduleless copper cathode deposits shown in Figure 1.3. Otherwise, additives can become really problematic that anodic dissolution rate will decrease or even stop due to the formation of anode passivation film (precipitation of solid copper sulfate, cuprous oxide Cu₂O and cupric oxide CuO onto the copper anode surface), leading to uneconomically high energy consumption and increasing residue scrap and voltage levels. Thiourea (Tu), as one of additives, is capable of adsorbing Cu⁺ and Cu²⁺ ions by forming complex compounds (i.e. Cu(Tu)⁺ and [Cu(Tu)₄]⁺). Since thiourea (very few amount, typically 0.2-1 ppm) can form complex with cuprous ions, it is often used in refineries to decrease the formation rate of the slimes layer on copper anode according to the literature [2-8].

Figure 1.3: Industrial production of copper cathode plate.
With increasingly low-grade copper ores being mined, it is difficult to handle growing concentrations of impurities in the copper industrial flowsheet. As far as electrorefining is concerned, during the industrial copper electrorefining process, various impurity elements are present in copper anode, including Fe, As, Bi, Sn, Ni, Sb, Se, Te and precious metal such as Au and Ag [1], [9]. Those impurities will not dissolve or deposit on the cathode as they are more noble than copper. Indeed, they settle down in the bottom of refining cells as anode slimes which are fully recyclable. Detrimental impurities such as As, Sb, Bi and Fe partially dissolve into the refining electrolyte from anode and accumulate to form a solution with the co-existence of various valence of Fe, As, Sb and Bi. In various copper refineries, the concentration of Fe can reach up to 3g/L or even more, which considerably affects current efficiency during the production due to its higher reduction potential from Fe(III) to Fe(II) [1]. The high amount of Fe also leads to the difficulties during the extraction of arsenic [10]. Other impurity ions (As, Sb and Bi) then gradually form anode and/or floating slimes, not only possibly entering copper cathode by electrolyte entrainment, but also influencing the migration of copper cations onto cathode within cells. This can cause problems during processes of copper production including anode passivation, cathode contamination (co-deposition with copper or mechanical inclusion), and low current efficiency, etc., which, as a result, worsen commercial copper cathode quality and increase operating costs [11-18]. Among those, one of the main challenges is the formation of floating slimes which is believed to be caused by the co-existence of various valence of As, Sb (III and V) and Bi(III) in the electrolyte.
1.2 Options for impurities removal

To remove those impurities from the electrolyte, various methods have already been proposed and applied in industry, including in-situ impurity control, solvent extraction, ion exchange resin, chemical precipitation, adsorption by activated carbon, etc.

1.2.1 In-situ impurity control

The slightly soluble impurities as antimony and bismuth are the most concern in the copper refinery. The precipitation is the main cause of copper cathode contamination. When the precipitate forms, it reports to cathode. To reduce antimony and bismuth contamination, the concentration of pentavalent arsenic should be increased in the electrolyte. Both trivalent antimony and bismuth arsenate are slightly soluble. Because of this, increasing the concentration of As(V) can lower down the solubility of As(III) and Bi(III). As the As concentration continues to increase, the solubility of Sb and Bi continues to decrease. When the As(V) attains a value of 15-20 g/L, Sb and Bi concentration will be depressed to less than 100 ppm in the electrolyte and no longer contaminate the copper cathodes [19]. The use of high concentration of As(V) in the refineries has the advantageous of causing most of the Sb and Bi to report in the slimes, where it can be recovered as saleable salts.

1.2.2 Solvent extraction and ion exchange

Arsenic can be extracted from the partially treated electrolyte by solvent extraction. The preferred solvent is tributyl phosphate (TBP). In order to improve the distribution coefficient of arsenic acid between TBP and tankhouse electrolyte, sufficient sulfuric acid is added to the partially treated electrolyte to increase its sulfuric acid concentration to about 600 g/L [19]. The
arsenic acid is recovered from the loaded TBP by stripping with water. A washing stage may be required for the loaded solvent to recover sulfuric acid. It should be mentioned that the solvent extraction is both purification of the electrolyte and arsenic disposal.

The electrolyte bleed stream, preferably after decopperizing, is passed through a short ion-exchange bed containing an anion-exchange resin that preferentially adsorbs sulfuric acid and rejects salts. By alternately passing decopperized electrolyte and water through the ion-exchange bed, it is possible to separate the salts from the acid. Although a complete separation of the sulfuric acid is not accomplished, 80–90% can be recovered [19]. This gives the opportunity for recovering saleable Bi and Sb compounds and minimizes the process costs.

LIX 1104SM reagent is an effective extractant for removing antimony (III) from sulfuric acid solution. The selectivity of the system against other metallic species is good, with an extraction order: Sb (III) > As (V) > Fe (III). Neither copper (II) nor sulfuric acid are extracted [20]. Antimony (III) can be recovered using HCl at low O/A phase ratios ([Sb (III)]/[LIX 1104SM]). Riveros et al. [21] stated that both Sb(III) and Sb(V) can be extracted by aminophosphonic resins, such as Duolite C-467, from copper electrolytes. However, whereas Sb(III) is readily eluted with HCl and EDTA, Sb(V) is eluted extremely slowly with HCl and is not amenable to elution with EDTA or other common complexing agents. This is probably because that Sb(V) may build up in the resin phase, leading to the formation of insoluble antimony compounds within the resin beads.

1.2.3 Adsorption of impurities onto activated carbon

Main advantages of the carbon adsorption process relied in its use in various modes: carbon-in column (CIC), carbon-in pulp (CIP) and carbon-in-leach (CIL); but since being the
adsorption process is, in principle, an anion exchange phenomenon, it is restricted only to the surface of the activated carbon; thus, in comparison to ion exchange resins, the loading capacity of activated carbon is relatively small. On the other hand, solvent extraction processing seems to have more favorable kinetics and metal separation possibilities than those of activated carbon. The extent of impurities removal can be enhanced using a greater carbon/solution ratio or using a countercurrent device [22].

Antimony and arsenic adsorption onto activated carbon can be used for separating these impurities from copper electrolytes and recycling the electrolyte to the electrorefining cells since neither copper nor sulfuric acid is loaded in the carbon.

1.2.4 Co-precipitation of impurities

The co-precipitation method for impurities removal in copper electrorefining has been recently developed to observe the microstructure and molecular form by adjusting the ratio of the species in compound under different valence and concentration. It was found that As (V) and Sb (V) in the electrolyte could form arsenato antimonic acid (AAAc). Self-purification in copper electrolyte could be promoted with mixed oxides of Sb(III) and Sb(V) reacting with As(V) to form arsenato antimonates precipitates, and the concentration of As, Sb, Bi all decreased in the electrolyte. The formation of arsenato antimonates and removal efficiency highly depend on mole ratio of As/Sb/Bi [23-26]. If the mole ratio of As/Sb/Bi in copper anode is controlled properly, and arsenic concentration is maintained in the ranges of 7–15 g/L, most of the arsenic, antimony and bismuth in the copper electrolyte can be deposited into anode slimes in the form of arsenato antimonates expressed as follows:
\[
aH_3\text{AsO}_4 + b\text{H}[\text{Sb(OH)}_6] + c\text{MeO}^+ \rightarrow \text{Me}_c\text{As}_a\text{Sb}_b\text{O}_{(3a+5b+c/2+1)}\text{H}_{(a+5b-2c+2)}x\text{H}_2\text{O} + c\text{H}^+ + (a + b + c/2 - 1-x)\text{H}_2\text{O} \quad (1.3)
\]

where Me=As(III), Sb(III) and Bi(III); \(a \geq 1\), \(b \geq 1\), and \(c \leq (3a+b)\). The possible precipitates can form according to the following reactions:

\[
\text{SbO}^+ + H_3\text{AsO}_4 \leftrightarrow \text{SbAsO}_4 \downarrow + H^+ + H_2\text{O} \quad (1.4)
\]
\[
\text{HSb(OH)}_6 + \text{HAsO}_2 \leftrightarrow \text{AsSbO}_4\downarrow + 4\text{H}_2\text{O} \quad (1.5)
\]
\[
\text{Bi}^{3+} + H_3\text{AsO}_4 \leftrightarrow \text{BiAsO}_4 \downarrow + 3H^+ \quad (1.6)
\]
\[
\text{HSb(OH)}_6 + 3\text{Bi}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Bi}_3\text{SbO}_7 \downarrow + 9\text{H}^+ \quad (1.7)
\]

After further investigations, it was also pointed out that the influence of As (III) ion initial concentration on the removal rate of Sb and Bi could reach 53% and 52% respectively by adding As (III) ion in various concentrations to the solution containing \(\text{H}_2\text{SO}_4\), \(\text{Cu}^{2+}\), Sb (III, V) and Bi (III) ions and characterizing the slime structure [27].

1.3 Summary

The disadvantages of above methods are also obvious, including the increase the production cost, serious solution contamination, entrainment of non-target ions, less selectivity and so on. The amount of these aqueous species of each detrimental element with valence distribution is still unknown due to limited detection method. Therefore, it is hard to apply these methods to industrial copper refining production. Complete removal of these impurity species seems to be very difficult.

Clearly, all the methods above rely on the valence distribution of those impurity ions. To determine valence distribution, titration method is vastly used but may not provide accurate results and sometimes exists great errors. This could result in discrepancy between theoretical
prediction and experimental fact. On the other hand, some types of impurity ions and molecules are in favor of precipitates generation according to above-mentioned methods and are inevitably present in copper electrorefining solutions. From an economic point of view, removal of these beneficial species is not recommended unless higher efficiency or complete removal is achieved. Attempts are needed to minimize the impact of impurities on copper production. Perhaps, the quantification of valence distribution of those impurity ions, i.e. by controlling of the amount of impurity elements with different valence (III or V for As, Sb, Bi; II or III for Fe), can provide a deeper understanding of the electrolyte and hence describe the behavior of those impurity ions with different valence. To do so, a systematic study on thermodynamic modeling and speciation in related hydrometallurgical solutions is needed.

1.4 Thermodynamic modeling and speciation studies based on hydrometallurgy

Speciation study usually connects with thermodynamic modeling and calculation of a particular solution system to obtain distribution and concentration of chemical species. The prerequisites for thermodynamic model include various identified inorganic species and their thermodynamic data (Gibbs free energy, entropy and equilibrium constants) in either acidic or alkaline condition over temperature.

1.4.1 Speciation in Fe(II)-Fe(III)-H₂SO₄-H₂O system up to 150°C

Some authors have done a plenty of pioneering research on speciation studies in the field of hydrometallurgical copper. The speciation modeling of Fe(II, III)-H₂SO₄-H₂O system was carried out at 25°C and 50°C by Casas et al. [28] in the early 2000’s. The selected Fe species
include Fe$^{2+}$ and FeSO$_4^o$ for Fe(II), and Fe$^{3+}$, FeSO$_4^+$, Fe(SO$_4$)$_2^-$ and FeH(SO$_4$)$_2^o$ for Fe(III) with formation reactions at 25°C listed below.

\[
\begin{align*}
    \text{H}^+ + \text{SO}_4^{2-} & \leftrightarrow \text{HSO}_4^- & \log K_f^\circ = 2.25 \quad (1.8) \\
    \text{Fe}^{2+} + \text{SO}_4^{2-} & \leftrightarrow \text{FeSO}_4^o & \log K_f^\circ = 2.25 \quad (1.9) \\
    \text{Fe}^{3+} + \text{SO}_4^{2-} & \leftrightarrow \text{FeSO}_4^+ & \log K_f^\circ = 4.04 \quad (1.10) \\
    \text{Fe}^{3+} + 2\text{SO}_4^{2-} & \leftrightarrow \text{Fe}((\text{SO}_4)_2^2- & \log K_f^\circ = 5.38 \quad (1.11) \\
    \text{Fe}^{3+} + \text{H}^+ + 2\text{SO}_4^{2-} & \leftrightarrow \text{FeH}((\text{SO}_4)_2^o & \log K_f^\circ = 8.10 \quad (1.12)
\end{align*}
\]

The total concentrations of Fe and H$_2$SO$_4$ are up to 1.3M and 2.2M respectively. Each concentration of Fe(II) and Fe(III) were experimentally determined by volumetric titration and chemical analyses. The B-dot equation was used for calculation of ionic activity coefficients of all participating species over temperature. The results show that most of Fe(II) and Fe(III) species distribute as free Fe$^{2+}$ (78–83%) and FeH(SO$_4$)$_2^o$ (93.9–96.6%) severally in solutions containing 200 g/L H$_2$SO$_4$, 27 g/L Fe(II) and 23 g/L Fe(III). The results were finally validated by solution conductivity measurements.

The same thermodynamic modeling and solution system with different compositions, validation method and temperature range were developed based on chalcopyrite (CuFeS$_2$) leaching from 25°C to 150°C by Yue et al. [29]. The Fe species including Fe(II) and Fe(III) were further specified in sulfuric acid system. Compared with the previous work by Casas et al. [1], two more iron bisulfate ions FeHSO$_4^+$ and FeHSO$_4^{2+}$ were considered here. The existence of FeHSO$_4^+$ and FeHSO$_4^{2+}$ is quite arguable. Rudolph et al. [30] stated that existence of FeHSO$_4^+$ and FeHSO$_4^{2+}$ contradicts with Raman spectroscopy, in which no evidence of contact ion pairs between HSO$_4^-$ and Fe cations has been found. These two iron bisulfate species can not fit with Raman results because bisulfate (SO$_4^{2-}$) ion was considered as a non-complexing anion. This
relates to whether HSO$_4^-$ can act as a ligand. The H$_2$SO$_4$ solution usually follows two steps of deprotonation process depending on pH.

$$
H_2SO_4_{(aq)} \leftrightarrow H^+ + HSO_4^- \quad (1.13)
$$

$$
HSO_4^- \leftrightarrow H^+ + SO_4^{2-} \quad (1.14)
$$

In extreme acidic solutions (about pH<1), H$_2$SO$_4$ deprotonates almost completely to form HSO$_4^-$ and H$^+$ ions. Fully protonated H$_2$SO$_4$ only accounts for minor amounts that can be neglected. HSO$_4^-$ bisulfate complex at pH>2 will deprotonate forming SO$_4^{2-}$ and H$^+$ [31]. In the case of copper electrowinning (pH is around or even less than 0), the predominant sulfate complex species is always HSO$_4^-$ even at high temperature.

Furthermore, some authors pointed out that Raman spectrophotometry is only sensitive to contact ion-pair complexes such as Fe$^{2+}$SO$_4^{2-}$ but not to hydrated (outer sphere) complexes such as Fe$^{2+}$(H$_2$O)$_n$HSO$_4^-$, which might exist [32-33]. In addition to iron bisulfate ions, similar species such as AlHSO$_4^{2+}$, NiHSO$_4^+$ and MgHSO$_4^+$ could also exist in aqueous sulfate solutions. Because without inclusion of such species in these speciation models, a large discrepancy occurs between theoretical results from modeling and experimental results from literature when increasing H$_2$SO$_4$ concentration (>1M H$_2$SO$_4$), while inclusion of such species will always give a better fit. Conversely, at low H$_2$SO$_4$ concentration (<0.1M H$_2$SO$_4$), there will be no difference between these results. This may be attributed to the formation of above metal-sulfate ionic species under high sulfate condition.

Besides, FeHSO$_4^+$ and FeHSO$_4^{2+}$ have been vastly used in iron speciation-related research and numerous papers can be found. These two species have also been collected in some chemistry-field books [34-35] and commercial geochemical software EQ3/6. Therefore, these
two species with relevant thermodynamic data were selected in speciation model of chalcopyrite leaching solutions by Yue et al. [29].

\[ \text{Fe}^{2+} + \text{H}^+ + \text{SO}_4^{2-} \leftrightarrow \text{FeHSO}_4^+ \quad \log K_f = 1.08 \quad (1.15) \]

\[ \text{Fe}^{3+} + \text{H}^+ + \text{SO}_4^{2-} \leftrightarrow \text{FeHSO}_4^{2+} \quad \log K_f = 3.48 \quad (1.16) \]

The neutral species FeH(SO$_4$)$_2^0$ was excluded due to its instability under the CuFeS$_2$ leaching conditions and inclusion of this species always gave a poor fit to the measured experimental data. The thermodynamic modeling was carried out by summarizing mass and charge balance equations, chemical equilibrium relationship, activity coefficient using B-dot equation, and Criss-Cobble method (also see **Chapter 3**) for calculation of high-temperature equilibrium constants. The solutions consist of H$_2$SO$_4$ 30 g/L and Fe(III) 10g/L with nominal Fe$^{3+}$/Fe$^{2+}$ ratio (total amount of Fe(III) to Fe(II) initially added to solutions) being 1:1, 10:1, 100:1 and 1000:1 in correspond to total amount of Fe(II). The species distribution results indicated that most of Fe(II) and Fe(III) dissolved as free Fe$^{2+}$ and FeSO$_4^+$ respectively and both are over percentage of 60% on their own state from 25°C to 150°C. The experimental oxidation and reduction potential (ORP) was carried out to validate the developed model by using redox free Fe$^{3+}$/Fe$^{2+}$ couple and the Nernst equation. The ORP also refers to open circuit potential (OCP). This work provides a comprehensive understanding on thermodynamic model and speciation calculation in Fe(II)-Fe(III)-H$_2$SO$_4$-H$_2$O system at or above room temperature. Experimental ORP measurements as a validation method to thermodynamic model seems to be easier and give more information about studied solution systems. It provides an insight into redox reactions. Monitoring and control redox potentials is very important in industrial hydrometallurgical processes.
1.4.2 Speciation in aqueous Cu-As-H$_2$SO$_4$ solutions

Copper sulfate system is a very important system in hydrometallurgical copper process, mostly including electrowinning and electrorefining. Arsenic has the tendency to accumulate in industrial metallurgical circuits, which affects the metal production performance. Casas et al. [36] has investigated thermodynamic modeling on aqueous speciation in As(III, V)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions at 25°C. The studied the solutions contain 0-0.16M CuSO$_4$, 0.3-0.5M H$_2$SO$_4$, and 0-0.1M As. Chemical analyses were performed to determine the solution concentration. Modeling was carried out using a set of defined species, components and reactions occurring in the solutions in terms of mass balance and chemical equilibrium relationship. The major Cu(II) species were found to be Cu$^{2+}$, CuSO$_4^0$ and CuHSO$_4^+$, and H$_4$AsO$_5^+$ and H$_3$AsO$_4^0$ for As(III), and H$_2$AsO$_4^-$ and H$_3$AsO$_4^0$ for As(V). Their reactions are summarized below.

$$\text{Cu}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{CuSO}_4^0 \quad \log K_r^0 = 2.36 \quad (1.17)$$

$$\text{Cu}^{2+} + \text{H}^+ + \text{SO}_4^{2-} \leftrightarrow \text{CuHSO}_4^+ \quad \log K_r^0 = 2.34 \quad (1.18)$$

$$\text{H}_2\text{AsO}_3^- + \text{H}^+ \leftrightarrow \text{H}_3\text{AsO}_5^0 \quad \log K_r^0 = 9.23 \quad (1.19)$$

$$\text{H}_2\text{AsO}_5^- + 2\text{H}^+ \leftrightarrow \text{H}_4\text{AsO}_5^+ \quad \log K_r^0 = 8.94 \quad (1.20)$$

$$\text{H}_2\text{AsO}_4^- + \text{H}^+ \leftrightarrow \text{H}_3\text{AsO}_4^0 \quad \log K_r^0 = 2.27 \quad (1.21)$$

Due to this non-ideal solutions, activity and activity coefficients were evaluated by using the extension of Debye-Hückel model, B-dot equation. The speciation model was solved using the EQ3/6 thermodynamic code [37]. The temperature effect on species distribution was simulated. The results show that concentration of copper bisulfate anion (CuHSO$_4^+$) increases greatly with increasing temperature from 15% at 25°C to 60% at 80°C approximately. Concentrations of Cu$^{2+}$ and CuSO$_4^0$ decrease with increasing temperature in the approximate range of 58% to 30% and 38% to 11% respectively from 10°C to 80°C. Major arsenic H$_3$AsO$_4^0$
and arsenious \( \text{H}_3\text{AsO}_3^- \) species are relatively steady over temperature, being 49% and 40% in total arsenic respectively. Other arsenic compounds are the present in concentrations lower than 10%. Ionic conductivity measurements and calculation was carried out for comparison in order to validate developed model.

### 1.4.3 Speciation and reduction potentials of metal ions in concentrated chloride and sulfate solutions

As reported by Senanayake and Muir [38], hydrolysis of As, Sb, Bi and Fe ions in acid solutions can result in the formation of a range of hydroxo-complexes according to the solution pH. The species distribution are highly dependent on solution pH. 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. Sulfate association of Fe(III) or Fe(II) is much stronger than its water association with proton, and thereby Fe species mostly distribute as iron sulfate complexes in sulfate media as shown in Figure 1.4. The speciation is sensitive to pH, but, of course, is dependent on the ratio of \( \text{SO}_4^{2-}/\text{Fe} \).
Figure 1.4: Effect of pH on species distribution of Fe(III) and Fe(II) in sulfate solution at 25°C. Conditions: total SO$_4^{2-}$ = 1M; Fe(III) = Fe(II) = 0.1M [38].

Conversely, sulfate association is not the case with As(III), Sb(III) and Bi(III), which predominantly exist as hydrolyzed MO$^+$ species at low pH. The reported case of hydrolysis of trivalent M(III) ions follows the order As(III)>Sb(III)>Bi(III) in the sulfate solutions to form HMO$_2$ species. The effect of pH on species distribution of As(III), Sb(III) and Bi(III) in aqueous system at 25°C is shown in Figure 1.5.
Figure 1.5: Effect of pH on species distribution of As(III), Sb(III) and Bi(III) in water at 25°C [38].

It was also mentioned that pH<3 is required to produce unhydrolyzed M$^{3+}$ ions, in which the lowest pH for As(III) and highest for Bi(III), while the Sb(III) ions in the middle range. The reported hydrolyzation reactions and corresponding stability constants for As(III), Sb(III) and Bi(III) are listed below.

\[
\begin{align*}
\text{AsO}^+ + \text{H}_2\text{O} &\leftrightarrow \text{HAsO}_2^{0+} + \text{H}^+ & \log K_f = -0.34 & (1.22) \\
\text{SbO}^+ + \text{H}_2\text{O} &\leftrightarrow \text{HSbO}_2^{0+} + \text{H}^+ & \log K_f = -0.87 & (1.23) \\
\text{Bi}^{3+} + 2\text{H}_2\text{O} &\leftrightarrow \text{Bi(OH)}_2^{2+} + 2\text{H}^+ & \log K_f = -4.00 & (1.24)
\end{align*}
\]

The predominant As(III), Sb(III) and Bi(III) species are summarized to be AsO$^+$ and HAsO$_2^{0+}$ (or H$_3$AsO$_4^{0+}$) for As(III), SbO$^+$ and HSbO$_2^{0+}$ (or H$_3$SbO$_5^{0+}$) for Sb(III), and Bi$^{3+}$ and BiO$^+$ (or Bi(OH)$_2^{2+}$) for Bi(III), respectively.
1.4.4 Thermodynamic modeling and electrodialysis in $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-As-Sb-H}_2\text{O}$ at 25°C

Speciation model regarding $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-As-Sb-H}_2\text{O}$ solution was carried out with emphasis on electrodialysis (ED) based on copper electrorefining electrolytes [39]. Electrodialysis allows the separation of ions according to their charge state. The solution that needs to be treated is named working solution (WS). By using membranes in an electrical field, anion membranes allow anions to pass while hindering the passage of cations. Cation membranes do the opposite. When current flows through the cell, anions and cations will be concentrated in concentrate compartment (CC) as WS is continuously consumed. The transport rate of Cu species is faster than As species, which could lead to separation method for Cu and As in electrorefining solutions. A schematic illustration of electrodialysis process is shown in Figure 1.6.

![Figure 1.6: Transport direction of main species in As-Sb-CuSO₄-H₂O system. AM = anion membrane; CM = cation membrane; A = anolyte; C = catholyte; CC = concentrate compartment; WS = working solution [39].](image-url)
The authors also summarized possible species in the solutions by thermodynamic modeling, which consists of a set of equations representing equilibrium relationships for ionic reactions along with component mass balance in the system. B-dot equation was used for activity coefficient calculation. It proved that B-dot equation is applicable not only in binary or ternary solution systems, but also in quaternary systems. As concluded from thermodynamic modeling, the As species are presented as H$_3$AsO$_4^-$ and H$_2$AsO$_4^-$ for As(V), and H$_3$AsO$_5^-$ and AsO$_4^{3-}$ for As(III). The speciation of Sb is similar to As, including H$_2$SbO$_4^-$ (or Sb(OH)$_6^-$) and H$_3$SbO$_4^-$ (or H$_2$Sb(OH)$_6^-$) for Sb(V), and SbO$_4^{3-}$ and H$_3$SbO$_3^-$ for Sb(III). Copper species are in form of Cu$^{2+}$, CuSO$_4^{3-}$ and CuHSO$_4^+$. The model calculation indicates that species distribution is strongly dependent on pH, but weakly dependent on both solution concentration and temperature. The speciation model was further validated through experimental electrical conductivity of electrolytes. The quantification of Cu, As and Sb species can be possibly removed based on their charge state in the copper electrorefining.

1.4.5 Solubility study in Sb(III)-Sb(V)-H$_2$SO$_4$-H$_2$O at 25°C

In addition, antimony solubility and speciation in aqueous sulfuric acid at 298K were also reported by casas et al. [40], in which the species of Sb were similar to that of the above literature, with exception of H$_2$SbO$_3^-$ and H$_4$SbO$_4^+$ (or Sb(OH)$_4^+$). The possible Sb(III) species include H$_2$SbO$_3^-$, H$_3$SbO$_5^-$ and H$_4$SbO$_3^+$ (or SbO$^+$). The possible Sb(V) species include H$_2$SbO$_4^-$ (or Sb(OH)$_6^-$), H$_3$SbO$_4^-$ (or H$_2$Sb(OH)$_6^-$) and Sb(OH)$_4^+$. The bulk solutions are made of 20-50g total Sb and 0-6M H$_2$SO$_4$. The specific interaction (SIT) model is used to calculate activity coefficients of dissolved species. This model is capable of predict activity coefficient in concentrated solutions of ionic strength up to 3-4M [41]. It includes non-specific electrostatic
long-range interactions from Debye-Hückel term. It also involves short range specific cation-anion, ion-molecule and molecule-molecule interactions, describing the concentration dependence of complex equilibria. The speciation results show that the concentration of dissolved species for antimony was highly dependent of solution acidity. Several species can be formed at various pH and temperature, with the principal ones being $\text{H}_3\text{SbO}_3^0$ and $\text{H}_3\text{SbO}_4^0$. At acidity $< 2$ mol/kg, $\text{Sb}_2\text{O}_5$ (V) is mainly distributed as undissociated antimonic acid $\text{H}_3\text{SbO}_4^0$ and small amounts of $\text{H}_4\text{SbO}_4^+$ and $\text{H}_2\text{SbO}_4^-$. At higher acidity, the predominant species are $\text{H}_3\text{SbO}_4$ and $\text{H}_2\text{SbO}_4^-$. In contrast, $\text{Sb}_2\text{O}_3$ (III) is mainly dissolved as undissociated antimonous acid $\text{H}_3\text{SbO}_3^0$ and $\text{H}_4\text{SbO}_3^+$ at all studied solution acidities. Comparison of ionic conductivity of tested solutions from experimental measurements and theoretical calculation was made for model validation, thus allowing the prediction of Sb(III) and Sb(V) solubilities at various solution acidities.

1.5 Scope of the present work

In the present study, we aim to develop a complicated thermodynamic speciation modeling in aqueous solutions most relevant to industrial copper electrorefining condition, targeting on quantification of impurity ions including Fe(II and III), Cu(II), As(III and V), Sb(III and V) and Bi(III) in sulfuric acid solutions from 25°C to 70°C. The speciation modeling results will be used to calculate redox potential using the Nernst equation and then validated by comparing with experimental oxidation and reduction potential (ORP) measurements. ORP is chosen as it is easy to measure and highly related to the redox couple, current density and impurity behavior in the studied solutions and temperature. The total concentrations of targeted elements are $\text{H}_2\text{SO}_4$ 185 g/L, Fe 1-6 g/L, Cu 40-50 g/L, As 5 g/L, Sb 0.2 g/L, Bi 0.1 g/L.
Controlling of the amount of impurity elements with different valence can provide a new insight and deeper understanding into the electrolyte, the behavior of those impurity ions and thus the formation mechanism of floating slimes. This can assist chemistry control (amount of As, Sb and Bi) during copper anode casting and electrolyte in tank house. Detailed modeling and experimental results regarding redox potential and species distribution in several aqueous systems, along with effect of temperature, pH, ionic strength and nominal Fe$^{3+}$/Fe$^{2+}$ ratios (total concentration of Fe(III) to Fe(II) initially added to the solutions) will be discussed, and hence to shed light on potential optimization of refining process parameters.
Chapter 2: Thermodynamic data identification, collection, and evaluation

2.1 Introduction

When impurity elements are present in sulfuric acid solutions, they generally distribute as soluble species including simple cations or anions, neutral species, charged ionic complexes, and solid precipitates. Moreover, there are some factors that can influence the equilibrium state of those solution systems such as various solvents, species activities, concentrations, temperatures, solubilities, and electric motive force [42].

In order to understand the detailed speciation distribution throughout the entire work, the Thermodynamic model of the Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H_2SO_4 system was firstly separated into aqueous Fe(II, III)-Cu(II)-H_2SO_4 to test the compatibility of the speciation model and then As(III, V)-Sb(III, V)-Bi(III)-H_2SO_4 systems will be combined because of relatively lower amounts of total As, Sb and Bi compared to those of total H_2SO_4 and Cu(II) in electrorefining solutions. The species from each sub-system including Fe(II, III)-H_2SO_4-H_2O, Cu(II)-H_2SO_4-H_2O, As(III, V)-H_2SO_4-H_2O, Sb(III, V)-H_2SO_4-H_2O and Bi(III)-H_2SO_4-H_2O will be analyzed respectively, and finally considered as an entire system.

2.2 Species and thermodynamic data in Fe(II, III)-Cu(II)-H_2SO_4-H_2O solutions

Modeling the speciation requires reliable values of the thermodynamic properties (such as ΔG_f° and S°) for all species existing in the system. These properties include the standard Gibbs free energy of species to calculate the equilibrium constants from 25°C to 70°C, and the activity coefficients of species to describe the non-ideal thermodynamic behavior. Criss-Cobble ion correspondence entropy method is used to calculate equilibrium relationship at room or elevated temperature. Details about this method are presented in Section 3.4.
2.2.1 Species and thermodynamic data in Fe(II, III)-H₂SO₄-H₂O solutions

Sulfate association of Fe(III) or Fe(II) is much stronger than its water association with proton. Fe species mostly distribute as iron sulfate complexes in sulfate media [38]. In aqueous Fe(II, III)-H₂SO₄-H₂O solutions, species including H⁺, Fe²⁺, Fe³⁺, SO₄²⁻, HSO₄⁻, FeHSO₄⁺, FeSO₄⁰, FeHSO₄²⁺, Fe(SO₄)₂−, FeSO₄⁺ and H₂O already have been identified from 25°C to 150°C depending on the solution conditions [28-29, 43]. Fe₂O₃ is excluded due to its formation at relatively higher temperature and will not be considered in this work.

Reactions involved in sulfuric acid solutions were also collected and reviewed from above published literature, together with their standard equilibrium constants and related thermodynamic data as listed in Table 2.1.

2.2.2 Species and thermodynamic data in Cu(II)-H₂SO₄-H₂O solutions

For Cu(II) species in H₂SO₄, it has been widely reported that copper(II) sulfate pentahydrate, CuSO₄·5H₂O, could readily dissolve in sulfuric acid to form species including Cu²⁺ and CuSO₄⁰ [36, 43-46]. These aqueous neutral (CuSO₄⁰) and ionic species (Cu²⁺) were found to be very stable under solutions with high acidity. In addition, Horányi [47] reported that addition of Cu²⁺ ions in the form of perchlorate to a system containing SO₄²⁻ or HSO₄⁻ ions may result in a decrease in the concentration of those ions which may be ascribed to the formation of CuSO₄⁰ or CuHSO₄⁺ molecules or ion-pairs. This suggests the possible existence of copper bisulfate ion complex, CuHSO₄⁺, as one of Cu(II) species. Then, the value of Log $K_f^p = 2.34$ for CuHSO₄⁺, was reported and collected in the stability constants of metal complex database by Smith et al. [48] and was also employed in the MINTEQ software [49]. Following that, copper bisulfate ion complex, CuHSO₄⁺, has been included in speciation studies by different researchers
in various fields such as copper electrorefining and electrowinning, electrodialysis, leaching, mining and ecosystem [36], [39] [50-55]. In this work, we figured out that the inclusion of this species, CuHSO$_4^+$, always gave a better fit to the experimentally measured data. Hence, it is believed that CuHSO$_4^+$ is a stable species under the conditions of temperature and solution composition studied in the present acidic iron copper sulfate solutions and thus it is included in the present study.

In addition, the thermodynamic data ($\Delta G^\circ$ and $S^\circ$) for Cu$^{2+}$ was reported by Bard et al. [56], but for other Cu(II) species such as CuSO$_4^0$ and CuHSO$_4^+$ data could not be found directly from published literatures. Hence, an estimation of those data was made based on equilibrium constants of reactions.

$$\text{Cu}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{CuSO}_4^0 \quad (2.1)$$

$$\text{Cu}^{2+} + \text{H}^+ + \text{SO}_4^{2-} \leftrightarrow \text{CuHSO}_4^+ \quad (2.2)$$

The Log $K_f^\circ = 2.36$ for Reaction 2.1 at 25°C was published by Casas et al. [44] and Cifuentes et al. [43] in sulfuric acid solutions. The same value was also reported in MINTEQ 3.1 software [49], which generally agrees with the value (Log $K_f^\circ = 2.35\pm0.05$) recommended by IUPAC after rigorous review from various sources [45]. Thus Log $K_f^\circ = 2.36$ for the above reaction was employed in the study, hence leading to a calculated value of $\Delta G_f^\circ = -692.40$ kJ/mol for CuSO$_4^0$ at 25°C. As to CuHSO$_4^+$, similarly, $\Delta G_f^\circ = -692.29$ kJ/mol was estimated using the reported Log $K_f^\circ = 2.34$ at 25°C for Reaction 2.2 from the literature [36], [48-51].

As to the entropy ($S^\circ$) for the two Cu(II) species, the published Log $K_f^\circ$ values of 2.36 at 25°C and 2.46 at 35°C for CuSO$_4^0$ [43-44], [49], and 2.34 at 25°C and 3.45 at 60°C for CuHSO$_4^+$ [36], [48-51] were used for this calculation. Firstly, van’t Hoff equation was used to calculate enthalpy change of the formation reactions, $\Delta H_f^\circ$ and is expressed below:
\[
\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ_r}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]  

(2.3)

Due to its negligible change under lower temperatures from 25°C to 60°C, it was assumed to be a constant. Secondly, entropy change $\Delta S^\circ$ of the formation reactions were calculated according to equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Finally, the $S^\circ$ for CuSO$_4^o$ and CuHSO$_4^+$ was estimated based on $\Delta S^\circ$ of Reaction 2.1 and Reaction 2.2, and the known $S^\circ$ of the remaining Cu$^{2+}$ and HSO$_4^-$ species. The $S^\circ$ of 27.10 and 170.66 J K$^{-1}$ mol$^{-1}$ for CuSO$_4^o$ and CuHSO$_4^+$ were thus obtained, respectively.

Please note that for the sake of maintaining internal consistency, the Log$K_f^\circ$ of all the species partaking in these equilibria are based on the values reported in the same sources. Table 2.1 shows the summary of main species and their standard thermodynamic data both from literatures and estimation, as well as equilibrium formation constants in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions at 25°C.
<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^o$ (kJ/mol)</th>
<th>$S^o$ (J/mol)</th>
<th>Species and Formation Reactions</th>
<th>Log $K_f^o$ at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>−744.63</td>
<td>20.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSO$_4^-$</td>
<td>−756.01</td>
<td>131.8</td>
<td>H$^+$ + SO$_4^{2-}$ ↔ HSO$_4^-$</td>
<td>1.98</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>−91.2</td>
<td>−107.1</td>
<td></td>
<td></td>
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<tr>
<td>FeHSO$_4^+$</td>
<td>−841.99</td>
<td>134.19</td>
<td>Fe$^{2+}$ + H$^+$ + SO$_4^{2-}$ ↔ FeHSO$_4^+$</td>
<td>1.08</td>
</tr>
<tr>
<td>FeSO$_4^+$</td>
<td>−848.67</td>
<td>3.26</td>
<td>Fe$^{2+}$ + SO$_4^{2-}$ ↔ FeSO$_4^+$</td>
<td>2.25</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>−16.7</td>
<td>−280.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeHSO$_4^{2+}$</td>
<td>−775.48</td>
<td>34.97</td>
<td>Fe$^{3+}$ + H$^+$ + SO$_4^{2-}$ ↔ FeHSO$_4^{2+}$</td>
<td>2.48</td>
</tr>
<tr>
<td>FeSO$_4^+$</td>
<td>−784.38</td>
<td>−5.93</td>
<td>Fe$^{3+}$ + SO$_4^{2-}$ ↔ FeSO$_4^+$</td>
<td>4.04</td>
</tr>
<tr>
<td>Fe(SO$_4$)$_2^-$</td>
<td>−1524.6</td>
<td>423.16</td>
<td>Fe$^{3+}$ + 2SO$_4^{2-}$ ↔ Fe(SO$_4$)$_2^-$</td>
<td>5.38</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>−237.18</td>
<td>69.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>65.7</td>
<td>97.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuSO$_4^+$</td>
<td>−692.40</td>
<td>27.10</td>
<td>Cu$^{2+}$ + SO$_4^{2-}$ ↔ CuSO$_4^+$</td>
<td>2.36</td>
</tr>
<tr>
<td>CuHSO$_4^+$</td>
<td>−692.29</td>
<td>170.66</td>
<td>Cu$^{2+}$ + H$^+$ + SO$_4^{2-}$ ↔ CuHSO$_4^+$</td>
<td>2.34</td>
</tr>
</tbody>
</table>

NOTE: Thermodynamic data ($\Delta G^o$ and $S^o$) for Cu$^{2+}$, CuSO$_4$ and CuHSO$_4^+$ were collected and estimated based on $\log K_f^o$ values at different temperatures reported from the literature [36], [43-44], [48], [50-51], [56] (see text for details). Other thermodynamic data ($\Delta G^o$, $S^o$ and Log$K_f^o$) were taken directly from the literature [28-29], [43], [56].
2.3 Species and thermodynamic data in As(III, V)-Sb(III, V)-Bi(III)-H₂SO₄-H₂O solutions

2.3.1 Ion interactions among As, Sb and Bi in copper electrorefining

As, Sb and Bi behave differently in aqueous acidic and alkaline solutions. The distribution of various species in aqueous solutions is dependent on its potential to pH domain according to Pourbaix diagram [57]. Aqueous species involved in the present study were identified and critically assessed from available sources.

Tremendous work has been conducted so far regarding the formation mechanism of slimes brought up by As, Sb and Bi. Wang et al. [58] has revealed that the formation of arsenato antimononic acid (AAAc) to various species is caused by combination of As(V) and Sb(V) through Sb-O-Sb and As-O-Sb structural bond in aqueous refining solutions, which is considered as pioneering work elucidating the formation mechanism of floating slimes. The existence of arsenato antimonates was later confirmed by examining floating slimes precipitates using infrared spectroscopy [23]. It is also suggested by Wang et al. [24] that 7 g/L of arsenic in the electrolyte is required to generate sufficient slime fall to reduce floating slime formation. Major slime compounds were also identified by XRD analysis including crystalline SbAsO₄, BiAsO₄, As₂O₃, Sb₂O₃, Bi₂O₃ [11], [26], [59-60].

The presence of above crystalline compounds or amorphous slimes mainly depends on oxidation state and concentration of As, Sb and Bi as well as temperature. As, Sb and Bi initially entering into refining solutions and after hydrolyzation are in trivalent state of AsO⁺, H₃AsO₃⁰, SbO⁺, H₃SbO₃⁰, Bi³⁺ and BiO⁺, then partially oxidized to pentavalent state forming H₃AsO₄⁰ and H₃Sb(OH)₆⁰ by the air (O₂) dissolved in the refining electrolyte, while Bi species always remain in trivalent state [24], [27], [61-63]. Furthermore, Sb(V) plays an important role in the formation of floating slimes. Absence of Sb(V) cannot lead to the precipitates of arsenato antimonates. The
quantity of floating slime increases with increasing concentration of Sb(V) according to the literature [9], [23-24], [60], [64-65]. Because the oxidation rate of As\(^{3+}\) is notably faster than that of Sb\(^{3+}\), As(III) oxidizing to As(V) by dissolved O\(_2\) takes place prior to the same process of Sb(III) to Sb(V). The content of Sb(III) and Sb(V) strongly depends on concentration and valence of As in industrial solutions [62], [66]. Wang et al. [24] stated that maintaining mole ratio of As(III)/As(V) < 0.09 is critical to the oxidation reaction of Sb(III) to Sb(V). Moreover, copper deposits become more brittle with increasing concentrations of Sb. It was found that when [Sb] > 300 ppm in the electrolyte, brittle copper deposits are produced, and it has been confirmed through bend tests [67-68]. In commercial copper refineries, arsenic is commonly added to the anodes to maintain a molar ratio of As/(Sb+Bi)>2.0 to improve ductility of cathode starter sheet [69-70]. Therefore maintaining a certain content of As in refining solution is beneficial to control floating slime as it slows down oxidation rate of Sb(III) to Sb(V), thus inhibiting excessive generation of Sb(V). The amount of As, Sb and Bi can have an influence on their species distribution.

2.3.2 Species and thermodynamic data in As(III, V)-H\(_2\)SO\(_4\)-H\(_2\)O system

Arsenic species dissolved from its oxide forms in aqueous sulfuric acid solutions has been widely reported in hydrometallurgical literature. The principal As(III) species by dissolution of arsenic trioxide (As\(_2\)O\(_3\)) is arsenious acid, H\(_3\)AsO\(_3\)(aq), which remains undissociated in water and exist at nearly all pH values [36], [71-73]. However, under extreme acidic conditions, As\(^{3+}\) has strong tendency to hydrolyze and form arsenyl ion, AsO\(^+\) (or H\(_4\)AsO\(_5^+\)), typically at pH < -0.3 [74-77]. The pH effect on distribution of As(III) species and Eh-pH diagram of aqueous As(III) species are shown in Figure 2.1 and Figure 2.2, respectively.
Figure 2.1: The effect of PH on distribution of various arsenic (III) species [76].

Figure 2.2: Eh-pH equilibrium diagram for the system arsenic-water at 25°C and at unit activity of all species [77].
The species AsO\(^+\) is generated from the protonation of arsenious acid H\(_3\)AsO\(_3\)^\(o\) (or HAsO\(_2\)^\(o\)). Its formation refers to Reaction 2.4 according to published literature [36], [78-79]. Therefore, H\(_3\)AsO\(_3\)^\(o\) and AsO\(^+\) are selected as the major As(III) species in the present work since they were mostly mentioned in copper hydrometallurgical studies.

\[
\text{H}_3\text{AsO}_3^o + \text{H}^+ \leftrightarrow \text{AsO}^+ + 2\text{H}_2\text{O} \quad (2.4)
\]

Reliability of modeling on the current solutions highly depends on the thermodynamic data sources. Discrepancy between two different thermodynamic values of same species can result in great uncertainties when extrapolating LogK\(_f^o\) value for a given chemical reaction. For the purpose of maintaining internal consistency, the standard thermodynamic values of \(\Delta G_f^o\) and \(S^o\) for above two As(III) species were taken from the same source as reported by Bard et al. [56] to calculate equilibrium constants of Reaction 2.4 at 25°C. An exception is for the value of \(S^o(\text{AsO}^+)\) due to lack of direct data. Hu [80] has reasonably estimated this value in terms of Latimer’s method [81] using individual entropy contributions of the element (arsenic) and the ligand (oxygen). The value of \(S^o(\text{AsO}^+) = 15.52 \text{ J K}^{-1} \text{ mol}^{-1}\) was obtained by \(S^o(\text{AsO}^+) = S^o(\text{As}) + S^o(\text{O})\), thereby it was employed for model calculation in the current study.

In solutions with high concentration of H\(_2\)SO\(_4\), pentavalent arsenic (V) can be present as stable arsenic acid H\(_3\)AsO\(_4\)^\(o\) and arsenic anion H\(_2\)AsO\(_4\)^\(-\) according to pH effect on species distribution [36], [72], [76], [79], [82-84]. The pH effect on distribution of As (V) species is indicated in Figure 2.3.
Figure 2.3: The effect of pH on distribution of various arsenic (V) species [76].

\[ H_3AsO_4^\circ \text{ deprotonates at a somewhat higher pH based on Reaction 2.5} \ [84]. \text{ It is believed that As(V) will distribute mostly as } H_3AsO_4^\circ \text{ and a small percentage of } H_2AsO_4^- \text{.} \]

\[ H_3AsO_4^\circ \leftrightarrow H_2AsO_4^- + H^+ \quad (2.5) \]

The thermodynamic data of \( H_3AsO_4^\circ \) was taken from Bard et al.[56], and data of \( H_2AsO_4^- \) was referred from Nordstrom et al.[84] after critical review.

2.3.3 Species and thermodynamic data in Sb(III, V)-H_2SO_4-H_2O system

Antimony forms two oxygen acids, antimonous (Sb(III)) and antimonic (Sb(V)) acids. The first one, \( H_3SbO_3^\circ \) (also called antimony (III) hydroxide, \( Sb(OH)_3^\circ \) or \( HSbO_2^\circ \)), exists only as its salts, the antimonites. The second one, \( H_3SbO_4^\circ \) is found only as the hydrate, \( H_3SbO_4\cdot 2H_2O = H[Sb(OH)_6] \). These two Sb (III and V) acids can be prepared from their oxide
forms. There are three antimony oxides: the trioxide, Sb$_2$O$_3$, is the anhydride of antimonous acid; the pentoxide, Sb$_2$O$_5$, is the anhydride of antimonic acid; and the tetroxide, Sb$_2$O$_4$, is a mixed anhydride of these two acids [85].

The behavior of Sb (III) species is similar to that of As (III). Casas et al. [40] reported the speciation and solubility studies of both antimony (III) and antimony (V) in concentrated sulfuric acid solutions up to 6M. The solubility results show that the concentration of dissolved species for antimony was highly dependent of solution acidity. The major aqueous Sb(III) species are SbO$^+$ and H$_3$SbO$_3^\circ$. The same results were also noted by Senanayake and Muir [38]. The antimonyl ion, SbO$^+$ (or H$_4$SbO$_3^+$), forms similarly to AsO$^+$ under extreme acidic condition [38], [61], [72]. SbO$^+$ originates from protonation of antimonous acid H$_3$SbO$_3^\circ$ (or HSbO$_2^\circ$), which is shown in Reaction 2.6 [38], [62], [86-88]. Therefore, it will be selected for modeling calculation as one of Sb (III) species as well as SbO$^+$ and H$_3$SbO$_3^\circ$ in the present work. Thermodynamic data of $\Delta G^\circ$ and $S^\circ$ for the three Sb(III) species were all taken from literature [56].

$$H_3SbO_3^\circ + H^+ \leftrightarrow SbO^+ + 2H_2O \quad (2.6)$$

Conversely, the species of Sb(V) differs from that of As(V). Pentavalent Sb(V) exists mainly as Sb(OH)$_6^-$ at pH > 2.7 and H$_3$SbO$_4^\circ$ at pH < 2.7 in aqueous solutions [89]. Casas et al. [40] pointed out the concentration of aqueous antimony (III and V) species is highly dependent on solution acidity. Antimonic acid, H$_3$SbO$_4^\circ$ (or HSb(OH)$_6^\circ$), was considered as the major dissolved Sb(V) species from Sb$_2$O$_5$ in sulfuric acid systems. Baes and Mesmer stated that Sb(V) forms a series of polymeric ionic complex such as Sb$_{12}$(OH)$_{64}^{4+}$ to Sb$_{12}$(OH)$_{67}^{7-}$ as a function of solution pH with concentration of Sb(V) greater than 0.001M, below which, Sb(V) occurs as Sb(OH)$_5^\circ$ (often written as hydrated HSb(OH)$_6^\circ$) or Sb(OH)$_6^-$ depending on pH value of solutions.
The formation of HSB(OH)$_6^0$ is summarized in Reaction 2.7 with LogK$_f^\rho$ = -2.72 [86-87], [90].

Additionally, pKa = 2.55 (LogK$_f^\rho$ = -2.55) for Reaction 2.7 was mentioned by Perrin [91] under (CH$_3$)$_4$NH$_4$Cl solutions with ionic strength I=0.5M when Sb concentration is less than 10$^{-3}$ M. The same dissociation constant pKa = 2.55 for HSB(OH)$_6^0$ was also announced by Wiberg [85]. HSB(OH)$_6^0$ is considered monobasic acid, approximately as strong as acetic acid. It forms salts (Hexahydroxoantimonate (V)) with the formula M[SB(OH)$_6$]. This value will not be considered in the present study because of the inconsideration of ionic strength in the solutions, and not much detailed information could be found from the original source.

\[
\text{HSB(OH)$_6^0$} \leftrightarrow \text{Sb(OH)$_6^-$} + \text{H}^+ \quad \text{LogK}_f^\rho = -2.72 \quad (2.7)
\]

Since the total concentration of Sb(V) is very low in this work, it is predicted that most amount of Sb(V) distributes as oxidation state of HSB(OH)$_6^0$ while minor percentage as Sb(OH)$_6^-$ in the solutions with high acidity. Furthermore, hydrated antimonic acid (HSB(OH)$_6^0$) is generally believed to form by oxidation of trivalent SbO$_2^+$ with dissolved O$_2$ in refining electrolyte. It has been widely mentioned in the laboratory research of floating slime formation, crystalline phase analysis and valence effect on impurity removal on the basis of copper electrorefining [24], [26-27], [61-62]. HSB(OH)$_6^0$ and Sb(OH)$_6^-$ are thus selected as the main Sb(V) species in the current solutions.

The standard thermodynamic data ($\Delta G_f^\rho$ and $S^\circ$) regarding Sb(OH)$_6^-$ and HSB(OH)$_6^0$ are not directly available form literature. An estimation method is therefore needed to obtain these values. Smith and Martell [90] has only reported the value of $\Delta G_f^\rho$($\text{Sb(OH)$_5^-$}$) = -986.5 kJ mol$^{-1}$, while no other corresponding thermodynamic data ($S^\circ$ and $\Delta H_f^\rho$) is available. Since formation of HSB(OH)$_6^0$ equals to Sb(OH)$_5$ + H$_2$O, the $\Delta G_f^\rho$(HSB(OH)$_6^0$) = -1223.7 kJ mol$^{-1}$ can be easily
calculated by the sum of $\Delta G_f^\circ(Sb(OH)_6^\circ)$ and $\Delta G_f^\circ(H_2O)$. The way to obtain $\Delta G_f^\circ(HSb(OH)_6^\circ)$ is also applicable to calculate entropy of $S^\circ(HSb(OH)_6^\circ)$ for reactions of hydrolyzation. Pitman et al. [87] has extrapolated formation energy $\Delta G_f^\circ(Sb(OH)_6^\circ) = -1225.9$ kJ mol$^{-1}$ based on equilibrium formula of $2Sb(OH)_6^- + 2H^+ \leftrightarrow Sb_2O_5 + 7H_2O$ by collecting solubility data in HCl of various concentration. If this value is used, it leads to a Log$K_f^\circ = 0.39$ on Reaction 2.7 that differs a lot with above-noted Log$K_f^\circ = 2.72$. In addition, the extrapolation does not take consideration of solution ionic strength, which is the same case for pKa=2.55 of $HSb(OH)_6^\circ$ reported by Wiberg [85]. It will not be adopted in the present study. By using chemical equilibrium calculation ($\Delta G_f^\circ(HSb(OH)_6^\circ) = -1223.7$ kJ mol$^{-1}$ and Log$K_f^\circ = -2.72$) on Reaction 2.7, a value ($\Delta G_f^\circ = -1208.17$ kJ mol$^{-1}$) of $Sb(OH)_6^\circ$ is achieved and will be used for model simulation.

To our knowledge, no value of $S^\circ(Sb(OH)_6^-)$ or $S^\circ(HSb(OH)_6^\circ)$ has been ever published before. A method was introduced from Yue et al. [29] to assess an unknown $S^\circ$ value of a species, simply using Equation 2.8 based on the known $\Delta S^\circ$ and $S^\circ$ of the remaining species from Reaction 2.7. Besides, the calculation herein requires formation enthalpy of $\Delta H_f^\circ(Sb(OH)_6^-)$, which still remains unavailable from sources. However, sufficient thermodynamic data regarding $Sb(OH)_6^-$ involved in Reaction 2.9 at different temperatures from various sources has been compiled by Lothenbach et al. [92], in which equilibrium constant Log$K_f^\circ = -15.72$ at 293K from Pitman et al. [87] and Log$K_f^\circ = -15.19$ at 300K from Haight [93] both in KOH solutions were evaluated.

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S^\circ \quad (2.8)$$

$$Sb(OH)_6^- + 2e^- \leftrightarrow Sb(OH)_4^\circ + 2OH^- \quad (2.9)$$

These above two Log$K_f^\circ$ values at 293K and 300K for Reaction 2.9 were adopted in this work, thus allowing to calculate formation enthalpy change ($\Delta H_f$) by using van’t Hoff equation
Since variation from 293K to 300K is very close to room temperature, the formation enthalpy of Sb(OH)$_6^{3-}$, Sb(OH)$_4^{-}$ and OH$^{-}$ only leads to a small deviation from their standard values at 298K. It can be assumed that the above calculated formation enthalpy change ($\Delta H_f$) equals to standard formation enthalpy change ($\Delta H_f^o$) at 298K. Accordingly, the $\Delta H_f^o$(Sb(OH)$_6^{3-}$) = -1577.01 kJ mol$^{-1}$ is acquired and then plugged into Equation 2.8 based on Reaction 2.9, resulting in $S^o$(Sb(OH)$_6^{3-}$) = 11.17 J mol$^{-1}$ K$^{-1}$ (relevant data of Sb(OH)$_4^{-}$ and OH$^{-}$ also taken from ref [56]). The $\Delta H_f^o$(HSb(OH)$_6^{0}$) = -1478.6 kJ mol$^{-1}$ was obtained from literature [56], [71]. Therefore, based on the known $\Delta G_f^o$, $\Delta H_f^o$ and $S^o$ values for species Sb(OH)$_6^{3-}$, and known $\Delta G_f^o$ and $\Delta H_f^o$ values for species HSb(OH)$_6^{0}$, the $S^o$(HSb(OH)$_6^{0}$) = 393.32 J mol$^{-1}$ K$^{-1}$ can be attained from Reaction 2.7 according to Equation 2.8 by equilibrium relationship.

2.3.4 Species and thermodynamic data in Bi(III)-H$_2$SO$_4$-H$_2$O system

Bismuth only exists in trivalent state in electrorefining solutions [24], [26-27], [61-62]. The effect of pH on species distribution of Bi(III) in water at 25°C has been studied by Senanayake and Muir [38], in which BiO$^+$ (or Bi(OH)$_2^+$) and Bi$^{3+}$ coexist in acidic solutions at low pH<3. It has been commonly assumed that Bi$^{3+}$ ions initially entering into refining solutions from anode hydrolyze to BiO$^+$ as indicated by Reaction 2.10. Both BiO$^+$ and Bi$^{3+}$ can potentially react with As(V) and Sb(V) to produce crystalline precipitates and slime compounds [24], [26], [61].

$$\text{BiO}^+ + 2\text{H}^+ \leftrightarrow \text{Bi}^{3+} + \text{H}_2\text{O} \quad (2.10)$$

Thermodynamic data of the two Bi(III) species were taken from SUPCRTBL software [94], which agree with the values compiled in HSC 7.0 database [95] that takes advantage of the Criss-Cobble principle to calculate equilibrium relationships at elevated temperature, as reported
by Mambote et al. [42] and Hiskey [61]. SUPCRTBL was used in this work because it is equipped with a more recent mineral database of Holland and Powell [96] and modifies the computer code to accommodate the different heat capacity function, volume as a function of temperature and pressure, mineral phase transition, etc. It provides sufficient thermodynamic data for the two targeted Bi(III) cations, while $S^\circ$($\text{BiO}^+$) is unavailable in HSC 7.0 database.

**Table 2.2** shows the summary of adopted As(III, V), Sb(III, V) and Bi(III) species and their standard thermodynamic data (Gibbs free energy and entropy) both from literature and estimation, as well as equilibrium formation constants at 25°C.
### Table 2.2: Thermodynamic data and equilibrium formation constants at 25°C for the main species in aqueous As(III, V)-Sb(III, V)-Bi(III)-H₂SO₄-H₂O solutions.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>Ref</th>
<th>$S^\circ$ (J/mol)</th>
<th>Ref</th>
<th>Species and Formation Reactions</th>
<th>Log $K_f^\circ$ 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$AsO$_3$</td>
<td>-639.9</td>
<td>[56]</td>
<td>196.6</td>
<td>[56]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsO$^+$</td>
<td>-163.8</td>
<td>[56]</td>
<td>12.52</td>
<td>[80]</td>
<td>H$_3$AsO$_3$ + H$^+$ $\leftrightarrow$ AsO$^+$ + H$_2$O</td>
<td>-0.31</td>
</tr>
<tr>
<td>H$_2$AsO$_4^-$</td>
<td>-753.575</td>
<td>[84]</td>
<td>106.55</td>
<td>[84]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_3$AsO$_4$</td>
<td>-766.42</td>
<td>[56]</td>
<td>188</td>
<td>[56]</td>
<td>H$_2$AsO$_4^-$ + H$^+$ $\leftrightarrow$ H$_3$AsO$_4$</td>
<td>2.30</td>
</tr>
<tr>
<td>SbO$^+$</td>
<td>-175.64</td>
<td>[56]</td>
<td>22.33</td>
<td>[56]</td>
<td>H$_3$SbO$_3$ + H$^+$ $\leftrightarrow$ SbO$^+$ + 2H$_2$O</td>
<td>0.91</td>
</tr>
<tr>
<td>H$_3$SbO$_3$</td>
<td>-644.8</td>
<td>[56]</td>
<td>116.3</td>
<td>[56]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(OH)$_6^-$</td>
<td>-1208.17</td>
<td>Est</td>
<td>11.17</td>
<td>Est</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSb(OH)$_6^-$</td>
<td>-1223.7</td>
<td>Est</td>
<td>393.32</td>
<td>Est</td>
<td>Sb(OH)$_6^-$ + H$^+$ $\leftrightarrow$ HSb(OH)$_6$</td>
<td>2.72</td>
</tr>
<tr>
<td>BiO$^+$</td>
<td>-122.591</td>
<td>[94]</td>
<td>79.914</td>
<td>[94]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>95.73</td>
<td>[94]</td>
<td>-188.28</td>
<td>[94]</td>
<td>BiO$^+$ + 2H$^+$ $\leftrightarrow$ Bi$^{3+}$ + H$_2$O</td>
<td>3.30</td>
</tr>
</tbody>
</table>

#### 2.4 Precipitates among As, Sb and Bi during copper electrorefining

Trivalent As(III) is initially dissolved into solution during electrorefining, then oxidized with dissolved O$_2$ to As(V). This process takes place prior to the oxidation of Sb(III) to Sb(V). The presence of adequate As(V) can promote the formation of SbAsO$_4$, thus decreasing the amount of Sb in solution by precipitation to slimes [11], [97-98]. SbAsO$_4$ has been found in commercial slimes [99-101]. XRD powder diffraction has confirmed that SbAsO$_4$ has crystal structure in either synthetic solution precipitates or leached anode slimes [26], [69], [101]. The formation reaction of SbAsO$_4$ can be found in Chapter 1.2. Antimonate precipitate of AsSbO$_4$
was reported in arsenic-rich anode slimes from the Copper Division of Southwire in the United States and other refineries [102-103]. As stated by Xiao et al. [101] that antimonate of $\text{AsSbO}_4$ and $\text{BiSbO}_4$ can also be found in the precipitate from the Sb-rich solution containing Sb(V), As(III) or Sb(V), Bi(III) ions through the possible reaction below:

$$\text{Bi}^{3+} + \text{H}2\text{Sb(OH)}_6^0 \leftrightarrow \text{BiSbO}_4^+ + 3\text{H}^+ + 2\text{H}_2\text{O} \quad (2.11)$$

$$\text{AsO}_4^- + \text{H}2\text{Sb(OH)}_6^0 \leftrightarrow \text{AsSbO}_4^- + \text{H}^+ + 3\text{H}_2\text{O} \quad (2.12)$$

Existence of $\text{BiAsO}_4$ has been widely reported in electrorefining solutions by XRD detection [23], [26], [59-60], [63], [69]. This precipitate with crystalline structure forms in Bi-rich solutions. The formation reaction of $\text{BiAsO}_4$ is shown as follows [26], [61]:

$$\text{Bi}^{3+} + \text{H}_3\text{AsO}_4^0 \leftrightarrow \text{BiAsO}_4^+ + 3\text{H}^+ \quad (2.13)$$

Addition of arsenic at the smelting process is addressed to maintain the proper ratio of $\text{As}/(\text{Sb+Bi})$. Moats et al. [104] has concluded that operational $\text{As}/(\text{Sb+Bi})$ molar ratios and practices in numerous industrial refineries should be maintained at or above 2 to reduce the presence of floating slimes and contamination of the cathode.
Chapter 3: Model development and calculation

3.1 Introduction

The conceptualization of basic speciation model was proposed by Rafal et al. [105] based on mathematical methodology to systematically describe species behavior in an ionic system. In hydrometallurgical process, deposition or precipitate of different salts are known to be determined by the ionic composition. An exact description of a solutions system involving with various metal ions and ligands in terms of concentration is an important task.

Applying speciation model in aqueous system can provide an abundance of information which is difficult to obtain by experimental work. Because of the lack of analytical techniques for in-situ measurements of ions and ionic complexes especially at high temperatures, thermodynamic modeling with experimental validation is a very useful tool to predict the behavior of inorganic species in complex aqueous systems at given conditions, and therefore obtain important data and information most relevant to industrial processes.

3.2 Construction of thermodynamic model

The speciation computation involves the chemical equilibrium equations from 25°C to 70°C, mass and charge balance relationship, B-dot equation and ionic strength for calculation of the concentration of each individual chemical species in a multicomponent chemical system. For modeling calculation at above 25°C, thermodynamic data of each species incorporating standard formation free energy ($\Delta G_f^\circ$) and entropy ($S^\circ$) is required to calculate equilibrium relationship through Criss-Cobble method. An example for Fe(II, III)-Cu(II)-As(III, V)-Sb(III, V)-Bi(III)-H$_2$SO$_4$ aqueous solution system is illustrated in this section.
3.2.1 Chemical equilibrium equations

The first step of constructing chemical speciation model is to specify the various types of species (such as ion, ionic complex and molecule), components and reactions involved in studied solutions at different pH range. Since the studied solutions is highly acidic (pH is usually less than 0), hydroxide ions (OH⁻) will not be considered for this model calculation. Only species in acidic condition are selected. Species collection can be referred to Chapter 2.

The second step is to list up a set of relevant equations that express the equilibrium relationships based on equilibrium constant (K) with a number of unknown concentrations of target species. The calculation of K is based on reaction free reaction change and is shown below:

\[
a \langle A \rangle + b \langle B \rangle \rightarrow c \langle C \rangle + d \langle D \rangle \quad (3.1)
\]

\[
\Delta G_r = \Delta G_r^o + RT \ln \frac{a_c a_d}{a_a a_b} \quad (3.2)
\]

\[
K = \frac{a_c a_d}{a_a a_b} \quad (3.3)
\]

When solutions reach to equilibrium state, Equation 3.2 can be simplified to \( \Delta G^o = -2.303RT\log K^o \), where \( R = 8.314 \text{ J/k·mol} \) is ideal gas constant, \( T(K) \) is temperature on the Kelvin scale. The activity of species, \( a \), represents thermodynamic concentration or active concentration and frequently expresses as \( a = \gamma \cdot C \), where \( \gamma \) is the activity coefficient (between 0 and 1). This coefficient takes into account the non-ideal characteristics of a mixture and it is solved herein by B-dot equation (see next section); \( C \) is the molar concentration of species. When \( \gamma = 1 \), the molar concentration \( C \) and activity \( a \) are numerically equal. The chemical equilibrium equations are shown in Table 2.1 and Table 2.2.
3.2.2 Mass and charge balance

Molal concentration (mol/kg H$_2$O) rather than molarity (mol/L) will be used to avoid volume and density change of solution at elevated temperature. The 5 solution systems in the present study are Fe(II, III)-H$_2$SO$_4$, Fe(II, III)-Cu(II)-H$_2$SO$_4$, Fe(II, III)-Cu(II)-As(III, V)-H$_2$SO$_4$, Fe(II, III)-Cu(II)-As(III, V)-Sb(III, V)-H$_2$SO$_4$ and Fe(II, III)-Cu(II)-As(III, V)-Sb(III, V)-Bi(III)-H$_2$SO$_4$. Mass and charge balance equation for components present in the Fe(II, III)-Cu(II)-As(III, V)-Sb(III, V)-Bi(III)-H$_2$SO$_4$ system, given as an example, are expressed in terms of total amount of Fe(II), Fe(III), Cu(II), As(III), As(V), Sb(III), Sb(V), Bi(III) and SO$_4^{2-}$ and total ionic charge of solutions, respectively as follows. The actual model construction including chemical equilibrium equations, mass and charge balance equations is highly dependent on solution compositions.

Mass balance:

\[
[\text{Fe(II)}] = C_{\text{Fe}^{2+}} + C_{\text{Fe(II)SO}_4} + C_{\text{FeSO}_4}
\]

\[
[\text{Fe(III)}] = C_{\text{Fe}^{3+}} + C_{\text{Fe(II)SO}_4} + C_{\text{Fe(III)SO}_4} + C_{\text{FeSO}_4'}
\]

\[
[\text{Cu(II)}] = C_{\text{Cu}^{2+}} + C_{\text{CuSO}_4} + C_{\text{Cu(II)SO}_4'}
\]

\[
[\text{As(III)}] = C_{\text{As(OH)}_3} + C_{\text{AsO}^{'}}
\]

\[
[\text{As(V)}] = C_{\text{As(OH)}_5} + C_{\text{H}_3\text{AsO}_4}
\]

\[
[\text{Sb(III)}] = C_{\text{SbO}^{'}} + C_{\text{H}_3\text{SbO}_3}
\]

\[
[\text{Sb(V)}] = C_{\text{Sb(OH)}_6} + C_{\text{H}_3\text{Sb(OH)}_6}
\]

\[
[\text{Bi(III)}] = C_{\text{BiO}^{'}} + C_{\text{Bi}^3'}
\]

\[
[\text{SO}_4^{2-}] = C_{\text{SO}_4^{2-}} + C_{\text{HSO}_4} + C_{\text{FeHSO}_4} + C_{\text{FeSO}_4} + C_{\text{Fe(II)SO}_4} + 2C_{\text{Fe(III)SO}_4} + C_{\text{FeSO}_4'} + C_{\text{CaSO}_4} + C_{\text{Ca(II)SO}_4'}
\]
Charge balance:

\[
\begin{align*}
&\text{C}_\text{H}^+ - 2\text{C}_{\text{SO}_4^{2-}} - \text{C}_{\text{HSO}_4} + 2\text{C}_{\text{Fe}^{2+}} + \text{C}_{\text{FeHSO}_4} + 3\text{C}_{\text{Fe}^{3+}} + 2\text{C}_{\text{Fe(HSO)}_4^{2-}} - \text{C}_{\text{Fe(SO)}_4^{2-}} + \text{C}_{\text{FeSO}_4} + 2\text{C}_{\text{Cu}^{2+}} + \\
&\text{C}_{\text{CuHSO}_4} + \text{C}_{\text{AsO}_4^{2-}} + \text{C}_{\text{H}_2\text{AsO}_4} + \text{C}_{\text{SbO}^+} - \text{C}_{\text{Sb(OH)}_6} + \text{C}_{\text{BiO}^+} + 3\text{C}_{\text{Bi}^{3+}} = 0
\end{align*}
\]

3.2.3 Ionic strength

Effective (or real) ionic strength, I, is also considered as a main parameter in the Debye–Hückel theory, which describes the deviations from ideality that happen in ionic solutions.

\[
I = \frac{1}{2} \sum z_i^2 C_i 
\]  \hspace{1cm} (3.4)

The term 1/2 means both ions (cation and anion) are considered. \( z_i \) is the charge number, \( C_i \) is the molal concentration (mol/kg H\(_2\)O) of ionic species. Ionic strength refers to a measure of the concentration of ions present in a particular solution. This concept is based on the dissociation that involves bases, acid, and salts in the presence of aqueous solution. It is representative of the interactions taking place between the ions (attraction and repulsion) of solutions and the ions in water. Ionic strength is also essential for species activity coefficient calculation. It is worth noting that the effective ionic strength varies in this study due to the variation of concentration of ionic species at different temperature (discussed in Chapter 5).

3.3 B-dot equation for activity coefficient

To develop the speciation model in the studied solutions, activity coefficients of species as a function of solution composition and temperature are required to describe the non-ideal thermodynamic behavior of solutions.

The activity coefficient of inorganic solutes can be calculated by using different models reported by Vasil’ev [106], Zemaitis et al. [107] and Pitzer [108]. However, Pitzer’s activity coefficient model is widely accepted [42], [105]. Pitzer’s equations are based on the virial
expansion theory and involved with a large set of interaction coefficients to model systems of
great complexity. The advantage of this model is that it can predict ionic speciation for
concentrated systems with ionic strength up to 10M, while others’ methods are not capable to do
so. Its disadvantage is also obvious. It consists of the large number of empirical parameters that
are temperature dependent, required to quantify the physico-chemical interactions among all the
components present in solution, and which limit its applicability. Consequently, this model will
not be adopted in this study.

An empirical extension of Debye-Hückel models, known as B-dot equation and proposed
by Helgeson was chosen in this work [109-110]. The validity of this expression has been
reported in aqueous solutions with ionic strength up to 1 molal within a temperature range of 0-
300°C. It has been employed by several authors for chemical speciation modeling in
hydrometallurgical applications [28], [29], [36], [50], [111]. Apparently, all the present solutions
are of high ionic strength larger than 1M. They are not diluted due to the existence of high
amount of 185g/L H$_2$SO$_4$ and 40~50g/L Cu(II). However, the parameters for this equation are
relatively easier to be found or estimated than those above-noted models. The validity of B-dot
equation will be examined in the studied aqueous Fe(II, III)-H$_2$SO$_4$ and Fe(II, III)-Cu(II)-H$_2$SO$_4$
systems, then further extended to solutions containing As(III, V), Sb(III, V) and Bi(III). The B-
dot equation is given by the following relationship:

$$\log \gamma_i = -\frac{A_i z_i^2 \sqrt{I}}{1 + a_i B_i \sqrt{I}} + B \cdot I$$

(3.5)

where $A_i$ (kg$^{0.5}$ mol$^{-0.5}$) and $B_i$ (kg$^{0.5}$ mol$^{-0.5}$ cm$^{-1}$) are defined as Debye-Hückel
parameters whose values only depend on the dielectric constant, density and temperature. $\hat{B}$ (kg
mol$^{-1}$) represents the characteristic B-dot parameter, with its value only depending on the
temperature. $a_i$ (Å) is the effective hard-core diameter of species $i$ and $z_i$ denotes the ionic charge
of species $i$. The effective or real ionic strength of the solution, $I$ (mol kg$^{-1}$), stands for a measure of concentration of charged species. $\hat{B}$ (kg mol$^{-1}$) is the characteristic B-dot parameter whose value depends only on the temperature. $A_\gamma$, $B_\gamma$, and $\hat{B}$ values were selected from literature [109-110], [112]. The Debye-Hückel parameters and B-dot values are shown in Table 3.1 from 25°C to 70°C.

**Table 3.1**: Debye-Hückel parameters ($A_\gamma$ and $B_\gamma$) and $\hat{B}$ values as a function of temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>$A_\gamma$ (kg$^{0.5}$ mol$^{-0.5}$)</td>
<td>0.5114</td>
</tr>
<tr>
<td>$B_\gamma$ (kg$^{0.5}$ mol$^{-0.5}$ cm$^{-1}$) (x10$^{-8}$)</td>
<td>0.3288</td>
</tr>
<tr>
<td>$\hat{B}$ (kg mol$^{-1}$)</td>
<td>0.0410</td>
</tr>
</tbody>
</table>

The first term is valid for long-range binary interactions (electrostatic) between anions and cations. The term “$\hat{B}$I” stands for a correction for short-range interactions between dissolved species [28], [36]. The only two species-specific parameters of charge ($z_i$) and hard-core diameter ($\hat{a}_i$) for species were taken from literature [29], [113-116]. The $\hat{a}$ value for Cu$^{2+}$ (6Å), CuHSO$_4^+$ (4Å), AsO$^+$ (4Å), H$_2$AsO$_4^-$ (4.5Å), SbO$^+$ (4Å), Sb(OH)$_6^-$ (4Å), Bi$^{3+}$ (9Å) and BiO$^+$ (4Å) and will be used to calculate activity coefficient by B-dot equation.

### 3.4 Model calculation from 25°C to 70°C

To estimate the standard Gibbs free energy for ionic species at elevated temperature, the HFK model has been widely used to calculate thermodynamic properties due to its coverage over a wider range of temperatures, pressures and dataset [117-118]. However, the model usually requires a large number of parameters i.e. temperature dependent term, aqueous solvent
volumetric and dielectric constants, and pressure properties, which makes the calculation of great complexity. Therefore, HFK model is not preferred here in the present work.

The Criss-Cobble ion entropy correspondence principle provides an optional method to carry out the same evaluation based on available thermodynamic data at room temperature [119-120]. This method has been reported to accurately predict temperature-dependent thermodynamic values up to 200°C [121] and yield valid modeling results under similar hydrometallurgical studies [29], [116]. Therefore, the Criss-Cobble method was selected in the present study.

The Gibbs formation free energy (ΔG^o_f,T) of the studied species above 70°C are obtained by the following expression:

$$\Delta G^o_{f,T} = \Delta G^o_{f,298} - S^o_{298} (T - 298) + \Delta C_p \int_{298}^{T} dT - T \Delta C_p \int_{298}^{T} \frac{dT}{T}$$  \hspace{1cm} (3.6)

In this equation, ΔG^o_{f,298} and S^o_{298} are standard Gibbs free energy and entropy of species at 298K. ΔC_p \int_{298}^{T} represents the mean value of partial molal heat capacity between two temperatures, 298K and T. Please note that the Criss-Cobble principle does not assume ΔC_p of proton (H^+) to be zero. To estimate ΔC_p of a certain aqueous species, the “absolute” standard partial molal ionic entropy at 298K, \( \overline{S}^o_{298} \), is firstly employed.

$$\overline{S}^o_{298}(i) = S^o_{298}(i) - 20.92Z$$  \hspace{1cm} (3.7)

Where S^o_{298} is the conventional (standard) entropy of species i, the number -20.92 means the absolute entropy of the H^+ ion in unit J mol^{-1} K^{-1} at 298K. Z denotes ionic charge. At temperature above 25°C, the absolute ion entropy can be obtained by the following equation:

$$\overline{S}^o_T(i) = a_i + b_i \overline{S}^o_{298}(i)$$  \hspace{1cm} (3.8)
The correspondence principle coefficients $a_t$ and $b_t$ depend on temperature and type of ions (simple anions, simple cations, oxyanions and acid-oxyanions) [119-120]. It was believed that this linear correspondence relationship can accurately predict the values of $S_\tau^\circ$ at least up to 150°C [121]. Consequently, $\Delta C_p \int_{298}^{T} \text{d}T$ can be calculated by the equation below:

$$\Delta C_p(i) \bigg|_{298}^{T} = \frac{S_\tau^\circ(i) - S_\tau^\circ_{298}(i)}{\ln(T/298)} \quad (3.9)$$

Finally, $\Delta G_{f,T}^\circ$ from 25°C to 70°C for each species of interest can be calculated by Equation 3.6 as well as reaction free energy change ($\Delta G_{r,T}^\circ$) from 25°C to 70°C. Thus the calculated equilibrium constants of the main formation reactions from 25°C to 70°C in this study are calculated as shown in Table 3.2.

In order to mathematically describe the chemistry of each studied solutions, calculation of thermodynamic modeling in a system requires several components, including (1) a maximum of 14 chemical equilibrium equations based on those formation reactions from 25°C to 70°C in Table 3.2, (2) activity coefficient calculation of B-dot equation, (3) formula of effective ionic strength of solutions, (4) a maximum of 9 componential mass balance equations in terms of total amount of Fe(II), Fe(III), Cu(II), As(III), As(V), Sb(III), Sb(V), Bi(III) and SO$_4^{2-}$ depending on solution compositions, and (5) one total ionic charge balance equation (the solution must remain electrically neutral) are required to solve a number of up to 23 unknowns as listed in Table 2.1 and Table 2.2. These non-linear equations were eventually solved in a Fortran code by Brent’s method [122-123]. Thereby, parameters including species concentrations, species activity coefficients, pH, ionic strength, and redox potentials can thus be obtained or calculated.
Table 3.2: Standard and calculated equilibrium constants for the main species in aqueous Fe(II, III)-Cu(II)-As(III, V)-Sb(III, V)-Bi(III)-H₂SO₄-H₂O solutions from 25°C to 70°C by Criss-Cobble method.

<table>
<thead>
<tr>
<th>Species and Formation Reactions</th>
<th>LogK° 25°C</th>
<th>LogKf° 40°C</th>
<th>LogKf° 50°C</th>
<th>LogKf° 60°C</th>
<th>LogKf° 65°C</th>
<th>LogKf° 70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺ + SO₄²⁻ ↔ HSO₄⁻</td>
<td>1.98</td>
<td>2.20</td>
<td>2.34</td>
<td>2.49</td>
<td>2.56</td>
<td>2.64</td>
</tr>
<tr>
<td>Fe²⁺ + H⁺ + SO₄²⁻ ↔ FeHSO₄⁺</td>
<td>1.08</td>
<td>1.59</td>
<td>1.91</td>
<td>2.22</td>
<td>2.37</td>
<td>2.52</td>
</tr>
<tr>
<td>Fe²⁺ + SO₄²⁻ ↔ FeSO₄°</td>
<td>2.25</td>
<td>2.37</td>
<td>2.46</td>
<td>2.54</td>
<td>2.59</td>
<td>2.63</td>
</tr>
<tr>
<td>Fe³⁺ + H⁺ + SO₄²⁻ ↔ FeHSO₄²⁺</td>
<td>2.48</td>
<td>3.11</td>
<td>3.50</td>
<td>3.87</td>
<td>4.05</td>
<td>4.22</td>
</tr>
<tr>
<td>Fe³⁺ + 2SO₄²⁻ ↔ Fe(SO₄)₂²⁻</td>
<td>5.38</td>
<td>4.78</td>
<td>5.73</td>
<td>6.62</td>
<td>7.06</td>
<td>7.48</td>
</tr>
<tr>
<td>Fe³⁺ + SO₄²⁻ ↔ FeSO₄⁺</td>
<td>4.04</td>
<td>4.50</td>
<td>4.79</td>
<td>5.08</td>
<td>5.22</td>
<td>5.37</td>
</tr>
<tr>
<td>Cu²⁺ + SO₄²⁻ ↔ CuSO₄°</td>
<td>2.36</td>
<td>2.52</td>
<td>2.62</td>
<td>2.72</td>
<td>2.77</td>
<td>2.82</td>
</tr>
<tr>
<td>Cu²⁺ + H⁺ + SO₄²⁻ ↔ CuHSO₄⁺</td>
<td>2.34</td>
<td>2.86</td>
<td>3.18</td>
<td>3.49</td>
<td>3.64</td>
<td>3.79</td>
</tr>
<tr>
<td>H₃AsO₄° + H⁺ ↔ AsO⁺ + H₂O</td>
<td>-0.31</td>
<td>-0.42</td>
<td>-0.50</td>
<td>-0.60</td>
<td>-0.65</td>
<td>-0.71</td>
</tr>
<tr>
<td>H₂AsO₄⁺ + H⁺ ↔ H₂AsO₄°</td>
<td>2.30</td>
<td>2.38</td>
<td>2.43</td>
<td>2.49</td>
<td>2.53</td>
<td>2.56</td>
</tr>
<tr>
<td>H₃SbO₅⁺ + H⁺ ↔ SbO⁺ + 2H₂O</td>
<td>0.91</td>
<td>0.96</td>
<td>0.98</td>
<td>0.97</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>Sb(OH)₆⁺ + H⁺ ↔ HSb(OH)₆°</td>
<td>2.72</td>
<td>3.56</td>
<td>4.10</td>
<td>4.62</td>
<td>4.87</td>
<td>5.12</td>
</tr>
<tr>
<td>BiO⁺ + 2H⁺ ↔ Bi₃⁺ + H₂O</td>
<td>3.31</td>
<td>2.65</td>
<td>2.25</td>
<td>1.87</td>
<td>1.68</td>
<td>1.51</td>
</tr>
</tbody>
</table>

3.5 ORP calculation and validation for speciation from 25°C to 70°C

It has been reported that the redox couple of Fe³⁺/Fe²⁺ plays an important role in determining the redox potentials in FeSO₄-Fe₂(SO₄)₃-H₂SO₄-H₂O solutions [29], [116], [124-126]. The standard electrode potential E° = 0.771V for Fe³⁺/Fe²⁺ redox couple has been widely used. Specifically, single ion activity coefficients and concentrations for free Fe³⁺ and Fe²⁺ ions (γferric and γferrous; Cferric and Cferrous) obtained from modeling at different temperatures can thus be employed to invoke the Nernst equation:
\[ E = E^\circ + \frac{2.303RT}{nF} \times \log \frac{\gamma_{\text{feric}}}{\gamma_{\text{ferrous}}} + \frac{2.303RT}{nF} \times \log \frac{C_{\text{feric}}}{C_{\text{ferrous}}} \] \quad (3.10)

The electrode potential \( E_T^\circ \) for Fe\(^{3+}/\text{Fe}^{2+} \) redox couple at above 25\(^\circ\)C vs SHE at 25\(^\circ\)C was determined by \( \Delta G_{r,T}^\circ = -nF E_T^\circ \) through Criss-Cobble calculation. This method was used to calculate the ORP values for both Fe(II, III)-H\(_2\)SO\(_4\)-H\(_2\)O and Fe(II, III)-Cu(II)-H\(_2\)SO\(_4\)-H\(_2\)O systems. The ORPs calculated by the Nernst equation from model results were finally used to compare with experimental ORPs.
Chapter 4: Materials and methods

4.1 Electrode preparation

A pure Pt electrode (99.9% of mass percentage, Sigma-Aldrich) in a diameter of 2mm was selected as working electrode. A graphite rod with diameter of 5mm and a saturated Ag/AgCl electrode with glass body (saturated with 4M KCl, Accumet®, Fisher Scientific) were used as a counter electrode (CE) and reference electrode (RE) respectively. The RE was connected to Luggin capillary to minimize IR drop. Before each test, CE was firstly degreased using ethanol and then rinsed with deionized water. The WE was activated in a 0.1M sulfuric acid solution according to a previously published method [127].

4.2 Electrolyte preparation

4.2.1 Electrolyte preparation for Fe(II, III)-Cu(II)-H₂SO₄-H₂O system

The composition of synthetic electrolyte in Fe(II, III)-Cu(II)-H₂SO₄-H₂O system were determined according to the typical industrial conditions of copper electrorefining and are shown in Table 4.1. The nominal Fe³⁺/Fe²⁺ ratios (the ratio of total Fe(III) to total Fe(II) initially added to the solution due to unknown concentration of Fe(III) and Fe(II)) were selected from 0.05 to 50 with a total Fe amount of 1-6 g/L. The typical sulfuric acid concentration is in a range of 150-220 g/L, and 185 g/L was selected as it is the most common concentration in the tank house. The copper concentration was selected based on the typical operating conditions for copper electrorefining, i.e., 40-50 g/L.
Table 4.1: Compositions of synthetic Fe(II, III)-H$_2$SO$_4$-H$_2$O and Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions, g/L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[H$_2$SO$_4$]</th>
<th>[Fe$^{3+}$]</th>
<th>[Fe$^{2+}$]</th>
<th>[Fe]$_{total}$</th>
<th>[Cu$^{2+}$]</th>
<th>Nominal [Fe$^{3+}$]/[Fe$^{2+}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>185</td>
<td>0.1429</td>
<td>2.8571</td>
<td>3</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>#2</td>
<td>185</td>
<td>0.1818</td>
<td>1.8182</td>
<td>2</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>#3</td>
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<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>#4</td>
<td>185</td>
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<td>1</td>
<td>3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>#5</td>
<td>185</td>
<td>1.6667</td>
<td>0.3333</td>
<td>2</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>#6</td>
<td>185</td>
<td>2.7273</td>
<td>0.2727</td>
<td>3</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>#7</td>
<td>185</td>
<td>5.8824</td>
<td>0.1176</td>
<td>6</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>#8</td>
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<td>0.1429</td>
<td>2.8571</td>
<td>3</td>
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<td>0.05</td>
</tr>
<tr>
<td>#9</td>
<td>185</td>
<td>0.1818</td>
<td>1.8182</td>
<td>2</td>
<td>45</td>
<td>0.1</td>
</tr>
<tr>
<td>#10</td>
<td>185</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>45</td>
<td>1</td>
</tr>
<tr>
<td>#11</td>
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<td>40</td>
<td>2</td>
</tr>
<tr>
<td>#12</td>
<td>185</td>
<td>1.6667</td>
<td>0.3333</td>
<td>2</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>#13</td>
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<td>2.7273</td>
<td>0.2727</td>
<td>3</td>
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<td>10</td>
</tr>
<tr>
<td>#14</td>
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<td>5.8824</td>
<td>0.1176</td>
<td>6</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>#15</td>
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<td>1.8182</td>
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</tr>
<tr>
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<tr>
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<td>45</td>
<td>5</td>
</tr>
</tbody>
</table>

The equivalent amount of concentrated H$_2$SO$_4$ (95.0%-98.0%, Fisher Scientific) was diluted in ultra-pure deionized water (18 MΩ.cm resistivity, Milli-Q) in a 1L beaker first, and then the corresponding amount of iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O, 99% for analysis ACS, Acros), iron (III) sulfate pentahydrate (Fe$_2$(SO$_4$)$_3$·5H$_2$O, 97%, Acros), and copper (II) sulfate pentahydrate (CuSO$_4$·5H$_2$O, 98%, Acros) were weighed and gradually dissolved in the diluted sulfuric acid solutions. Finally, all the solution was transferred into a 1L volumetric flask to finalize the solutions. The average density for the prepared solutions is ~1.11 g/cm$^3$ for Fe(II,
III)-H₂SO₄-H₂O system and ~1.20 g/cm³ for Fe(II, III)-Cu(II)-H₂SO₄-H₂O system, respectively, which was used to change the unit from “g/L solution” to “mol/kg water” for modeling calculation, correspondingly.

4.2.2 Electrolyte preparation for aqueous system containing Fe(II, III), As(III, V), Sb(III, V), Bi(III), Cu(II) and H₂SO₄

The compositions of synthetic electrolyte were determined according to the typical industrial conditions of copper electrorefining and are shown in Table 4.2. In industrial solutions, the concentration range of H₂SO₄ is 150-220 g/L, Fe 0.5-6 g/L, Cu 37-52 g/L, As 5-30 g/L, Sb 0.1-0.65 g/L and Bi 0.05-0.8 g/L. The total H₂SO₄ 185 g/L, Fe 2g/L, Cu(II) 42 g/L, As 5 g/L, Sb 0.2 g/L and Bi 0.1g/L were selected in the present synthetic solutions, as they are the most common concentrations in the tank house of copper refineries. The selected concentrations for these species were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) and Atomic absorption spectroscopy (AAS).

Nominal concentration ratio is also used to approximate the unknown concentration range of an impurity element with different valence state coexist in solutions. The nominal Fe³⁺/Fe²⁺ ratios (initial concentration ratio of total Fe(III) to total Fe(II)) were arranged to be 0.1:1, 1:1 and 10:1 with a constant concentration of total Fe being 2 g/L. The nominal As⁵⁺/As³⁺ ratios (initial concentration ratio of total As(V) to total As(III)) were set from 3:7 to 7:3 in order to observe its influence on ORPs as well as the nominal Sb⁵⁺/Sb³⁺ ratio (initial concentration ratio of total Sb(V) to total Sb(III)) being constant at 1:1.
**Table 4.2:** Compositions of synthetic aqueous solutions containing Fe(II, III), As(III, V), Sb(III, V), Bi(III), Cu(II) and H$_2$SO$_4$, g/L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H$_2$SO$_4$</th>
<th>[Fe]$^{tot}$</th>
<th>Nominal Fe$^{3+}$/Fe$^{2+}$</th>
<th>[As]$^{tot}$</th>
<th>Nominal As$^{5+}$/As$^{3+}$</th>
<th>[Sb]$^{tot}$</th>
<th>Nominal Sb$^{5+}$/Sb$^{3+}$</th>
<th>Bi(III)$_{tot}$</th>
<th>Cu(II)$_{tot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>185</td>
<td>2</td>
<td>0.1</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
<td>42</td>
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<tr>
<td>#5</td>
<td>185</td>
<td>2</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>0</td>
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<td>0</td>
<td>42</td>
</tr>
<tr>
<td>#6</td>
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<td>2</td>
<td>10</td>
<td>5</td>
<td>7:3</td>
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<td>0</td>
<td>0</td>
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</tr>
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<td>0.1</td>
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<td>3:7</td>
<td>0.2</td>
<td>1</td>
<td>0</td>
<td>42</td>
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<td>#9</td>
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<td>10</td>
<td>5</td>
<td>7:3</td>
<td>0.2</td>
<td>1</td>
<td>0</td>
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</tr>
<tr>
<td>#10</td>
<td>185</td>
<td>2</td>
<td>0.1</td>
<td>5</td>
<td>3:7</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>#11</td>
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<td>2</td>
<td>1</td>
<td>5</td>
<td>1</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>#12</td>
<td>185</td>
<td>2</td>
<td>10</td>
<td>5</td>
<td>7:3</td>
<td>0.2</td>
<td>1</td>
<td>0.1</td>
<td>42</td>
</tr>
</tbody>
</table>

The equivalent amount of concentrated H$_2$SO$_4$ (95.0%-98.0%, Fisher Scientific) was first diluted in ultra-pure deionized water (18 MΩ.cm resistivity, Milli-Q) in a 1L beaker, and then the corresponding amount of iron (II) sulfate heptahydrate (FeSO$_4$·7H$_2$O, 99% for analysis ACS, Acros), iron (III) sulfate pentahydrate (Fe$_2$(SO$_4$)$_3$·5H$_2$O, 97%, Acros), copper (II) sulfate pentahydrate (CuSO$_4$·5H$_2$O, 98%, Acros), arsenic (III and V) oxide (As$_2$O$_3$, 99.99% and As$_2$O$_5$, 99.9%, Alfa Aesar), antimony (III and V) oxide (Sb$_2$O$_3$, 99.99% and Sb$_2$O$_5$, 99.9%, Alfa Aesar) and bismuth (III) trioxide (Bi$_2$O$_3$, 99.999%, Alfa Aesar) were weighed and gradually dissolved in the diluted sulfuric acid solutions under agitation and heating at 70°C for 24 hours. Finally, all the solutions were transferred into a 1L volumetric flask to finalize the solutions at room temperature. The average density for the prepared solutions is 1.215 g/cm$^3$ which was used to change the unit from “g/L solution” to “mol/kg water” for modeling calculation, correspondingly.
### 4.3 Electrochemical measurements from 25°C to 70°C

The Schematic illustration of electrochemical tests for experimental ORP(OCP) measurements by potentiostat in aqueous Fe(II, III)-H₂SO₄, Fe(II, III)-Cu(II)-H₂SO₄, Fe(II, III)-As(III, V)-Cu(II)-H₂SO₄, Fe(II, III)-As(III, V)-Sb(III, V)-Cu(II)-H₂SO₄ and Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H₂SO₄ solutions is shown in **Figure 4.1**.

![Figure 4.1](image)

**Figure 4.1:** Schematic illustration of experimental ORP(OCP) measurements by potentiostat in aqueous solutions containing Fe(II, III), As(III, V), Sb(III, V), Bi(III), Cu(II) and H₂SO₄.

Electrochemical tests were performed using a standard three-electrode cell with five round glass ports. The cell has an integrated water jacket which was further connected to a water bath (Polyscience, PD07R-20) to control cell solution temperature by recirculation and heat...
transfer. \( \text{N}_2 \) gas with a high purity was sparged into testing solutions at a constant flow rate to eliminate dissolved oxygen before and during the whole tests. The cell off-gas was ejected through an Allihn condenser and deionized water, and finally discharged to a fume hood. The open circuit potentials (OCP) of the Pt working electrode, eventually as steady-state redox potentials or ORPs, were recorded by using a VersaSTAT 3F Potentiostat (AMETEK) along with a VersaStudio electrochemical software package (Princeton Applied Research).

All the measured potentials were corrected and referred to the SHE at 25°C. Details on the correction of procedure and methods could be found in a previous publication [29].

Chapter 5: Thermodynamic modeling in Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solution and its application to redox potential calculation up to 70°C

5.1 Introduction

Although several studies have recently examined the speciation of relevant aqueous solutions to quantify species distribution over a wide range of temperatures and pH by numerical thermodynamic modeling in CuSO$_4$-H$_2$SO$_4$ and Fe(II)-Fe(III)-H$_2$SO$_4$ systems on the basis of industrial copper production processes including leaching, electrowinning and electrorefining [28-29], [36], [43-44], [50], the speciation of Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O system over a wide range of temperature has hardly been investigated, and very few studies are available about the oxidation reduction potentials in the systems. In order to better elucidate the effect of impurity element Fe on the quality of cathode deposit and current efficiency during electrorefining, a detailed speciation study of the electrolyte is required so as to first quantify the species distribution of Fe and Cu in the Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions (including concentration and valence distribution of each element). In copper electrorefining, the impurity elements such as As, Sb, Bi can partially exist in aqueous electrolyte, and different valence of As, Sb and Bi can form floating slimes and enter into copper cathode by electrolyte entrainment. Fe (II and III) can have a chemical interaction with As, Sb and Bi (III or V) in the electrolyte. Speciation distribution and ORP determination in this study can provide new insight into the electrolyte and can also help better understand the effects of Fe on current efficiency due to its chemical and/or electrochemical interaction with copper cathode. Moreover, acidic iron sulfate solutions with copper ions are widely existing in the hydrometallurgical processes of copper production, i.e., leaching, SX/EW, thus the distribution of Fe and Cu in sulfate solutions is also of general importance.
The Fe(II, III)-H₂SO₄-H₂O system is firstly evaluated to extend its applicability when changing the iron chemistry and acid concentration compared with the previous results [30]. The total concentrations of Cu(II) and H₂SO₄ in the synthetic solutions are up to 50 g/L and 185 g/L respectively, while the total concentration of Fe is kept on up to 6 g/L, with nominal Fe³⁺/Fe²⁺ ratios (total concentration of ferric to ferrous) from 0.05 to 50 (selected due to the uncertainty of predominant valence of Fe, as discussed previously). The purpose of this design is to obtain the effects of high amount of Cu(II), acidity, and different nominal Fe³⁺/Fe²⁺ ratios on the species distribution and redox potentials, with an emphasis on the solution conditions during copper electrorefining. A detailed discussion regarding redox potential and species distribution between two aqueous systems before and after addition of Cu(II), along with temperature, pH, ionic strength and nominal Fe³⁺/Fe²⁺ ratios will be made.

5.2 Calculated species distribution in Fe(II, III)-H₂SO₄-H₂O system from 25°C to 70°C

In this section, the thermodynamic model of Fe(II, III)-H₂SO₄-H₂O system will be employed to evaluate the possibility of extending its applicability to the acidic iron sulfate solutions with a much higher acid concentration and different iron chemistry. Figure 5.1(a) to (f) present the results of the aqueous speciation (expressed as a percentage of the total ferric or ferrous) for tests #1 to #7 in Table 4.1 in Fe(II, III)-H₂SO₄-H₂O solutions with different nominal Fe³⁺/Fe²⁺ ratios of 0.05 to 50 from 25°C to 70°C. As observed under each testing temperature (25°C, 40°C, 50°C, 60°C, 65°C and 70°C), there is no apparent fluctuation of the percentage for each species, and the distribution curves tend to be very stable at nominal Fe³⁺/Fe²⁺ ratios from 0.05 to 50. However, under the same nominal Fe³⁺/Fe²⁺ ratio, the percentage of each species varies with temperature from 25°C to 70°C.
Percentage of Fe$^{2+}$ and Fe$^{3+}$ species

Nominal Fe$^{3+}$/Fe$^{2+}$ Ratio

(a)
Figure 5.1: Calculated species distribution diagram in aqueous Fe(II, III)-H₂SO₄·H₂O solution from 25°C to 70°C for samples #1 to #7 in Table 4.1 with nominal Fe³⁺/Fe²⁺ ratios of 0.05 to 50 (a) at 25°C; (b) at 40°C; (c) at 50°C; (d) at 60°C; (e) at 65°C, and (f) at 70°C. The sum of the percentage values of Fe(II) species is 100%, which is also the case for the Fe(III) species.

Under the 7 nominal Fe³⁺/Fe²⁺ ratios at different temperatures shown in Figure 5.1 (a) to (f), there is considerable difference between Fe(II) and Fe(III) species. Fe(II) species mainly distribute as free Fe²⁺ cations which always account for the largest percentage 70.92~77.59% of the total Fe(II). At temperatures below about 50°C, the neutral FeSO₄⁰ is the second predominant Fe(II) species, with an initial percentage of 19.22% at 25°C, and decreasing to 13.05% at 50°C. Its percentage keeps decreasing with temperature and eventually reaches to a minimum about 8.51% at 70°C. FeHSO₄⁺ cation is the least abundant Fe(II) species below 50°C, initially being 3.87% at 25°C, but its percentage gradually increases over temperature. It replaces neutral FeSO₄⁰ species to be the second dominant species when temperature is higher than 50°C, and its percentage ultimately increases to 20.3% at 70°C. This is different from the previous result that FeSO₄⁰ always represented the second most abundant Fe(II) species [29].
For Fe(III) species, FeSO$_4^+$ is always the predominant species for Fe(III), with its percentage in the range of 53.20~71.07% of total Fe(III), followed by FeHSO$_4^{2+}$ cations with its percentage ranging from 14.85% at 25°C to 32.94% at 70°C. This phenomenon is different from the previous result that Fe(SO$_4$)$_2^-$ represented the second most abundant Fe(III) species [30]. The remaining Fe(III) species are distributed as free Fe$^{3+}$ and Fe(SO$_4$)$_2^-$. From 25°C to 70°C, the single free Fe$^{3+}$ cations account for only 1.39~7.65% of total Fe(III) and its percentage keeps decreasing with temperature, while the amount of Fe(SO$_4$)$_2^-$ is around 0.66~13.00%.

In addition, under the same nominal Fe$^{3+}$/Fe$^{2+}$ ratios, in general, increasing the temperature from 25°C to 70°C results in an overall increase amount of FeHSO$_4^+$, FeHSO$_4^{2+}$, and Fe(SO$_4$)$_2^-$, but a decrease in the percentage of Fe$^{2+}$, FeSO$_4^-$, Fe$^{3+}$ and FeSO$_4^+$. The predominant species of Fe(II) and Fe(III) are free Fe$^{2+}$ cations and FeSO$_4^+$ complex respectively, which are similar to the results in the previous work when the nominal Fe$^{3+}$/Fe$^{2+}$ ratios were in the range of 1, 10, 100, 1000 [29] although the solution conditions used in these models are different. Casas et al. [28] reported similar results for the predominant Fe(II) species, which was free Fe$^{2+}$ cations as well when the nominal Fe$^{3+}$/Fe$^{2+}$ ratios were from 0.78 to 1.1.

Consequently, it could be concluded that the model developed previously for the Fe(II, III)-H$_2$SO$_4$-H$_2$O system remains applicable when changing the iron chemistry and acid concentration in this work compared with the previous results relevant to leaching conditions [29]. Changes of nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.05~50 and total Fe from 1-6 g/L under the same temperature do not have significant influence on species distribution in Fe(II, III)-H$_2$SO$_4$-H$_2$O quaternary aqueous system. Temperature variation plays a major role that influences species distribution in comparison to the nominal Fe$^{3+}$/Fe$^{2+}$ ratios and iron amount. Finally, it should be noted that, compared with the previous results [29], there is a slight change in the distribution of
some Fe(II) and Fe(III) species, especially at higher temperatures investigated in the current study, which is probably caused by the change of solution compositions such as the high acidity and/or minor change of iron chemistry in the solutions investigated in the current work.

5.3 Calculated species distribution in Fe(II, III)-Cu(II)-H₂SO₄-H₂O system from 25°C to 70°C

Figure 5.2 (a) to (f) show the calculated results of the aqueous speciation in Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions with different nominal Fe³⁺/Fe²⁺ ratios of 0.05 to 50 from 25°C to 70°C. The solution compositions are shown in Table 4.1 (#8–#14). Compared with the results in Figure 5.1 (a) to (f), high amount of copper (40, 45, 50 g/L) was added to simulate the solution conditions of copper electrefining.
As can be seen in Figure 5.2, a considerable proportion of Fe(II) still exists predominantly as free Fe$^{2+}$ in the range of around 67.02~72.13%, which is slightly lower than
that in Fe(II)-Fe(III)-H₂SO₄-H₂O system shown in Figure 5.1. This trend was still similar to that without the addition of copper. The percentage of FeHSO₄⁺ is in the range of 3.98% to 20.05% and almost equal to that of Fe(II, III)-H₂SO₄-H₂O solution. The proportion of FeSO₄²⁻ is within 12.17–25.60% and is relatively higher than that in the above quaternary system. Although from 25°C to 70°C the percentage of FeSO₄⁰ is continuously decreasing, it accounts for the second most common Fe(II) species when temperature is lower than 60°C. At higher temperatures 65°C and 70°C, FeHSO₄⁺ represented the second most abundant Fe(II) species. Furthermore, it should be noted that the least abundant Fe(II) species was FeHSO₄⁺ initially, and its percentage keeps increasing from 3.98% at 25°C to 20.05% at 70°C. FeHSO₄⁺ became the second dominant Fe(II) species when the temperature is higher than 60°C. These results are in good agreement with those shown in the Fe(II, III)-H₂SO₄-H₂O solution.

For Fe(III) species from 25°C to 70°C, FeSO₄⁺ remains the predominant species of Fe(III), with a proportion of 55.00–76.87%, which is slightly larger than that in Fe(II, III)-H₂SO₄-H₂O system shown in Figure 5.1. Free Fe³⁺ and complex FeHSO₄²⁺ cations only account for a minor percentage, about 0.88–5.42% and 11.67–25.00%, respectively, which are lower than those in Fe(II, III)-H₂SO₄-H₂O system under the same nominal Fe³⁺/Fe²⁺ ratios. The proportion of free Fe³⁺ decreases as a function of temperature, whereas the percentage of FeHSO₄²⁺ increases over temperature at all times. The percentage of Fe(SO₄)²⁻ is in the range of 1.08–22.34%, relatively larger than those of Fe(II, III)-H₂SO₄-H₂O system in general.

The Cu(II) species mainly distribute as Cu²⁺, CuSO₄⁰ and CuHSO₄⁺. CuSO₄⁰ is the least abundant Cu(II) species and its percentage decreases with temperature from 18.73% at 25°C to 4.10% at 70°C. The second most abundant Cu(II) species is free Cu²⁺ and its proportion decreases with temperature as well from 40.98% at 25°C to 14.57% at 70°C. By contrary, a
considerable proportion of Cu(II) exists in the form of CuHSO$_4^+$, and as the predominant species for Cu(II) its percentage increases substantially from 41.28% to 81.16% when increasing the temperature from 25°C to 70°C. This could be ascribed to the increasing stability of CuHSO$_4^+$ which is favored by higher temperature and high acidity of the solutions. The above-mentioned species distribution results of Cu(II) by thermodynamic modeling are also in agreement with those in the published literature [36], from which the concentrations of free Cu$^{2+}$ and neutral CuSO$_4$ decrease with temperature, whereas the concentration of copper bisulfate (CuHSO$_4^+$) increases with temperature ranging from 10°C to 80°C in the solutions with total Cu(II) and H$_2$SO$_4$ concentrations of 32 g/L and 49 g/L. The reported percentage and trend of each Cu(II) species is similar to those in the present work, although the solutions’ conditions are different. Therefore, it can be summarized from previous literature and present work that proportion of each Cu(II) species in the studied solutions over temperature is confirmed to be independent of total Cu concentration.

Based on the above discussion, it appears that the overall percentage trends of the distribution of Fe(II) and Fe(III) species do not have substantial changes after the addition of Cu(II). Moreover, under same temperature, with different nominal Fe$^{3+}$/Fe$^{2+}$ ratios, the distribution percentage of each Fe(II) and Fe(III) species has small variation compared to those of Fe(II, III)-H$_2$SO$_4$-H$_2$O solutions, but overall still remain stable. Therefore, it can be concluded from previous literature and present work that after the addition of Cu(II), the change of nominal Fe$^{3+}$/Fe$^{2+}$ ratios and total Fe concentration under same temperature only has a minor effect on species distribution. Only temperature variation exhibits a crucial effect on the distribution of Cu(II) species, as well as Fe(II) and Fe(III) species. The thermodynamic modeling has been
proven as an effective method to describe aqueous behavior of inorganic species at or above room temperature.

5.4 Comparison of redox potential between calculated results and experimental measurements from 25°C to 70°C

To validate the thermodynamic speciation model, a comparison of reversible potentials between experimental measurements performed in this work and model prediction values calculated by Nernst equation (Equation 3.10) was used. It is worth noting that this calculated potential is determined by the activity ratio of free ferric to free ferrous which can be obtained from the speciation results, i.e., by using the relative amounts of free ferric and ferrous and the accompanying activity coefficients in the solution, rather than the nominal concentration ratio of Fe$^{3+}$/Fe$^{2+}$ (the ratio of total Fe(III) to total Fe(II) initially added to the solution).
Figure 5.3: Comparison of the potentials predicted by thermodynamic modeling and measured by experiments vs SHE at 25°C (a) in various Fe(II, III)-H₂SO₄-H₂O solutions for tests #1 to #7, and (b) in Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions for tests #8 to #14 with nominal Fe³⁺/Fe²⁺ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C.

Figure 5.3 (a) and (b) show that the reversible potentials predicted by the model and measured by experiments with nominal Fe³⁺/Fe²⁺ ratios from 0.05 to 50 in both Fe(II, III)-H₂SO₄-H₂O and Fe(II, III)-Cu(II)-H₂SO₄-H₂O aqueous systems are in good agreement from 25°C to 70°C. The potential difference between experimental and calculated values is typically no more than 5 mV in general depending on the solution composition and temperature. The maximum root-mean-square error (RMSE) of potentials between model results and experimental values for each test in the two systems was calculated to be no more than 1.82% in correspond to experimental values from 25°C to 70°C. It seems that adding 40-50g/L Cu(II) does not have much impact on redox potential of solutions without Cu(II). The experimentally measured ORPs between solutions systems essentially maintain the same values, which can prove that redox Fe³⁺/Fe²⁺ couple still dominates in iron-copper-sulfate solutions. The comparison of
experimental and calculated results suggests that the model is qualitatively and quantitatively validated. Therefore, a conclusion can be drawn that the predicted distribution and concentration of each species are correct for either aqueous Fe(II, III)-H₂SO₄-H₂O or Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions in the studied temperature and composition ranges.

5.5 Applicability of the developed expression by comparison with experimental results from 25°C to 70°C

A novel expression was developed to predict the redox potential of the Fe³⁺/Fe²⁺ couple in the acidic iron sulfate electrolyte up to 150°C [29], and it is expressed as follows:

\[
E(\text{mV}) = -1 \times 10^{-3} \times [T(\text{K})]^2 + 0.91 \times T(\text{K}) + \frac{2.303 R}{nF} \times T(\text{K}) \times 10^3 \times \log \frac{C_{\text{feric, nominal}}}{C_{\text{ferrous, nominal}}} + 492
\]

(Equation 5.1)

Equation 5.1 has been reported to be capable of predicting redox potentials in acidic iron sulfate solutions without or with cupric ions (up to 6 g/L) over a wide range of solution compositions and temperatures [29], [116], [124], [126]. The redox potentials can be easily and accurately determined only by two variables of nominal Fe³⁺/Fe²⁺ ratios and temperature. Compared with those previously published results, much higher acidity and copper concentration were employed in this work. It is also of interest to determine whether ORP equation developed previously (Equation 5.1) remains applicable under conditions studied in the present work.
Figure 5.4: Comparison of the potentials calculated by Equation 5.1 and measured by experiments vs SHE at 25°C (a) in various Fe(II, III)-H₂SO₄-H₂O solutions for tests #1 to #7, and (b) in various Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions for tests #8 to #14 with nominal Fe³⁺/Fe²⁺ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C.

In Figure 5.4(a), it is suggested that the measured potentials are generally in good agreement with those calculated by Equation 5.1 in the studied Fe(II, III)-H₂SO₄-H₂O solutions with a much higher acid concentration. To further verify the applicability of this equation in the above solutions with high copper amount added, comparison of the potentials for Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions was carried out. As shown in Figure 5.4(b), the experimental results are in excellent agreement with those calculated by Equation 5.1 in the studied Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions. The potential difference, in general, is less than 3 mV with the nominal Fe³⁺/Fe²⁺ ratios of 0.05 to 50 from 25°C to 70°C. Hence, it proves that the expression developed previously can also be employed to predict the redox potential in either of the studied Fe(II, III)-H₂SO₄-H₂O or Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions, with a much higher acid and copper concentration.
5.6 Effect of high acid and copper concentration on redox potential

Based on the discussion in the previous two sections, it seems that either with much higher acid concentration or with the co-existence of higher amount of copper ions, the redox potential can still be solely determined by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple. Changing of those two parameters exerts no apparent influence on the prediction of redox potentials. Particularly, the addition of high amount of copper does not affect the redox potential for the above-mentioned two systems either calculated from model results or measured by experiment. The following discussion will explain in more details regarding this phenomenon.

After obtaining the speciation results for aqueous Fe(II, III)-H$_2$SO$_4$ and Fe(II, III)-Cu(II)-H$_2$SO$_4$ systems from thermodynamic modeling, the temperature dependence of the free ferric and ferrous ion concentrations and their ratios, together with their accompanying activity coefficients can be obtained to systematically study the reversible potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.

The temperature dependence of the calculated real $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (concentration ratio of free $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ ions) in the two solution systems under different nominal $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios is presented in Figure 5.5. The nominal $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios from 0.05 to 50 correspond to tests #1 to #14. It could be observed that, under each temperature the calculated real $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is much lower than the nominal ratio, and meanwhile under each given nominal $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio the calculated real ratios of $\text{Fe}^{3+}/\text{Fe}^{2+}$ substantially declines with temperature from 25°C to 70°C in the two studied systems. This implies that the real $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is markedly dependent upon temperature and the composition of the electrolyte for both of the systems. This trend was similar to that in a previous publication for the Fe(II)-Fe(III)-H$_2$SO$_4$-H$_2$O solutions when the nominal $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios are 1:1, 10:1, 100:1 and 1000:1 from 25°C to 150°C [29].
Figure 5.5: Calculated real Fe$^{3+}$/Fe$^{2+}$ ratios for test #1 to #7 in various Fe(II, III)-H$_2$SO$_4$-H$_2$O solutions, and test #8 to #14 in various Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O solutions with nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C.

The standard electrode potential of the Fe$^{3+}$/Fe$^{2+}$ couple ($E^\circ$, mV) at higher temperatures was calculated according to the method in a previous publication and increases linearly with temperature [29]. The obtained values agree well with those predicted at higher temperature by other authors [128-130].

As to the single ion activity coefficients for species involved in the present study, they were estimated by the above-mentioned B-dot equation (Equation 3.5). Calculated results show that the ratios of the activity coefficient for free ferric and free ferrous are typically only affected by temperature and remain practically constant at same temperature under different nominal
Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios. The ratios of the activity coefficient for free ferric and ferrous range from 0.321 at 25°C to 0.301 at 70°C (each is an average of the values under 7 different nominal Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios) for Fe(II, III)-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O system, and from 0.318 at 25°C to 0.299 at 70°C for Fe(II, III)-Cu(II)-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O system, with the temperature increasing from 25°C to 70°C. This ratio of activity coefficients also varies linearly with temperature. The obtained activity coefficient ratios for free ferric and ferrous were included in the term \((2.303RT/nF)\times\log (\gamma_{\text{ferric}}/\gamma_{\text{ferrous}})\) where this entire expression is defined here as \(E_1\) (mV), and which yields the potential values resulting from the single ion activity coefficients.

Apparently, the potential difference of \(E_1\) between the two systems with or without copper only depends on the log \((\gamma_{\text{ferric}}/\gamma_{\text{ferrous}})\) values. According to the calculated activity coefficient ratios for free ferric and ferrous above, in general the potential difference of \(E_1\) between the two systems is within 0.5 mV, which is negligible here. Therefore, the contribution of the ORP calculation from the activity coefficient ratios for free ferric and ferrous \((E_1)\) in the Fe(II, III)-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O and Fe(II, III)-Cu(II)-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O systems under studied temperature and nominal Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios could be assumed to be identical.

For the concentrations of free ferric and ferrous in the present study, they were obtained from thermodynamic speciation results. The obtained concentration ratios of free \(C_{\text{ferric}}\) to \(C_{\text{ferrous}}\) were included in the term \((2.303RT/nF)\times\log (C_{\text{ferric}}/C_{\text{ferrous}})\) for redox potential calculation. This entire term here is defined as \(E_2\), which is the third component of Equation 3.10. It is clearly seen in Figure 5.5 that, the calculated real Fe\textsuperscript{3+}/Fe\textsuperscript{2+} concentration ratios for tests #1 to #7 in the Fe(II, III)-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O solutions are almost identical to those for tests #8 to #14 in the Fe(II, III)-Cu(II)-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O solutions over all the nominal Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios and temperature, which leads to essentially same \(E_2\) for the two system with or without copper sulfate addition. This implies
that as $E^°$ is the same and $E_1$ is very stable at each temperature for both systems, the calculated reversible potential for the Fe$^{3+}$/Fe$^{2+}$ couple based on the sum of $E^°$, $E_1$ and $E_2$ remains essentially unchanged for the acidic iron sulfate solutions before and after the addition of high amount of copper.

From the above analysis of the model-calculated results, together with the fact that the experimental ORP values in the two solution systems are almost identical to each other, it seems that the redox potential of acidic iron sulfate solutions with much higher acid concentration and high copper amount can still be solely determined by the Fe$^{3+}$/Fe$^{2+}$ couple.

Based on above discussion, the proposed model was validated by reliable and accurate prediction of measured redox potentials. It proves that either with much higher acid concentration with or without the co-existence of higher amount of copper ions, the redox potential can still be solely determined by the Fe$^{3+}$/Fe$^{2+}$ couple. There is no apparent influence on the prediction of redox potentials caused by those two parameters. The expression developed previously can also be employed to predict the redox potential in much more complicated solutions. The speciation model and developed expression explain the change of redox potential with temperature for all nominal Fe$^{3+}$/Fe$^{2+}$ ratios.

It should be emphasized that the current work provides a set of thermodynamic data which has proved to be reliable to simulate the distribution of simple ion, ion complex and neutral molecule by thermodynamic modeling for the above-mentioned solutions, thus providing a new method to understand the behavior of species involved in acidic iron sulfate solution with copper.
Validation of the present model could not be extended to a wider range of composition concentrations and temperatures due to the generation or the presence of additional species. Further work is required in order to expand our understanding of these two systems.

5.7 Discussion on the effect of nominal Fe$^{3+}$/Fe$^{2+}$ ratio and T on redox potential

As discussed in Section 5.5 based on Equation 5.1, the redox potential could be easily and accurately determined based on the variables of temperature and nominal Fe$^{3+}$/Fe$^{2+}$ ratio. Please also note that at any given temperature, the redox potentials of the Fe(II, III)-H$_2$SO$_4$-H$_2$O and Fe(II, III)-Cu(II)-H$_2$SO$_4$-H$_2$O systems are solely determined by the nominal Fe$^{3+}$/Fe$^{2+}$ ratio and a temperature dependence of the same slope as the Equation 3.10. A detailed discussion on the effects of nominal Fe$^{3+}$/Fe$^{2+}$ ratio and temperature on redox potentials will be provided in this section.

As shown in Figure 5.3, speciation and experimental results indicate that for a given temperature the model-calculated and experimental-measured potentials increase considerably with the nominal Fe$^{3+}$/Fe$^{2+}$ ratios increasing from 0.05 to 50. However, from 25°C to 70°C, the potentials predicted by the model and measured by experiment increase gradually only when the nominal Fe$^{3+}$/Fe$^{2+}$ ratios are higher than 1:1. Interestingly, on the other hand, the predicted and measured potentials are relatively stable with the nominal Fe$^{3+}$/Fe$^{2+}$ ratios lower than 1:1 and no significant change was observed as the temperature increased. The reason for this unexpected behavior with nominal Fe$^{3+}$/Fe$^{2+}$ ratios lower than 1:1 lies in the fact that at each temperature, the real Fe$^{3+}$/Fe$^{2+}$ ratio in the solution is much lower in such a condition, typically lower than 0.1 and on the order of $10^{-2}$ or $10^{-3}$. Such small values will result in a large negative value for $E_2$. This implies that although the $E^\circ$ increases considerably with temperature, and $E_1$ is relatively stable
at each temperature, the calculated reversible potential for the Fe\(^{3+}/\text{Fe}^{2+}\) couple based on the sum of \(E^\circ, E_1\) and \(E_2\) remains essentially unchanged when the ratios are lower than 1:1. These trends are similar to our previous findings for the Fe(II, III)-H\(_2\)SO\(_4\)-H\(_2\)O solutions then the nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratios are 1:1, 10:1, 100:1 and 1000:1 in the temperature range of 25\(^{\circ}\)C-150\(^{\circ}\)C [29].

A similar trend was found regarding the potentials calculated by **Equation 5.1** with nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio employed, as shown in **Figure 5.4**. This unexpected behavior could be also explained by the analysis based on **Equation 5.1**. According to this Equation, the redox potential increases with the nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio under the same temperature. However, when nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio is larger than 1, the term \((2.303 R/nF) \times T(K) \times 10^3 \times \log (C_{\text{ferric, nominal}}/C_{\text{ferrous, nominal}})\) will contribute a positive value, hence resulting in an overall higher ORP value; When nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio is smaller than 1, this part will contribute a negative value, thus leading to an overall lower ORP value in solutions.

On the other hand, under the same nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio, temperature plays a very important role on ORP values with 1:1 as a critical nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio. When the nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio is smaller than 1, the term \((2.303 R/nF) \times T(K) \times 10^3 \times \log (C_{\text{ferric, nominal}}/C_{\text{ferrous, nominal}})\) in **Equation 5.1** will contribute a negative value (a much smaller negative value when increasing temperature from 25\(^{\circ}\)C to 70\(^{\circ}\)C). By contrast, when the nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio is larger than 1, this term will contribute a positive value (a much larger positive value when increasing temperature from 25\(^{\circ}\)C to 70\(^{\circ}\)C). Potential values contributed from other terms in the equation including “-1\times10^{-3}\times[T(K)]^2+0.91\times T(K)” plus the constant “492” remain relatively unchanged as a positive number over studied temperatures. As a result, it suggests that a positive and a negative componential ORP value can be obtained in solutions with nominal Fe\(^{3+}/\text{Fe}^{2+}\) ratio smaller than 1, but two positive componential ORPs can be obtained in solutions with nominal
Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio larger than 1. Consequently, as indicated in Figure 5.4, the ORP values remain increasing with temperature under the same nominal Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios when its values are higher than 1:1, but ORP values are relatively stable and do not show obvious increase under nominal Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios of 0.05 and 0.1 from 25°C to 70°C.

From the above discussion, the proposed model was validated by reliable and accurate prediction of measured redox potentials. It proves that either with much higher acid concentration with or without the co-existence of higher amount of copper ions, the redox potential can still be solely determined by the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} couple. There is no apparent influence on the prediction of redox potentials caused by those two parameters. The expression developed previously can also be employed to predict the redox potential in much more complicated solutions. The speciation model and developed expression explain the change of redox potential with temperature for all nominal Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios.

Validation of the studied thermodynamic model is limited to the range of solution compositions and temperatures in this work as a broader range may lead to the generation or presence of additional species. Additional experimental and theoretical work is needed to better understand the two solution systems.

5.8 Effect of total concentration of Cu(II) and Fe on ORP measurement

In order to completely verify ORP changes in Fe(II, III)-Cu(II)-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O system by different concentrations of total Cu(II) and Fe, 4 extra tests #15 to #18 were performed to only compare ORP values with tests #9 to #12 correspondingly, and their experimental and modeling values were plotted into Figure 5.6 and Figure 5.7. The equational values were also drawn as a reference included in the comparison.
Figure 5.6: Comparison of the potentials predicted by modeling with Equation 3.10, measured by experiments and calculated by Equation 5.1 vs SHE at 25°C for (a) #9 and #15, (b) #10 and #16 respectively from 25°C to 70°C in aqueous Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions.

To demonstrate the effect of total Cu(II) concentration on ORP, potential of test #15 was measured experimentally to compare with test #9 as well as their relative modeling results. The only difference between #9 and #15 is their concentration of total Cu(II), which are 45g/L and 40g/L respectively, while other parameters including nominal ratios, concentrations of H₂SO₄ and total Fe stay identical. As described in Figure 5.6(a), the model results for #9 and #15 generally coincide with each other, and likewise their experimental values are almost overlapped under same nominal Fe³⁺/Fe²⁺ ratios. The ORP difference between test #9 and #15 is typically less than 1mV from 25°C to 70°C in the aspect of experimental measurements and thermodynamic modeling. To minimize the experimental error, test #16 was conducted to pair with test #10 with respective total Cu(II) concentrations of 50g/L and 45g/L. Similar results are
observed in Figure 5.6(b), in which the difference of ORP values between test #10 and #16 in experiments and thermodynamic modeling is normally less than 2mV from 25°C to 70°C. The equational ORP values agree with experiments better than modeling. Therefore, it can be concluded that the variation of total Cu(II) concentration does not have significant effect on ORP measurement in the studied Fe(II, III)-Cu(II)-H₂SO₄-H₂O aqueous solutions from 25°C to 70°C.

To explain the effect of total Fe concentration on ORP, tests #17 and #18 were used to compare ORP results with test #11 and #12 respectively. The only constituent difference here is total Fe concentration. #17 shares the same components with #11 but total Fe quantity, which are 6g/L for the former, and 3g/L for the latter. To keep consistent analysis of the total Fe effect and minimize experimental error, the same procedures were performed for test #18 and #12 whose total Fe concentrations were 3g/L and 2g/L severally. Their corresponding experimental, modeling and equational ORP results are reflected in Figure 5.7 (a) and (b). As similar curves observed, the potentials from modeling and experiments at 25°C remain essentially unaltered. The potential difference between experiments and modeling from 25°C to 70°C on average is no more than 1mV. The equation-obtained values still agree with experiments better than modeling. Therefore, a conclusion can be drawn that increasing the concentration of total Fe plays a minor role in the ORP measurement from 25°C to 70°C.
Figure 5.7: Comparison of the potentials predicted by modeling with Equation 3.10, measured by experiments, and calculated by Equation 5.1 vs SHE at 25°C for (a) #11 and #17, (b) #12 and #18 respectively from 25°C to 70°C in aqueous Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions.

It seems that the change of concentrations of total Cu(II) and Fe does not have significant effect on ORP values in the studied solutions. This further reveals that addition of Cu does not form any extra redox couple in Fe(II, III)-Cu(II)-H₂SO₄-H₂O aqueous system. The only redox couple is still free ferric to ferrous ratio. Moreover, the change of total Fe concentration has no impact on free ferric to ferrous ratio of the redox couple, namely the free ferric concentrations always keep proportional to free ferrous concentrations in Fe(II, III)-Cu(II)-H₂SO₄ aqueous systems. Factors that significantly influence ORP values are testified to be nominal Fe³⁺/Fe²⁺ ratios and temperature, which are coincidentally in accordance with the two variables in Equation 5.1. Besides, in the above 4 pairs of tests with different nominal Fe³⁺/Fe²⁺ ratios, the ORP results obtained from equation present in better agreement with those of experiments than modeling. Results from equation are nearly identical to experimental values. This also proves
that the expression can provide an alternative way to theoretically predict total ferric to ferrous ratio based on known solution potential and temperature. Thus, the total concentration of Fe(III) and Fe(II) can be readily estimated by total Fe concentration. Furthermore, for each of the 8 tests shown in Figure 5.6 and Figure 5.7, the experimental data also demonstrates an excellent agreement with modeling results in the studied solutions. The deviation of ORP between two tests under same nominal Fe$^{3+}$/Fe$^{2+}$ ratio is reasonably within 6mV due to minor experimental errors, which are acceptable in the present work.

5.9 Analysis of calculated pH

pH is one of the key parameters in the industrial solutions. However, owing to the extreme acidic conditions, it is very challengeable to measure pH directly in the studied solutions. From the validated thermodynamic modeling results, the pH values for the solutions in test #1 to #14 can be calculated by the obtained activity of hydrogen ions in the present study. This provides an indirect way to study the pH of the solutions involved in this work.

The calculated pH for various solution compositions are shown in Figure 5.8 (a) and (b). It can be observed that the pH values of iron-sulfate/iron-copper-sulfate solutions are generally less than 0, in the range of -0.27 to -0.24 and -0.18 to -0.05 over the studied temperatures and nominal Fe$^{3+}$/Fe$^{2+}$ ratios. In both systems, under the same nominal Fe$^{3+}$/Fe$^{2+}$ ratio, the pH increases gradually with temperature up to 70°C. The increase of pH values shows the concentrations of H$^+$ ions in the two systems slightly decrease when the solution temperatures gradually increase from 25°C to 70°C. This implies that more protons are combined with free metal ions and sulfate anions to form more thermodynamically stable ionic complex at higher temperatures, resulting in the declining concentration of H$^+$ ions.
Figure 5.8: Calculated pH (a) in aqueous Fe(II, III)-H₂SO₄-H₂O system for samples #1 to #7; (b) in aqueous Fe(II, III)-Cu(II)-H₂SO₄-H₂O system for samples #8 to #14 with nominal Fe³⁺/Fe²⁺ ratios from 0.05 to 50 in the temperature range of 25°C to 70°C.

Moreover, under the same nominal Fe³⁺/Fe²⁺ ratio, the pH values in iron-sulfate solutions are overall lower than those in iron-copper-sulfate solutions at studied temperatures. This means that addition of copper sulfate results in an increase of pH, in other words, a decrease in concentration of H⁺ ions. This is mainly due to the fact that addition of sulfate anion leads to the ion association to form stable ionic complex which causes a decrease in the free H⁺ concentration in the solution.

5.10 Analysis of calculated real ionic strength

The calculated real ionic strength in Fe(II, III)-H₂SO₄-H₂O and Fe(II, III)-Cu(II)-H₂SO₄-H₂O solutions for tests #1 to #7 and tests #8 to #14 from 25°C to 70°C are shown in Figure 5.9 (a) and (b), which are lower than 2.34 and 3.1 mol/kg H₂O, respectively. As can be observed,
under same nominal Fe\(^{3+}/Fe^{2+}\) ratio, increasing temperatures from 25°C to 70°C results in a gradual decrease of the real ionic strength. This result may be due to ion association to form more stable species (from highly charged ions to less charged ion complexes) at higher temperatures, which will result in a decrease of the concentrations of species with higher charge such as Fe\(^{2+}\), Fe\(^{3+}\) and Cu\(^{2+}\) ions, as can be clearly observed in Figure 5.1 and Figure 5.2.

![Graph](image)

**Figure 5.9:** Calculated real ionic strength (a) in aqueous Fe(II, III)-H\(_2\)SO\(_4\)-H\(_2\)O system for samples #1 to #7; (b) in aqueous Fe(II, III)-Cu(II)-H\(_2\)SO\(_4\)-H\(_2\)O system for samples #8 to #14 with nominal Fe\(^{3+}/Fe^{2+}\) ratios from 0.05 to 50 in the temperature range of 25°C to 70°C.

The nominal ionic strengths for all the different nominal Fe\(^{3+}/Fe^{2+}\) ratios are in the range of 6.21~6.65 mol/kg H\(_2\)O for the Fe(II)-Fe(III)-H\(_2\)SO\(_4\)-H\(_2\)O solutions and 9.17~10.13 mol/kg H\(_2\)O for the Fe(II)-Fe(III)-Cu(II)-H\(_2\)SO\(_4\)-H\(_2\)O solutions. It is clear that the real ionic strength calculated by modeling results using the real concentration of charged species are much lower than those calculated using the nominal species concentrations in all cases. This is due to the fact
that the concentrations of the species with higher charges (such as Fe\(^{2+}\), Fe\(^{3+}\), Cu\(^{2+}\) and SO\(_4^{2-}\)) considerably diminish due to the formation of various complexes with lower charges (such as HSO\(_4^-\), FeHSO\(_4^+\), FeHSO\(_4^{2+}\), FeSO\(_4^+\), Fe(SO\(_4\))\(_2^-\) and CuHSO\(_4^+\)) or neutral species with no charges (FeSO\(_4^0\) and CuSO\(_4^0\)).

Although it was reported that B-dot equation was only valid for aqueous electrolyte solutions with moderate ionic strengths up to 1 molal in a range of 0–300°C [101-102], and the effective ionic strength of the solutions used in this study is still relatively high, the excellent agreement of reversible potentials between experimental measurements and model prediction justify the reasonable use of the B-dot model. This model has also been successfully used to evaluate the activity coefficients of dissolved species in aqueous sulfuric acid/metal sulfate systems with similar solution conditions and has given reasonable predictions through a wide range of temperature and solution composition [28-29], [36], [43], [114], [116], which also indicates its suitability for the present study. The use of other complicated activity models (such as Pitzer, electrolyte NRTL, Bromley-Zaemaitis and the mixed solvent electrolyte models) may have better described the non-ideal behavior of the ionic solutions examined in the present study, however, these models usually require a large amount of theoretical or experimental data (such as mean activity coefficient, osmotic coefficient and solubility) in order to obtain numerous interaction parameters by regression to calculate the activity coefficients. Such data are usually unavailable, especially at high concentrations and temperatures.

5.11 Conclusion

Speciation of Fe(II, III)-Cu(II)-H\(_2\)SO\(_4\)-H\(_2\)O aqueous systems was developed by thermodynamic modeling under conditions most relevant to the current industrial copper
electrorefining electrolyte from 25°C to 70°C. The model can help quantify the species distribution and provide fundamental data for a deeper understanding of Fe (II and III) and Cu behavior during copper electrorefining, especially for the effects of Fe(II, III) as impurity ions on current efficiency and formation of slimes due to its chemical or electrochemical interaction with other species.

The calculated distribution of each Fe(II and III) and Cu(II) species in the Fe(II)-Fe(III)-H2SO4-H2O and Fe(II)-Fe(III)-Cu(II)-H2SO4-H2O systems reveals that Fe(II) are primarily distributed as free Fe2+, FeHSO4+ and FeSO4°; Fe(III) are mainly distributed as free Fe3+, FeSO4+, FeHSO42+ and Fe(SO4)2−; Cu(II) is mainly dissolved as Cu2+, CuSO4° and CuHSO4+. Especially, after the addition of high amount of copper (40-50 g/L), the overall distribution trends of each Fe(II) and Fe(III) species do not have substantial changes.

The validity of the proposed model was confirmed by reliable and accurate prediction of measured redox potential throughout all solution conditions. The excellent agreement between measured potentials and those calculated by Equation 5.1 proves that this expression can also be employed to predict the redox potential in the studied solutions with a much higher acid and copper concentration. A detailed analyses of the model-calculated results in terms of the free ferric and ferrous ion concentrations ratios and their accompanying activity coefficients, together with the fact that the experimental ORP values in the two solution systems are almost identical to each other, strongly support that the redox potential of acidic iron sulfate solutions with much higher acid concentration and high copper amount can still be solely determined by the Fe3+/Fe2+ couple. The speciation model and developed expression explain the change of redox potential with temperature for all nominal Fe3+/Fe2+ ratios.
Furthermore, this work provides an alternative method of estimating the pH by the validated modeling results under extreme acidic conditions. As expected, the pH values of iron-sulfate/iron-copper-sulfate solutions are generally less than 0 over the studied conditions and increase gradually with temperature. The pH values in iron-sulfate solutions are overall lower than those in iron-copper-sulfate solutions. It is also worth noting that the real ionic strength calculated by the concentrations of ionic species based on modeling results is significantly lower than the nominal ionic strength calculated by nominal species concentrations. Although the effective ionic strength is still relatively high, the excellent agreement of redox potentials between experimental measurements and model prediction justify the reasonable use of B-dot model for the calculation of activity coefficients of dissolved species.

It should be emphasized that this work provides a reliable set of thermodynamic data and the model developed in this study is a feasible and promising method for the studies on the speciation of the Fe(II)-Fe(III)-Cu(II)-H₂SO₄-H₂O system over a wide range of solution conditions, allowing comprehensive description of Fe and Cu behavior such as valence distribution, redox potential calculation, and pH estimation in acidic iron sulfate solution with copper. The reliable prediction of redox potential by the speciation model and the developed expression with high accuracy is particularly valuable and attractive. Therefore, it can be expected that the findings in the present work will facilitate our further investigation on the speciation of more complicated acidic iron sulfate solutions containing As, Sb and Bi as well as solutions in other copper hydrometallurgical processes.
Chapter 6: Speciation and redox potentials in aqueous solutions containing Fe(II, III), As(III, V), Sb(III, V), Bi(III), Cu(II) and H$_2$SO$_4$ from 25°C to 70°C

6.1 Introduction

In electrorefining solutions, both anode and floating slimes are solid precipitates and particles formed through ion interactions. Crystalline precipitates or slime compounds tend to form when relevant species such as free ions, ionic complexes and neutral molecules reaches threshold concentration in refining solutions [61]. These slimes have been well identified by using various material characterization approaches. However, the behavior and temperature dependence of these impurity species in the liquid phase is still unclear. In particular, measuring in-situ concentration of various As, Sb, Bi and Fe species remains a challenge. Quantification of each species of interest is not applicable in practical terms. This leads to the poor control strategies for secondary/floating slimes as the distribution of various aqueous species is unknown. Additionally, Few publications are available on the redox potential in copper solutions containing impurity elements with multi-redox valence states, for example, As(V)/As(III), Sb(V)/Sb(III) and Fe(III)/Fe(II). The predominant redox couple has not been clearly determined. Thus, understanding the liquid-phase speciation and its impact on redox potential is of great importance to define the control strategy about impurities in copper electrorefining solutions.

This section aims to develop a thermodynamic modeling to quantify species distribution in 4 aqueous systems including Fe(II, III)-Cu(II)-H$_2$SO$_4$, Fe(II, III)-As(III, V)-Cu(II)-H$_2$SO$_4$, Fe(II, III)-As(III, V)-Sb(III, V)-Cu(II)-H$_2$SO$_4$ and Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H$_2$SO$_4$ from 25°C to 70°C. The model is initiated to describe the non-ideal behavior of selected Fe(II), Fe(III), Cu(II), As(III), As(V), Sb(III), Sb(V) and Bi(III) species as a function of temperature and solution composition. Thermodynamic data of each aqueous species involved in
modeling was critically assessed after considerable literature review. In present synthetic solutions (same tests #1~12 in Table 4.2, referred here as Table 6.1 for convenience), the concentration ratio of total Fe(III)/Fe(II), namely nominal Fe$^{3+}$/Fe$^{2+}$ ratio, was chosen at 0.1:1, 1:1 and 10:1, which is same case for As(V)/As(III) and Sb(V)/Sb(III) of nominal As$^{5+}$/As$^{3+}$ ratio and nominal Sb$^{5+}$/Sb$^{3+}$ ratio being 3:7 to 7:3 and 1:1, respectively. Experimental ORP measurements were carried out to validate thermodynamic model, as well as to investigate the predominant redox couple that contributes to the steady-state redox potential in the studied solutions. The valence distribution of above impurity species will be evaluated and discussed. This research is expected to provide optimization parameters for impurity control under relevant copper electrorefining process in terms of solution compositions and temperature.

<table>
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<tr>
<th>Sample</th>
<th>H$_2$SO$_4$</th>
<th>[Fe]$_{tot}$</th>
<th>Nominal Fe$^{3+}$/Fe$^{2+}$</th>
<th>[As]$_{tot}$</th>
<th>Nominal As$^{5+}$/As$^{3+}$</th>
<th>[Sb]$_{tot}$</th>
<th>Nominal Sb$^{5+}$/Sb$^{3+}$</th>
<th>Bi(III)$_{tot}$</th>
<th>Cu(II)$_{tot}$</th>
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6.2 Calculated species distribution in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions from 25°C to 70°C.
Figure 6.1: Calculated species distribution in aqueous Fe(II, III)-Cu(II)-H₂SO₄ solutions from 25°C to 70°C for test #1~3 in Table 6.1 with nominal Fe³⁺/Fe²⁺ ratios of 0.1 to 10 (a) at 25°C; (b) at 40°C; (c) at 50°C; (d) at 60°C; (e) at 65°C, and (f) at 70°C. The sum of the percentage of Fe(II), Fe(III) and Cu(II) species is 100% respectively.

Figure 6.1 (a) to (f) show the speciation results from modeling calculation in aqueous Fe(II, III)-Cu(II)-H₂SO₄ solutions with nominal Fe³⁺/Fe²⁺ ratio of 0.1:1, 1:1 and 10:1 from 25°C to 70°C. The solution compositions are listed in Table 6.1 (#1~3). It is seen that under each temperature, the distribution percentage of each species of Fe(II), Fe(III) and Cu(II) tends to be very stable at different nominal Fe³⁺/Fe²⁺ ratio from 0.1 to 10. However, the percentage of each species differs at each temperature (25°C, 40°C, 50°C, 60°C, 65°C and 70°C). The concentration of free Fe²⁺ is predominant species of total Fe(II), followed by FeSO₄⁻, accounting for 67.60~72.02% and 12.28~24.31% respectively, while FeHSO₄⁺ is the least abundant Fe (II) species with a proportion of 3.98~20.03% from 25°C to 70°C. FeSO₄²⁻ ion complex is the major species of total Fe(III), taking up 55.17~75.75%, free Fe³⁺ ions 0.97~5.38%, Fe(SO₄)₂⁻ 1.09~20.26% and FeSO₄⁺ 55.17~75.75% from 25°C to 70°C. In addition, most of Cu(II) species
distributes as CuHSO$_4^+$ with the proportion of 41.31~81.13%, free Cu$^{2+}$ 14.70~40.92% and CuSO$_4$ 4.15~17.83% ranging from 25°C to 70°C.

The distribution results in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions are similar to the those in the Section 5.3. The variation of concentration or percentage of each Fe(II, III) and Cu(II) species over temperature is due to their stability constant at different temperature from 25°C to 70°C. Evidently, from above modeling results, the nominal Fe$^{3+}$/Fe$^{2+}$ ratio from 0.1 to 10 does not exert any significant influence on the distribution of the dissolved species. Only temperature plays a major role on species distribution.

6.3 Calculated species distribution in aqueous Fe(II, III)-As(III, V)-Cu(II)-H$_2$SO$_4$ solutions from 25°C to 70°C
Percentage of Fe(II, III) and Cu(II) species

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

Fe$^{2+}$ FeHSO$_4^-$ FeSO$_4^{0-}$ Fe$^{3+}$ FeHSO$_4^{2+}$ Fe(SO$_4^{2-}$) FeSO$_4^{+}$ Cu$^{2+}$ CuSO$_4^{0-}$ CuHSO$_4^+$

Percentage of As(III) and As(V) species

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

H$_3$AsO$_3^{0-}$ AsO$_3^+$ H$_2$AsO$_4^{-}$ H$_3$AsO$_4^{0-}$

(b) (b')

(c) (c')
Figure 6.2: Calculated species distribution diagram in aqueous Fe(II, III)-As(III, V)-Cu(II)-H$_2$SO$_4$ solutions from 25°C to 70°C for test #4–6 in Table 6.1 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios of 0.1 to 10 for Fe(II), Fe(III), Cu(II), As(III) and As(V) species (a) and (a’) at 25°C; (b) and (b’) at 40°C; (c) and (c’) at 50°C; (d) and (d’) at 60°C; (e) and (e’) at 65°C; (f) and (f’) at 70°C. The sum of the percentage of Fe(II), Fe(III), Cu(II), As(III) and As(V) species is 100% respectively.

Figure 6.2 (a) and (a’) to (f) and (f’) present the speciation results in aqueous Fe(II, III)-As(III, V)-Cu(II)-H$_2$SO$_4$ solutions with same nominal Fe$^{3+}$/Fe$^{2+}$ ratio 0.1 to 10 and nominal As$^{5+}$/As$^{3+}$ ratio 3:7 to 7:3 from 25°C to 70°C. Compared with the results in Figure 6.1, a total of 5 g/L arsenic (III and V) was added in Fe(II, III)-Cu(II)-H$_2$SO$_4$ system to simulate species distribution (tests #4–6 in Table 6.1).

As can be observed, Fe(II) species still remains predominantly as free Fe$^{2+}$ ions within 67.47–71.94%, FeHSO$_4^+$ 3.98–19.98% and FeSO$_4$$^\circ$ 12.35–24.58%. A considerable amount of FeSO$_4^+$ exists as the most abundant Fe(III) species about 55.19–75.98% and the rest of Fe(III) makes up of free Fe$^{3+}$ ions 0.96–5.35%, FeHSO$_4$$^{2+}$ 12.23–24.58%, Fe(SO$_4$)$_2$ 1.11–20.58%. The Cu(II) species mainly distribute as free Cu$^{2+}$ 14.69–40.88%, CuSO$_4$$^\circ$ 4.17–18.05% and CuHSO$_4^+$ 41.26–81.07%. The distribution results for Fe(II, III) and Cu(II) in Fe(II, III)-As(III, V)-Cu(II)-
H$_2$SO$_4$ system are almost identical to those in Fe(II, III)-Cu(II)-H$_2$SO$_4$ system. It can be concluded that presence of As(III, V) has no effect on species distribution of Fe(II, III) and Cu(II) from 25°C to 70°C.

The modeling results of As(III, V) are shown in Figure 6.2 (a’) to (f’). It is noted that the percentage of H$_3$AsO$_3$ increases initially from 45.54% at 25°C to 56.50% at 70°C eventually. The distribution of AsO$^-$ is in an opposite trend. It starts to decrease from 54.46% at 25°C to 43.50% at 70°C. The observation for As(III) species distribution at 25°C is close to that in literature [38]. Furthermore, owing to the high acidity of the solutions, nearly all of As(V) species is dissolved as neutral H$_3$AsO$_4$ 99.24~99.43% over studied temperature, whilst only small amount of H$_2$AsO$_4$ about 0.57~0.75% exists in the solutions. This trend is similar to the reported results in literature [36], in which more than 98% of total As(V) is H$_3$AsO$_4$ and only about 2% is H$_2$AsO$_4^-$ at 25°C in aqueous 0.5M H$_2$SO$_4$ solutions. In summary, the distribution percentage of each dissolved As(III and V) species overall remains stable at each temperature although the nominal As$^{5+}$/As$^{3+}$ ratio varies from 3:7 to 7:3. It appears that the proportion of each As(III) and As(V) species is independent of total concentration of As(III) and As(V) from 25°C to 70°C. Temperature still has a major effect on speciation distribution.

6.4 Calculated species distribution in aqueous Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H$_2$SO$_4$ solutions from 25°C to 70°C
Percentage of Fe(II, III) and Cu(II) species

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

Fe$^{2+}$, Fe$^{3+}$, Fe(SO$_4$)$_2^-$, FeHSO$_4^+$, FeSO$_4^-$, Cu$^{2+}$, Cu$^{3+}$, Cu$^{2+}$(SO$_4$)$_2^-$, CuHSO$_4^+$

(a)

Percentage of As, Sb (III, V) and Bi(III) species

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

H$_3$AsO$_3^+$, AsO$_3^-$, H$_2$AsO$_4^-$, H$_3$AsO$_4^{30}$, SbO$^+$, H$_3$SbO$_3^+$, Sb(OH)$_6^-$, HSb(OH)$_6^{30}$, BiO$^+$, Bi$^{3+}$

(b)

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

(a')

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

(b')
Percentage of Fe(II, III) and Cu(II) species

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

Fe$^{2+}$
FeHSO$_4^-$
Fe$^{3+}$
FeSO$_4^{2-}$
Cu$^{2+}$
CuHSO$_4^-$

Percentage of As, Sb (III, V) and Bi(III) species

Nominal Fe$^{3+}$/Fe$^{2+}$ ratio

H$\textsubscript{3}$AsO$_3^-$
H$\textsubscript{2}$AsO$_4^-$
H$\textsubscript{3}$AsO$_4^{3-}$
Sb$\textsubscript{2}$(OH)$_6^-$
HSb(OH)$_6^-$
Bi$\textsubscript{3}^+$
BiO$^+$

(c)

(c')

(d)

(d')
Figure 6.3: Calculated species distribution diagram in aqueous Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H₂SO₄ solution from 25°C to 70°C for test #7~12 with nominal Fe³⁺/Fe²⁺ ratios of 0.1 to 10, As⁵⁺/As³⁺ ratio of 7:3 to 3:7, and Sb⁵⁺/Sb³⁺ ratio of 1 for Fe(II), Fe(III), Cu(II), As(III), As(V), Sb(III), Sb(V) and Bi(III) species (a) and (a’) at 25°C; (b) and (b’) at 40°C; (c) and (c’) at 50°C; (d) and (d’) at 60°C; (e) and (e’) at 65°C; (d) and (d’) at 70°C. The sum of the percentage of Fe(II), Fe(III), Cu(II), As(III), As(V), Sb(III), Sb(V) and Bi(III) species is 100% respectively.
Figure 6.3 (a) and (a’) to (f) and (f’) show the thermodynamic speciation results in both aqueous Fe(II, III)-As(III, V)-Sb(III, V)-Cu(II)-H₂SO₄ (tests #7~9) and Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H₂SO₄ (tests #10~12) in solutions listed in Table 6.1 with nominal Fe³⁺/Fe²⁺ ratio 0.1 to 10, nominal As⁵⁺/As³⁺ ratio 3:7 to 7:3, and a constant nominal Sb⁵⁺/Sb³⁺ ratio 1:1 from 25°C to 70°C. Since the species distribution for tests #7~9 and #10~12 is all identical to each other excluding Bi(III) due to its small amount, analysis of tests #7~12 are combined in the same diagram for convenience.

For Fe(II) and Fe(III) species, the percentage of Fe²⁺ is 67.47~71.93%, FeHSO₄⁺ 3.98~19.98%, FeSO₄⁰ 12.35~24.59%, Fe³⁺ 0.96~5.34%, FeHSO₄²⁺ 12.22~24.57%, Fe(SO₄)₂⁻ 1.11~20.59% and FeSO₄⁺ 55.19~75.98%. For Cu(II) species, the percentage of Cu²⁺ is 14.77~40.9%, CuSO₄⁰ 4.23~18.05% and CuHSO₄⁻ 41.26~81.07%. For As(III) and As(V) species, the percentage of H₃AsO₄⁰ is 45.55~56.52%, AsO⁺ 43.48~54.45%, H₂AsO₄⁻ 0.57~0.75% and H₃AsO₄⁻ 99.25~99.43%. It can be noticed that concentrations of Fe(II, III), Cu(II) and As(III, V) species are nearly the same as those in Figure 6.1 and Figure 6.2. This indicates that addition of 0.2 g/L Sb(III, V) with nominal Sb⁵⁺/Sb³⁺ ratio 1:1 and 0.1 g/L Bi(III) practically does not change the proportion of the rest of the dissolved species.

Speciation results for Sb(III), Sb(V) and Bi(III) species are reflected in Figure 6.3 (a’) to (f’). As expected, distribution percentage of each Sb(III and V) and Bi(III) species, in general, remains stable at all studied temperature points. Most of Sb(III) species is distributed as SbO⁺ about 95.12~97.27% increasing with temperature, and H₃SbO₃⁰ decreases from 4.88% at 25°C to 2.72% at 70°C. In addition, a significant proportion of Sb(V) species is neutral H₃Sb(OH)₆⁰, which is around 99.73~99.997% in a declining trend, while the percentage of Sb(OH)₆⁻ is only 0.003~0.27% in an increasing trend from 25°C to 70°C.
Because the total concentration of Bi(III) is quite small (0.1 g/L) only including BiO\(^+\) and Bi\(^{3+}\) species, the distribution of Bi(III) species from 25°C to 70°C was estimated by using one mass balance equation and one equilibrium equation with the same activity coefficients of AsO\(^+\) and free Fe\(^{3+}\) in Fe(II, III)-As(III, V)-Sb(III, V)-Cu(II)-H\(_2\)SO\(_4\) system. For Bi(III) species, BiO\(^+\) is the least abundant, increasing from 0.003% at 25°C to 0.22% at 70°C, and free Bi\(^{3+}\) is the predominant Bi(III) species decreasing from 99.997% at 25°C to 99.78% at 70°C. Moreover, similar results were also found in literature that more than 90% percent of Sb(III) and Bi(III) distribute as SbO\(^+\) and Bi\(^{3+}\) in acidic solutions when pH is below zero (also under similar conditions: Sb(III)=Bi(III)=10\(^{-4}\) M) [38]. The distribution of each species strongly depends on temperature and is weakly dependent on concentration. The developed model has been confirmed to be practicable and accurate on the speciation of a complicated aqueous Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H\(_2\)SO\(_4\) system.

6.5 Experimental ORPs from 25°C to 70°C

It has been known that redox couple of free Fe\(^{3+}/Fe^{2+}\) is predominant to determine solution ORPs in aqueous FeSO\(_4\)-Fe\(_2\)(SO\(_4\))\(_3\)-H\(_2\)SO\(_4\) and FeSO\(_4\)-Fe\(_2\)(SO\(_4\))\(_3\)-CuSO\(_4\)-H\(_2\)SO\(_4\) systems up to 150°C [29], [116], [124-126]. It is of interest to investigate whether the presence of As(III, V) and Sb(III, V) still affect ORPs in iron-dominant solutions. Since the solution compositions of tests #10~12 are identical to those of tests #7~9 except for Bi(III) with a small amount as shown in Table 6.1, analysis of tests #10~12 is only shown to be necessary in the previous species distribution section. In addition, Bi(III) has no significance on ORP due to its single valence in the present work. The experimental ORP values between tests #10~12 and #7~9 are also nearly equivalent. Tests #10~12 will not be discussed in the following sections.
Figure 6.4: Comparison of the experimental ORPs for tests #1, 4 and 7 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 0.1:1, tests #2, 5 and 8 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 1:1, and tests #3, 6 and 9 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 10:1 in various solutions from 25°C to 70°C. Please refer to Table 6.1 that tests #1~3 are for aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions, tests #4~6 for Fe(II, III)-As(III,V)-Cu(II)-H$_2$SO$_4$ solutions, and tests #7~9 for Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H$_2$SO$_4$ solutions.

The experimental ORP results are shown in Figure 6.4 for tests #1~9 from 25°C to 70°C. As can be seen, adding 5g/L As(III, V) with 3 different nominal As$^{5+}$/As$^{3+}$ ratios into Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions has no evident impact on ORPs in Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions. The measured redox potentials for tests #1~3 are generally in accordance with those of tests #4~6 under same nominal Fe$^{3+}$/Fe$^{2+}$ ratio from 0.1 to 10. Furthermore, similar observation was also found that the presence of additional Sb(III), Sb(V) with nominal Sb$^{5+}$/Sb$^{3+}$ ratio 1 in aqueous Fe(II, III)-As(III,V)-Sb(III, V)-Cu(II)-H$_2$SO$_4$ solutions does not lead to substantial
change on ORPs in comparison to both tests #1~3 and #4~6. The deviation of ORPs between the 3 systems is less than 6mV on average over studied temperature under same nominal Fe$^{3+}$/Fe$^{2+}$ ratio. Tests #1, 4 and 7 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 0.1 actually have an almost same ORP value, which is also the case for tests #2, 5 and 8 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 1, and tests #3, 6 and 9 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 10. It appears that addition of As(III, V) and Sb(III, V) to aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions does not have any apparent influence on redox potential over temperature.

Theoretically, redox couple is likely to form spontaneously in aqueous solutions when two different valence states of a same element coexist, for instance Fe(III)/Fe(II), As(V)/As(III) and Sb(V)/Sb(III). Each couple is expected to have its own contribution to steady-state redox potential. More potential variations should be observed in the presence of As(III, V) and Sb(III, V) than in their absence. However, adding As(III, V) and Sb(III, V) gradually to Fe(II, III)-Cu(II)-H$_2$SO$_4$ system does not exhibit any effect on redox potential. It seems that the measured experimental ORPs from 25°C to 70°C are all determined by Fe(III)/Fe(II) under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 0.1 to 10, which, in fact, is redox free Fe$^{3+}$/Fe$^{2+}$ couple as discussed above. To further verify the effect of As(III, V) and Sb(III, V), calculation of redox potentials using Fe$^{3+}$/Fe$^{2+}$ couple from modeling results was carried out in the next section.

6.6 Calculated ORPs vs experimental ORPs from 25°C to 70°C
Potentials by Experiments and Modeling vs SHE at 25°C (mV)

(a) Tests #1~3

(b) Tests #4~6
Figure 6.5: Comparison of the potentials predicted by thermodynamic modeling and measured by experiments vs SHE at 25°C (a) in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions for tests #1~3, (b) in Fe(II, III)-As(III, V)-Cu(II)-H$_2$SO$_4$ solutions for tests #4~6, and (c) in Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H$_2$SO$_4$ solutions for tests #7~9 with relative nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.1 to 10, 1 As$^{5+}$/As$^{3+}$ ratio 3:7 to 7:3 and Sb$^{5+}$/Sb$^{3+}$ ratio 1 from 25°C to 70°C.

As can be seen in Figure 6.5 (a) to (c), the redox potentials calculated using the Nernst equation (Equation 6.1, which is same as Equation 3.10) and measured by experiments for tests #1~9 in Table 6.1 with nominal Fe$^{3+}$/Fe$^{2+}$ ratio from 0.1 to 10 in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$, Fe(II, III)-As(III, V)-Cu(II)-H$_2$SO$_4$ and Fe(II, III)-As(III, V)-Sb(III, V)-Cu(II)-H$_2$SO$_4$ solutions are in good agreement from 25°C to 70°C. This explains the fact that redox potentials for tests under the same nominal Fe$^{3+}$/Fe$^{2+}$ ratio have equivalent values of experimental ORPs as shown in Figure 6.4.

\[
E_T = E_T^o + \frac{2.303RT}{nF} \times \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \quad (6.1)
\]
The average potential deviation is no more than 4mV, 6mV and 7mV in the above three systems respectively. The maximum root-mean-square error of potentials between model results and experimental values for each test in above three systems was calculated to be no more than 1.71% in correspond to experimental values from 25°C to 70°C. It clearly indicates a quantitative validation to the developed speciation model by experimental ORP measurements. Therefore, a conclusion can be drawn that the calculated distribution and concentration of each species from Section 6.2 to 6.4 are accurate in the studied systems and temperature.

Figure 6.6 shows the calculated activity ratios of redox couple of free Fe$^{3+}$/Fe$^{2+}$ for tests #1~9 in Table 6.1 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 0.1 to 10 as a function of temperature. It is clear that the calculated activity Fe$^{3+}$/Fe$^{2+}$ ratios for tests #1, 4 and 7 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 0.1 are overlapped, in other words, are equal to each other from 25°C to 70°C. This is also the case for tests #2, 5 and 8 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 1 and tests #3, 6 and 9 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 10. The calculated results of activity Fe$^{3+}$/Fe$^{2+}$ ratios under the 3 nominal Fe$^{3+}$/Fe$^{2+}$ ratios for tests #1~9 provide a reasonable explanation for experimental results in Figure 6.4. Thus, the modeling ORPs can be fully calculated using free Fe$^{3+}$/Fe$^{2+}$ couple and above Equation 6.1 to compare with experimental values.

The concentrations (C$_{\text{ferric}}$ and C$_{\text{ferrous}}$) and single-ion activity coefficients (γ$_{\text{ferric}}$ and γ$_{\text{ferrous}}$) of free Fe$^{3+}$ and Fe$^{2+}$ ions at each temperature were obtained from modeling results. Concentration ratios of C$_{\text{ferric}}$/C$_{\text{ferrous}}$ for tests #1, 4 and 7 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 0.1 are almost identical, with average value ranging from 0.007 at 25°C to 0.001 at 70°C. The same case is also found for tests #2, 5 and 8 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 1, with average C$_{\text{ferric}}$/C$_{\text{ferrous}}$ ratio ranging from 0.074 at 25°C to 0.014 at 70°C, and tests #3, 6 and 9 under nominal Fe$^{3+}$/Fe$^{2+}$ ratio 10, with average C$_{\text{ferric}}$/C$_{\text{ferrous}}$ ratio ranging from 0.747 at 25°C to 0.145 at 70°C. In contrast,
single-ion activity coefficients ratios of $\gamma_{\text{ferric}}/\gamma_{\text{ferrous}}$ for tests #1~9 under nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.1 to 10 are nearly identical at all times and is only in a liner relationship with temperature. This is due to the same B-dot parameters used in Equation 3.5 with negligible difference. The average $\gamma_{\text{ferric}}/\gamma_{\text{ferrous}}$ ratio is 0.318 to 0.299 from 25°C to 70°C.

The standard electrode potential of free Fe$^{3+}$/Fe$^{2+}$ couple ($E^\circ$) is known to be 0.771V. The $E_T^\circ$ at elevated temperature was calculated using Criss-Cobble method [111-112]. Thereby, the modeling ORP values can be calculated simply by potential contributions from $E_T^\circ$(Fe$^{3+}$/Fe$^{2+}$) and activity Fe$^{3+}$/Fe$^{2+}$ ratios involved in Equation 6.1. Since $E_T^\circ$(Fe$^{3+}$/Fe$^{2+}$) is always identical for tests #1~9, and activity Fe$^{3+}$/Fe$^{2+}$ ratios are identical for tests #1, 4 and 7 (or tests #2, 5 and 8)
or tests #3, 6 and 9), this implies that calculated ORP values from modeling results remain essentially unchanged under the same nominal Fe$^{3+}$/Fe$^{2+}$ ratio but varying under the different ones over studied solutions and temperature.

In summary, the excellent agreement of redox potentials between experimental measurements and modeling calculation has firmly verified the predominance of redox free Fe$^{3+}$/Fe$^{2+}$ couple in the present work. Existence of 5g/L As(III, V) and/or 0.2g/L Sb(III, V) in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions has no effect on redox potentials. The redox potential can still be solely determined by the free Fe$^{3+}$/Fe$^{2+}$ couple, in spite of that, some extra redox couples may simultaneously exist. Please also note that validation of the studied thermodynamic model is limited to the current range of solution compositions and temperatures. Further experimental and theoretical work is needed to extend this model to a wider solution range.

6.7 Applicability of the developed expression
Figure 6.7: Comparison of the potentials calculated by Equation 6.2 and measured by experiments vs SHE at 25°C (a) in aqueous Fe(II, III)-Cu(II)-H$_2$SO$_4$ solutions for tests #1~3, (b) in Fe(II, III)-As(III, V)-Cu(II)-H$_2$SO$_4$ solutions for tests #4~6, and (c) in Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-H$_2$SO$_4$ solutions for tests #7~9 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.1 to 10, As$^{5+}$/As$^{3+}$ ratio 3:7 to 7:3 and Sb$^{5+}$/Sb$^{3+}$ ratio 1 in the temperature range of 25°C to 70°C.
Based on above analysis, the contribution to redox potentials in the present solutions has been confirmed to be dependent of free $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple. The Equation 5.1 has been pointed out in literature that it can be used to estimate redox potentials in iron-dominated acidic sulfate solutions up to 150°C [29]. Therefore, it is also used herein to find its applicability to the studied solutions in this chapter and is expressed as Equation 6.2 for convenience.

$$E(\text{mV}) = -1 \times 10^{-3} \times [T(K)]^2 + 0.91 \times T(K) + \frac{2.303 R}{nF} \times T(K) \times 10^3 \times \log \frac{C_{\text{ferric, nominal}}}{C_{\text{ferrous, nominal}}} + 492 \quad (6.2)$$

As demonstrated in Figure 6.7, the measured potentials are generally in good agreement with those calculated by Equation 6.2. The potential difference in overall less than 5mV under nominal $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios and temperature studied in the present work. Therefore, it can be confirmed that the previously developed expression is applicable to predict redox potentials in the studied solutions not only involving Fe(II and III), but also containing As(III and V) and Sb(III and V) from 25°C to 70°C.

6.8 Analysis of calculated pH and ionic strength

Measuring pH is a quite challenge in industrial electrorefining solutions due to their high acidity (typically pH<0). From the thermodynamic modeling results, it can provide the needed concentration and activity coefficient of H$^+$ ion to calculate pH value. Figure 6.8 (a) shows the estimated pH for various solution compositions in the present study.
Figure 6.8: Calculated (a) pH and (b) effective ionic strength in various solutions for tests #1~9 in Table 6.1 with nominal Fe$^{3+}$/Fe$^{2+}$ ratios from 0.1 to 10 in the temperature range of 25°C to 70°C.

The pH increases slightly from -0.17 to -0.07 in the temperature range of 25°C to 70°C under all studied nominal Fe$^{3+}$/Fe$^{2+}$ ratios. The increase of pH over temperature is due to the fact that more complex ions come into being such as FeHSO$_4^+$, FeHSO$_4^{2+}$, CuHSO$_4^+$ and HSb(OH)$_6^-$.

In fact, more protons are consumed by combining with free metal ions to form more thermodynamically stable ionic complexes and neutral species, giving rise to the declining concentration of H$^+$ ions. This also explains that distribution of dissolved aqueous species is highly dependent on pH and temperature.

The effective ionic strengths of the present solutions calculated from modeling results are shown in Figure 6.8 (b), which generally are lower than 3.0 mol/kg H$_2$O in a declining trend over temperature. The drop of ionic strength is because ion association of higher charged ions such as Fe$^{2+}$, Fe$^{3+}$ and Cu$^{2+}$ in solutions leads to the formation of more stable and less charged ionic complexes such as FeHSO$_4^+$, FeHSO$_4^{2+}$, FeSO$_4^+$, Fe(SO$_4$)$_2^-$ and CuHSO$_4^+$, and neutral...
species such as FeSO₄⁺, CuSO₄⁺, H₃AsO₄⁻, H₃AsO₄° and HSb(OH)₆⁻ as indicated in Figure 6.1 to Figure 6.3.

6.9 Conclusion

In this work, thermodynamic speciation model was developed to simulate current industrial copper electrorefining solutions up to 70°C. Compared with previous work, behavior of various impurity As(III, V), Sb(III, V) and Bi(III) species in aqueous Fe(II, III)-Cu(II)-H₂SO₄ solution from 25°C to 70°C has been illustrated in detail. Results reveal that distribution percentage of each Fe(II, III) and Cu(II) species including free Fe²⁺, FeHSO₄⁺, FeSO₄°, free Fe³⁺, FeSO₄⁺, FeHSO₄²⁺, Fe(SO₄)₂⁻, Cu²⁺, CuSO₄° and CuHSO₄⁺ is almost identical to that in Section 5.2 and 5.3 in the presence of As(III, V), Sb(III, V) and Bi(III).

As(III, V) primarily distributes as H₃AsO₄°, AsO⁺, H₂AsO₄⁺ and H₃AsO₄°; Sb(III, V) primarily dissolves as SbO⁺, H₃SbO₃°, HSB(OH)₆⁻ and Sb(OH)₆⁻; Bi(III) primarily dissolves as BiO⁺ and Bi³⁺. Concentrations of dissolved species were quantified through model calculation depending on solution compositions as well as their corresponding activity coefficients. Temperature plays a crucial role on species distribution.

Presence of As(III, V) and Sb(III, V) in aqueous Fe(II, III)-Cu(II)-H₂SO₄ solutions does not have any effect on ORPs over studied temperature under the same nominal Fe³⁺/Fe²⁺ ratio, and redox potentials in all 3 solution systems are shown to be identical, despite of solution compositions. The redox couple of free Fe³⁺/Fe²⁺ from Fe(III)/Fe(II) has been proved to be predominant although As(V)/As(III) and Sb(V)/Sb(III) may exist at same time. Furthermore, calculated ORPs by Equation 6.1 and experimental ORPs are in accordance that quantitatively validates the proposed model.
The good agreement of ORPs between **Equation 6.2** and experimental values confirms the suitability of the **Equation 6.2** to a broader range of solution compositions (**Table 6.1**). It can provide an alternative method to easily estimate ORPs in Fe$^{3+}$/Fe$^{2+}$ couple dominated solutions. As expected, calculated pH values in the present solutions are generally less than 0, increasing with temperature due to formation of ionic complex that consumes more proton. It is worth noting that the ionic strength in this study decreases with temperature due to formation of less charged ionic complexes and neutral molecules. The excellent agreement of ORPs between experimental measurements and model prediction justifies the reasonable use of B-dot model for activity coefficients calculation at high ionic strength up to 3M.

The present chapter provides a set of reliable thermodynamic data that enables researchers to study aqueous speciation over a wide range of solution compositions and temperature with high accuracy. The developed model allows systematic description of species behavior such as valence distribution, redox couple determination, ORP calculation, and pH/ionic strength estimation, thus, to obtain important optimization parameters of impurity control during copper production.
Chapter 7: Conclusions and future work

Aqueous speciation in Fe(II, III)-Cu(II)-H₂SO₄ solution from 25°C to 70°C has been demonstrated in detail in Chapter 5. The aqueous species are well identified, collected, and estimated after considerable literature review. It is shown to be reliable to simulate the species distribution under industrial copper electrorefining conditions. Speciation results show that Fe(II) still distributes as free Fe²⁺, FeHSO₄⁺ and FeSO₄⁻; Fe(III) distributes as free Fe³⁺, FeSO₄⁺, FeHSO₄²⁺ and Fe(SO₄)²⁻. Cu(II) dissolves as Cu²⁺, CuSO₄₀ and CuHSO₄⁺. Concentration of each species has been quantified through thermodynamic calculation as well as each accompanying ionic activity coefficient. Other parameters including activity, redox potential, pH and ionic strength were obtained from modeling results. Experimental redox potential (ORP) measurements have confirmed the validity of the developed model by comparing with the calculated ORPs using the Nernst equation (Equation 3.10 or Equation 6.1). Both Fe(II, III)-H₂SO₄ and Fe(II, III)-Cu(II)-H₂SO₄ aqueous systems were extended to a broader range of concentration of H₂SO₄ (185g/L) and Cu(II) (40~50g/L) in comparison to the previously developed model of Fe(II)-Fe(III)-H₂SO₄-H₂O system under chalcopyrite leaching conditions. Analysis suggests that Fe(II, III)-H₂SO₄ solutions with a high H₂SO₄ and Cu(II) concentration can still be solely determined by Fe³⁺/Fe²⁺ couple. The results also prove the suitability of B-dot equation at high solution ionic strength up to 3M, applicability of a previously developed expression (Equation 5.1) for ORP prediction, and reliability of the selected thermodynamic data.

Based on above theoretical and experimental results, an extension of Fe(II, III)-Cu(II)-H₂SO₄ model was made in solutions, containing additional As(III), As(V), Sb(III), Sb(V) and Bi(III) impurity elements with concentrations still based on industrial conditions from 25°C to
70°C. Aqueous species of As, Sb and Bi were also critically identified and assessed including $H_3AsO_3^0$, AsO$^+$, $H_2AsO_4^-$, $H_3AsO_4^0$, SbO$^+$, $H_3SbO_3^0$, Sb(OH)$_6^-$, HSb(OH)$_6^0$, BiO$^+$ and Bi$^{3+}$ from available sources as well as their thermodynamic data. Similarly to above Fe(II, III)-Cu(II)-$H_2SO_4$ model, important parameters, for example, concentration, activity coefficient, activity, redox potential, solution ionic strength and pH were thus calculated and obtained. Detailed results are presented in Chapter 6. This proved that the developed thermodynamic model is capable to carry out computational calculation in such complicated solutions systems and compositions. Experimental ORP measurements have validated the developed models by comparing with modeling ORPs using the Nernst equation. An important finding is that redox potentials in Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-$H_2SO_4$ solutions can be still determined by redox Fe$^{3+}$/Fe$^{2+}$ couple from Fe(III)/Fe(II) even with the presence of As(III)/As(V) and Sb(III)/Sb(V), neither of which can serve as an oxidant or reductant. Hence, the predominance of redox Fe$^{3+}$/Fe$^{2+}$ couple has been confirmed in Fe(II, III)-As(III, V)-Sb(III, V)-Bi(III)-Cu(II)-$H_2SO_4$ solutions by both modeling and experimental results. Furthermore, it has been verified that the previously developed expression with only two variables (nominal Fe$^{3+}$/Fe$^{2+}$ ratio and temperature) is capable of predicting ORPs in acidic sulfate solutions with high accuracy.

The findings of this work provide a deeper understanding on speciation in copper electorefining solutions. The thermodynamic and speciation model is practically valuable as it reveals the quantification analysis of impurity species and redox potential determination over a broad range of temperatures. Thus, it can potentially facilitate the impurity removal of those detrimental elements with higher efficiency during industrial operation in hydrometallurgical processes.
Since the amount of total 5g/L As(III, V) is obviously higher than that of 2g/L Fe(II, III), potential variation was expected during experimental testing. However, the results were still observed to be redox Fe(III)/Fe(II) dominated. The predominance of redox Fe$^{3+}$/Fe$^{2+}$ couple thus brings some interesting thinking whether redox species of free Fe$^{3+}$ and Fe$^{2+}$ cation can still form a redox couple in solution systems excluding As and Sb. It is known that cobalt (II, III) and nickel (II, III) also exist in copper electrorefining solutions with notable amount. Compared to copper, they could be regarded as byproduct when being extracted from slimes. However, these sorts of metals are of great value nowadays due to their higher demand in the field of related alloy, electrical vehicle and battery products. It will be interesting to see if the speciation or concentration of these elements (Co and Ni) with various valence states can be calculated or quantified in aqueous form by means of theoretical modeling and experimental testing according to the present methods. Determination of redox potential and/or redox couple over operating temperature will be also interesting to find. This possibly can improve the extractive efficiency not only in copper electrorefining solutions, also in other related electrometallurgical processes. To do so, more investigations and focus on speciation study of metal-water systems are needed in the future.
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potential and stability of FeCl_2^+ to 90°C. Thermodynamic properties of Fe^{3+}(aq) and ferric-
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