Phase equilibria of selected sulfide impurity systems at elevated temperatures

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Abstract

More complex ore bodies have to be utilized in order to meet the increasing demand for metals in the World. Together with growing use of secondary raw materials, metal production feeds are containing higher impurity levels than the processes are originally designed to operate with. Common to all impurities is the fact that they need to be eliminated from the product in an effective way. Phase diagram information and thermodynamic descriptions of phases in complex sulfide systems at elevated temperatures will help in the development of pyrometallurgical processes.

In this thesis, phase stability information about the FeS-PbS, Cu_2S-PbS, Fe-O-S, Cu_2S-PbS-ZnS, As_2S_3-Cu_2S, As_2S_3-PbS and As_2S_3-Cu_2S-PbS systems above 500 °C has been measured using isothermal equilibration-quenching experiments. The main interests in the experiments were in the formation of liquid phase. Based on these results and literature information where available, phase diagrams of these systems have been estimated.

Thermodynamic descriptions in a wide temperature and composition range for phases of the FeS-PbS, Cu-Pb-S, PbS-ZnS and Cu_2S-PbS-ZnS systems have been derived applying the CALPHAD method and MTDATA software, using the experimental data found during the work of this thesis and critically evaluated literature information. The association solution model was used for the molten phase and the experimental data was fitted by the least squares method.

The new experimental data presented within this thesis enables a more accurate description of the systems studied and provides new information about phase stabilities in these systems. The created thermodynamic assessments allow accurate predictions of phase equilibria and thermodynamic properties. The phase equilibria information provided in this thesis may be used to evaluate and give more accurate knowledge of different pyrometallurgical processes, including evaluation of molten phase formation in impure zinc sulfide roasting and component distributions copper smelting and refining.

A! Aalto-yliopisto

Tekijä
Hannu Johto

Väitöskirjan nimi
Valittujen sulfidiepäpuhtaussysteemien faasitasapainot korkeissa lämpötiloissa

Julkaisija Kemian tekniikan korkeakoulu

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Tiivistelmä

Epäpuhtauksien määrä metallinvalmistusprosessien syötteissä on kasvanut kun käyttöön on otettu monimutkaisempia rikasteita sekä sekundäärisiä raakaaineita usein korkeammalle tasolle kuin prosessit on alun perin suunniteltu operoitavaksi. Kehitettäessä prosesseja hallitsemaan epäpuhtauksien poisto tehokkaammin sekä ympäristöystävällisemmin on hyödyllistä olla systeemin faasipiirrosten sekä termodynaamisten ominaisuuksien tuntemusta. Tässä työssä määritettiin kokeellisesti vakiolämpötilassa suoritetuilla tasapainotuskokeilla systeemien FeS-PbS, Cu_2S-PbS, Fe-O-S, Cu_2S-PbS-ZnS, As_2S_3-Cu_2S, As_2S_3-PbS ja As_2S_3-Cu_2S-PbS faasitasapainoja yli 500 ºC lämpötiloissa keskittyen erityisesti sulan faasin muodostumiseen. Näiden kokeiden sekä kirjallisuudesta löytyvän aikaisemman kokeellisen tutkimustiedon perusteella luotiin systeemeille faasitasapainopiirrokset.

Kokeellisen työn lisäksi suoritettiin CALPHAD-metodia hyödyntäen MTDATA-ohjelmistolla termodynaamiset kuvaukset systeemeistä FeS-PbS, Cu-Pb-S, PbS-ZnS ja Cu_2S-PbS-ZnS laajalla lämpötila-sekä koostumusalueella. Sovituksissa käytettiin sulan faasin kuvaukseen assosiaattimallia ja sovitus tehtiin pienimmän neliösumman menetelmällä perustuen tämän työn kokeellisiin tuloksiin sekä kriittisesti arvioituun kirjallisuudessa esitettyyn kokeelliseen tietoon.

Tässä työssä esitetty kokeellinen tieto sekä tehdyt termodynaamiset sovitukset tarjoavat tutkittujen sulfidisysteemien aikaisempaa tarkemman faasitasapainokuvaukset sekä mahdollistavat systeemien termodynaamisten ominaisuuksien ennustamisen. Faasitasapainoja osassa tutkituista systeemeistä ei ole aikaisemmin kuvattu kirjallisuudessa. Esitettyä tasapainopiirrostietoa voidaan käyttää hyödyksi kehitettäessä ja analysoitaessa metallurgisia prosesseja ja ilmiöitä, mukaan lukien sulafaasin muodostuminen epäpuhtaan sinkkisulfidin pasutuksessa sekä epäpuhtauksien käyttäytyminen kuparin pyrometallurgisessa valmistuksessa.

Preface

This doctoral thesis carried out in the research group of Metallurgical Thermodynamics and Modelling (TDM) at Aalto University School of Chemical Technology during the years 2010 – 2014 and in the PYROSEARCH research group at the University of Queensland, Brisbane, Australia, during the year 2012.

I am deeply grateful to my supervisor and advisor professor Pekka Taskinen for all encouragement and support during this thesis project. His expertise in the field of metallurgy has been great source of learning for me and a great professional inspiration.

I would like to thank the staff and friends in the TDM research group during these years for all the help I have got but also giving me enjoyable environment. Especially I would like to thank Dr. Iina Vaajamo for being my roommate and problem sharer during this work and my office neighbors, Dr. Petri Kobylin and Lis.Sc. Hannu Sippola for all the pleasant discussions. I would also like to thank Professor Guven Akdogan from Stellenbosch University, RSA, guidance and interest towards my work and Dr. John Gisby from NPL, UK, for helping me with MTDATA.

I want to thank Professor Evgueni Jak for enabling part of this work to be conducted under his professional supervision at PYROSEARCH. I would also like to thank Dr. Hector M. Henao for continuous guidance during my stay in Brisbane and Ms. Suping Huang and Mr. Imam Santoso for valuable help.

From Outotec I would like to thank M.Sc. (Chem.) Jouni Pihlasalo and Dr. Maija Metsärinta for their interest towards my work and valuable discussions during these years.

List of Publications

The thesis consists of an overview and of the following publications, which are referred to in the text by their Roman numerals.

I   **Hannu Johto**, Pekka Taskinen, "Experimental research and thermodynamic model of the FeS-PbS system", In: Proceedings of European Metallurgical Conference 2011 (EMC), Düsseldorf, June 26-29, 2011, Volume 4, ISBN 978-3-940276-39-1 (pp. 1127-1136).

II   **Hannu Johto**, Pekka Taskinen, "Phase stabilities and thermodynamic assessment of the system Cu-Pb-S", Minerals Engineering 42 (2013) 68–75.

III   **Hannu Johto**, Hector M. Henao, Evgueni Jak and Pekka Taskinen, "Experimental study on the phase diagram of the Fe-O-S system", Metallurgical and Materials Transactions B 44, 6 (2013), 1364-1370, DOI 10.1007/s11663-013-9923-8.

IV   **Hannu Johto** and Pekka Taskinen,"Phase diagram of the system Cu_2S-PbS-ZnS at 873-1273 K", Canadian Metallurgical Quarterly, 2013, DOI 10.1179/1879139513Y.0000000105.

V   **Hannu Johto** and Pekka Taskinen, "Phase diagram of the system As_2S_3-Cu_2S-PbS at 773-1173 K", Accepted for publication in Canadian Metallurgical Quarterly.

iv

Author's contribution

Publication I: "Experimental research and thermodynamic model of the FeS-PbS system"

The author performed the literature survey and thermodynamic assessment of the system. The experimental part was planned and performed by the author with the experimental set-up designed by the author. The author analyzed the results, wrote the first version of the manuscript and edited the final version based on the input from the co-author.

Publication II: "Phase stabilities and thermodynamic assessment of the system Cu-Pb-S"

A literature survey and the thermodynamic assessment were done by the author. The author planned the equilibration experiments and executed them with the experimental set-up designed by the author. The author analyzed the results, and wrote the manuscript with the help of the co-author.

Publication III: "Experimental study on the phase diagram of the Fe-O-S system"

The phase diagram experiments were planned by the author, together with Professor Jak and Dr. Henao. The author performed the experiments with the experimental set-up designed at the University of Queensland. The analysis of results was performed by the author together with Dr. Henao and Professor Jak. The author wrote the manuscript and edited the final version based on the input from the co-authors.

Publication IV: "Phase diagram of the system $Cu_2S–PbS–ZnS$ at 873-1273 K"

The experimental part was planned and carried out by the author with the experimental set-up designed by the author. The author performed the thermodynamic assessment and the literature search. The author analyzed the results, and wrote the manuscript with the help of the co-author.

Publication V: "Phase diagram of the system As$_2$S$_3$-Cu$_2$S-PbS at 773–1173 K"

The phase stability experiments were planned and carried out by the author with the experimental set-up designed by the author. The author analyzed the results and wrote the manuscript with the help of the co-author.

List of symbols and abbreviations

Symbols

A-G	coefficients of Gibbs energy temperature dependence function
A-I	Polynomial terms of temperature dependent interaction parameter
a-n	coefficients of heat capacity function
c	number of compounds
C_i	the calculated value of property i
C_p	molar heat capacity, constant pressure
E_i	the experimental value of property i
G	Gibbs free energy
H	enthalpy
L	temperature dependent interaction parameter
l	number of sublattices
N	number of sites in sublattice
n	number of moles
$P_l(Y)$	reference matrix for sublattice
R	gas constant
S	entropy
T	temperature
U_i	uncertainty associated with the experimental value E
v	composition term
W_i	weight factor assigned to property i
x	mole fraction
y	site fraction
Ω	temperature dependent interaction parameter

Superscripts

n	order of polynomial
id	ideal
ex	excess
o	standard state
mix	mixing
ass	associate
reg	associate interaction term
ref	frame of reference
s	sublattice

Subscripts

I	compound
$i,j,k,-n$	components
i	property
n	order of polynomial
va	vacancy

Abbreviations

CALPHAD	CALculation of PHAse Diagrams
EDS	Energy Dispersive Spectrometer
EPMA	Electron Probe X-ray Microanalysis
MIRO	Minerals Industry Research Organization, UK
MTDATA	Thermochemical software from NPL
MTOX	Metal-oxide-sulfide-fluoride thermodynamic database
NPL	National Physical Laboratory, UK
SDD	Silicon Drift Detector
SEM	Scanning Electron Microscope
SER	Stable Element Reference
SGTE	Scientific Group Thermodata Europe
STP	Standard temperature and pressure
UNARY	Thermodynamic database for pure elements

Table of Contents

1. Introduction

1.1 Background

A significant part of the world's base metals production is produced from sulfide minerals [1,2]. The sulfide minerals in the Earth's crust are mainly located in mixed complex multi-metallic ore bodies which also contain various other sulfide minerals that are difficult to liberate [3]. Thus, the current tendency is towards using concentrates with higher impurity levels because more complex ore bodies are needed to meet the increasing global demand for metals and because of depletion of simpler and richer orebodies [4]. In addition, the increasing use of secondary raw materials can introduce components that do not exist in the primary ore-bearing raw materials for the metal making process [5].

It is common to all impurities that they have to be eliminated from product metal in an environmentally sustainable and effective way, without the loss of valuable metals. The impacts of the increasing amount of impurities in the pyrometallurical metal smelting process are currently not well established, and needs to be studied more so as to be able to control better.

The main production route for zinc is from sulfide concentrates with high temperature roasting in fluidized bed reactors followed by leaching and electrowinning [2]. In the zinc sulfide roasting, impurities such as As, Cu, Fe and Pb have been indicated to be the source of various production problems [6-9]. The dominant copper production route in the World from sulfuric concentrates is matte smelting in a flash furnace followed by converting step to produce crude copper [1]. In this process, the removal of impurities such as arsenic and lead from product copper is essential because of their adverse effects on the product and on the environment during the smelting process [10-12]. A better understanding of all these process phenomena demands more accurate and broader phase stability information about complex sulfide systems.

Thermodynamic calculations can be used to evaluate and optimize the parameters of industrial processes for best recovery of precious materials and treatment of impurities with changes in feed material and other process modifications [13, 14]. The phenomena in metal making processes are complex, often difficult, or impossible to investigate experimentally, and therefore thermodynamic calculations are an effective tool when dealing with detailed chemical processes at elevated temperatures. However, reliable thermodynamic calculations require an internally consistent and dependable thermodynamic database, which needs to be created based on experimental information.

1.2 Objective of the thesis

The aim of this thesis was:
1. To produce phase diagram information about the FeS-PbS, Cu_2S-PbS, Fe-O-S, Cu_2S-PbS-ZnS, As_2S_3-Cu_2S, As_2S_3-PbS and As_2S_3-Cu_2S-PbS systems, and
2. To create thermodynamic model parameters for the phases of the FeS-PbS, Cu-Pb-S, PbS-ZnS and Cu_2S-PbS-ZnS sulfide systems, to be stored in a thermochemical database

The experiments were aimed at producing phase diagram information in equilibrium conditions about the systems under consideration. Although phase diagrams of the FeS-PbS, Cu_2S-PbS, Fe-O-S and Cu_2S-PbS-ZnS systems can be found in the literature, the experimental information was used to confirm the previous data with more accurate measurement methods and to widen the experimentally covered temperature and composition areas with new scientific information. The experimental information available in the literature about the studied systems from 1907 to today have been presented and evaluated in Publications and is not repeated in this compendium. The experimental information of the pseudoternary As_2S_3-Cu_2S-PbS system within this thesis is new scientific information not previously available in the literature.

The phase diagram data obtained on the FeS-PbS, Cu-Pb-S, and Cu_2S-PbS-ZnS systems were used together with critically evaluated literature data to produce thermodynamic assessments of these systems using associate model and MTDATA software [15]. In addition, the PbS-ZnS system was thermodynamically assessed based on critical evaluated literature data. The assessments in the thesis have been made in collaboration with the National Physical Laboratory (NPL) and Mineral Industry Research Organization (MIRO) in order to expand their existing MTOX (metal-oxide-sulfide-fluoride)

thermodynamic database, which covers equilibria data for metallic, oxide, sulfide and fluoride systems related to various metal smelting and refining processes [14,16,17]. The thermodynamic descriptions created in the thesis were aimed to obtain more accurate phase equilibria predictions in a wide temperature range and with full internal consistency, which makes them suitable for use with other thermodynamic assessments.

2. Phase diagram experiments

The experimental part of the thesis was performed using an equilibration–quenching technique. This method makes it possible to measure the compositions of all the condensed phases in equilibrium at the experimental conditions [18]. In a case with two phases in equilibrium, this means the determination of a tie-line. The advantage of the selected method is the possibility of direct measurements of the compositions of all the condensed phases present in the sample as well as the independence of the tie-line from the bulk composition of the sample, when the analysis of the compositions is performed after the experiment. Therefore, the results are not affected by uncertainties in the initial mixture or changes in the bulk composition caused by vaporization or undetected reactions with the sample holder made by material not intended to include to the study [19]. One further advantage of this method is the more accurate determination of the actual sample temperature at the equilibrium than in methods using temperature ramping, like differential scanning calorimetry or differential thermal analysis [18].

Altogether three different experimental set-ups were used, which are described in detail in the publications. In publications I, II, IV and V, the experiments were performed in evacuated and sealed silica tubes due the high vapor pressures of the compounds present. The experimental part of publication III was performed using either an inert or controlled active gas atmosphere.

2.1 Materials used in the experiments

The equilibration experiments were performed using commercial pure metal, sulfide and oxide powders. Mixtures of various compositions were prepared by weighing the powders and mixing them using an agate mortar and pestle.

The quartz glass ampoules used in the experiments in publications I,II, IV and V were made by Lasilaite Oy, (Porvoo, Finland) from high-grade synthetic fused silica glass with a total metallic contamination of less than 5 ppm. The

experiments in inert or controlled gas atmospheres in the Fe-O-S system presented in publication III were performed using high purity iron foil as the sample holder in the form of metallic iron or at controlled oxygen partial pressure and temperature in pre-oxidized envelopes.

2.2 Equipment and experimental procedure

The experimental part of the thesis was performed using three different experimental set-ups, two of which were designed and built at Aalto University, Espoo, Finland and one at the University of Queensland, Brisbane, Australia. The overall experiment practice in all of the publications is similar but the implementation changes. The procedure is to equilibrate the sample at a controlled temperature and quenching it with cold water after a defined time.

The phase diagram study in publications I and partly in II were performed using a Lenton chamber furnace, (Hope Valley, UK) the UAF 16/10. In the experiments using the chamber furnace, the ampoules were placed in the hot zone of the furnace and the temperature was raised to 1150 °C to pre-melt the sample inside the ampoule and then cooled in a controlled way down to the equilibration temperature. After the selected equilibration time was past, counting from the point when of the correct temperature was reached, the ampoule was removed from the furnace with a pair of tongs and quenched in an ice water mixture.

For the experiments in publications IV, V and partly II, a vertical tube furnace, a Lenton (Hope Valley, UK) CSC 12/90/450, with a 30-mm inner diameter alumina working tube was installed in a fume hood. Through the furnace working tube, a steel wire was installed in such a manner that it enabled the wire to lift and drop the ampoule from outside the fume hood. The procedure with ampoules using the tube furnace was similar to that with the chamber furnace, but the quenching was done by releasing the lifting wire and letting the sample to drop into the ice water below instead of lifting the sample with tongs. This method enables faster quenching and is safer for the person performing the experiments. The schematic illustration of the experimental set-up is presented in Figure 1.

S-type thermocouple

A steel wire to lift and drop the ampoule

Lenton tube furnace

Sample in a ampoule inside a steel wire basket

PC to collect temperature data

Keithley -Voltmeters

furnace control unit

ice water

Glowe box
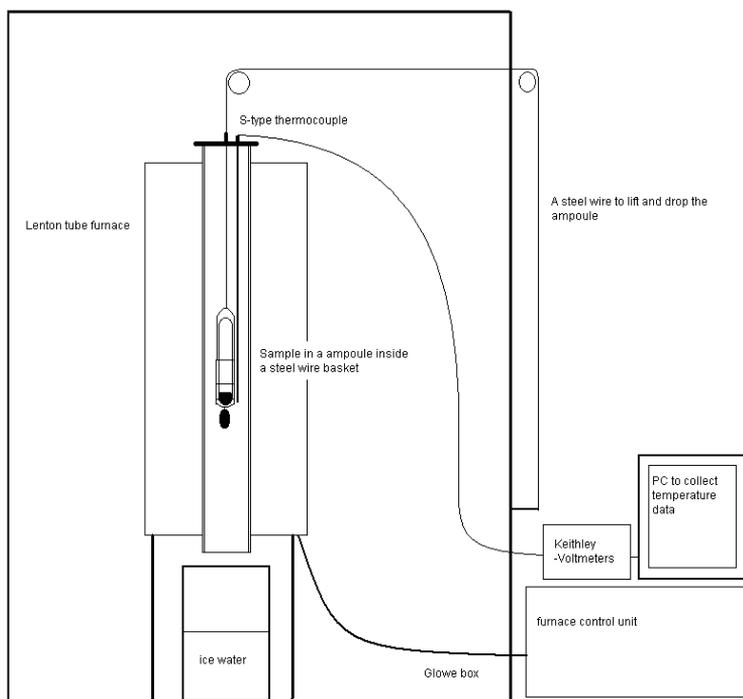
Figure 1 Schematic picture of the experimental set-up used in the publications IV, V and partly II.

During these experiments, the sample creates its own gas phase from the evaporating compounds present, which is in equilibrium with the condensed phases present in the sample. When the gas composition is in equilibrium with the condensed phases, no more evaporation takes place and the equilibrium amounts of the compounds with high vapor pressure remain in the condensed phases.

The experiments in publication III were performed using a set-up designed and built by the PYROSEARCH research group at the University of Queensland, Australia [19, 20]. The experimental set-up was vertical electrical resistance furnace with a 30-mm inside diameter alumina reaction tube with sealed cold ends. The sample was introduced into the furnace from the bottom of the furnace and suspended by a sample holder made of iron or platinum wire. The selected gas mixture or an inert gas was introduced into the reaction tube and the tube was flashed for more than 10 minutes before the sample was raised into the uniform temperature hot zone of the furnace. The correct gas mixtures to achieve selected oxygen partial pressure at a set temperature, with the volumetric gas compositions, were calculated by means of MTDATA

thermodynamic software using the MTOX database. The flow rates of gases to the furnace were controlled using glass capillary flow meters, introducing the gas mixture into the bottom of the furnace. The total flow rate of the gas inside the furnace was between 300 and 600 ml/min (STP). The sample was first pre-melted at a temperature 50-100 °C higher than the experimental temperature for 15 minutes before decreasing the temperature back for the equilibration. After the selected equilibration time was completed, the bottom of the furnace working tube was immersed in iced water, the lower end was opened, and the specimen was then rapidly quenched by dropping it into the water.

The advantage of the technique used to study the Fe-O-S system is that the sample holder used is reactive and a part of the system studied, thus eliminating any effect on the equilibrium of the sample holder made from a material not part of the system under investigation.

The achievement of equilibrium is an important issue in the type of experiments performed in the thesis and the most common source of uncertainty [18, 19]. During analysis, the homogeneity of the phases was checked by performing the analysis in different locations of the sample. Different equilibration times were also applied to confirm the achievement of equilibrium between the phases during the experiments before selecting the final equilibration time, which depended on the system studied. In the selected systems, experiments with different starting compositions were tested to ensure the achievement of equilibrium from different directions.

2.3   Analysis technique

After quenching, the ampoules in publications I, II, IV and V were broken down and the sample was separated from the quartz glass parts. The sample was then cut in half lengthwise and a polished section for SEM analysis was prepared from one half using standard wet methods in such a manner that the entire cut surface from the center of the sample could be examined. The analyses of the samples were performed using a LEO 1450 (Carl Zeiss Microscopy GmbH, Jena, Germany) scanning electron microscope with a Link Inca X-Sight 7366 Energy EDS- analyzer utilized with X-max 50 SDD detector (Abingdon, Oxfordshire, UK). In the composition analyses, the average uncertainty was within ±1.5 wt. % based on calculated standard deviations of multiple point analysis.

In the experiments presented in publication III, after quenching the sample was dried on a hot plate, crushed into pieces, and mounted in epoxy resin. The

specimen was then polished using conventional metallographic polishing techniques and carbon coated for metallographic observation and microanalysis. The compositions of various phases were measured using a JEOL (Japan Electron Optics Ltd, Tokyo, Japan) 8200L EPMA equipped with wavelength dispersive detectors. The oxygen content in the samples was not measured directly in the current study by means of EPMA; the analysis was performed by measuring directly only the sulfur and iron content of the samples. The oxygen content was calculated by subtracting the analyzed weight percentages of Fe and S from the total 100 wt. %. This procedure was not optimal and had a high degree of uncertainty due to the limitations in oxygen analysis. However, it is believed it still provides more accurate phase compositions compared with bulk analysis methods because the highly uncertain physical phase separation is not needed in the current technique. The assumed overall accuracy regarding the different elements is within 1 wt. % for iron, within 2 wt. % for sulfur and within 3 wt. % for calculated oxygen. The oxygen analysis method was tested by performing a set of experiments oxidizing iron samples with a known gas atmosphere and comparising the results of oxygen content calculations from the EPMA analysis with the compositions calculated by means of MTDATA thermodynamic software using the MTOX database from the Fe-O phase diagram.

3. Thermodynamic models and assessment procedure

Computational thermodynamic modelling is commonly used for predicting the thermodynamic properties of complex multicomponent systems. Most often calculations are based on global minimization of the Gibbs energy of the system, which is calculated with computer software using thermodynamic data for all the phases in the system [21]. The Gibbs energy approaches minimum when a closed system at constant temperature, pressure and amounts of components approaches an equilibrium state.

The Gibbs energy can be defined as

$$G = H - TS \tag{1}$$

where H is enthalpy, S entropy and T temperature. The temperature dependency of the Gibbs energy can be described using empirical power series of heat capacity [22]

$$C_p = a + bT + cT^{-2} + dT^2 + \sum e_n T^n \tag{2}$$

where $a...e_n$ are coefficients fitted to experimental data. From the basic thermodynamic equations for enthalpy and entropy and using Equations (1) and (2), the temperature dependency can be derived for Gibbs energy

$$G = A + BT + CT\ln T + \sum D_n T^n \tag{3}$$

where A and B are constants that can be calculated for standard values of enthalpy and entropy and from the coefficients of heat capacity Equation (2). The terms $C...D_n$ can be derived from the C_p Equation (2). The integers represented by n in Equation (3) typically receive the values 2,3 and -1. [22, 23]

Equation (3) is used in this work for the Gibbs energy of pure species. For stoichiometric compounds with no measured heat capacity, the temperature dependency of Gibbs energy can be estimated using the Kopp-Neumann rule [24], i.e. that the heat capacity of the compound is equal to the stoichiometric

average of the heat capacities of the elements. The Gibbs energy of a compound will then be

$$G = a_0 + a_1 T + \sum_i n_i G_i \qquad (4)$$

The enthalpy, and therefore also Gibbs energy, have no absolute values and therefore a reference state needs to be defined. A reference state widely used, including in the SGTE database [22] and data books of Barin [23], is the standard element reference, SER, which for the enthalpy of an element in the stable form at 298.15 K and 1 bar pressure is defined to be 0. Enthalpy using this reference state is denoted as H^{SER} and Gibbs energy G^{HSER}.

3.1 Description of solution phases

The Gibbs energy for a solution phase can be calculated as a sum of all the Gibbs energies of the species in equilibrium in the system [13]

$$G = \sum_i^n n_i G_i \qquad (5)$$

where n_i is the amount of species i and G_i is the partial Gibbs energy of a species $i...n$. The Gibbs energy of a species in a solution phase can thus be given as

$$G_i = G_i^0 + {}^{id}G_i + {}^{ex}G_i \qquad (6)$$

where G_i^0 is the contribution of the pure components of the phase to the Gibbs energy, ${}^{id}G_i$ is the ideal mixing contribution, and ${}^{ex}G_i$ is the contribution of non-ideal interactions between the species. The non-ideal interaction is also known as the Gibbs excess energy of mixing. Additional terms associated with pressure or magnetism can be added to Equation (6), but they are not used in this thesis because limited influence on total Gibbs energy. Combining Equations (5) and (6), the Gibbs energy of a solution phase can be written as

$$G = \sum_i^n x_i G_i^0 + {}^{id}G^{mix} + {}^{ex}G^{mix} \qquad (7)$$

where x_i is the mole fraction of species i, ${}^{id}G^{mix}$ is the ideal mixing contribution and ${}^{ex}G^{mix}$ is the excess mixing contribution to the Gibbs energy.

3.1.1 Substitutional solution model

For simple mixtures, like gas and a simple solid or liquid phase, the ideal Gibbs energy of mixing can be described by a random distribution of species in the lattice without interaction energy. This model is called the ideal substitutional solution model. In this approach, the enthalpy of mixing and the excess Gibbs energy of mixing are zero and therefore the Gibbs energy of an ideal mixing of the phase is

$$^{id}G^{mix} = RT \sum_i x_i ln x_i \tag{8}$$

Combining equation (7) with Equation (8), the Gibbs energy of a solution phase can be given as

$$G = \sum_i^n x_i G_i^0 + RT \sum_i x_i ln x_i + {}^{ex}G^{mix} \tag{9}$$

For the liquid phase, a regular solution model was used to describe the excess Gibbs energy. In this model, the excess Gibbs energy is given in binary system as

$$^{ex}G^{mix} = x_i x_j \Omega \tag{10}$$

where Ω is a temperature dependent interaction parameter. Equation (10) is often not enough to describe a system and thus it is modified to a more mathematically efficient form. One widely used modification is Redlich-Kister polynomials, where the interaction energies are considered to change with the composition [25]. With this modification, Equation (11) is the obtained

$$^{ex}G^{mix} = x_i x_j \sum_{n=0}^m {}^n L_{ij} (x_i - x_j)^n \tag{11}$$

where $^n L_{ij}$ is a temperature dependent interaction parameter estimated from experimental data and n is the order of each polynomial term, starting from zero. The polynomial L is described as temperature dependent

$$^n L_{ij} = A_n + B_n T + C_n T ln T + D_n T^2 + \cdots + I_n T^{-9} \tag{12}$$

By using the Muggianu [26] interpolation method, as used by MTDATA software, the excess Gibbs energy might be written in ternary system as

$$^{ex}G^{mix} = x_i x_j \sum_{n=0}^m {}^n L_{ij} (x_i - x_j)^n + x_j x_k \sum_{n=0}^m {}^n L_{jk} (x_j - x_k)^n +$$
$$x_i x_k \sum_{n=0}^m {}^n L_{ik} (x_i - x_k)^n + x_i x_j x_k (v_i \, {}^0 L_{ijk} + v_j \, {}^1 L_{ijk} + v_k \, {}^2 L_{ijk}) \tag{13}$$

where $v_i ... v_k$ are defined as

$$v_i = x_i + \frac{1 + x_i + x_j + x_k}{3} \tag{14a}$$

$$v_j = x_j + \frac{1 + x_i + x_j + x_k}{3} \tag{14b}$$

$$v_k = x_k + \frac{1 + x_i + x_j + x_k}{3} \tag{14c}$$

The temperature dependent interaction parameters are similarly described with the polynomials shown in Equation (12) and can be optimized from experimental data.

3.1.2 Associate model
The liquid phase can also be described as a substitutional solution of elements and compounds formed by the components of the system. These compounds are called associates. In this case, the thermodynamic properties of the liquid phase depend predominantly on the Gibbs energy of formation of these associates rather than interactions between the components. [27-31]

For a simple binary system A-B, where a single associate A_iB_j forms and the liquid contains n_{A1} and n_{B1} moles of non-associated A and B and m_{AiBj} moles of associate A_iB_j. The mole fractions of the compounds in the binary system containing 1 mole of A and B atoms are

$$x_A = n_A + in_{AiBj} \tag{15a}$$

$$x_B = n_B + jn_{AiBj} \tag{15b}$$

$$x_{AB} = n_{AiBj} \tag{15c}$$

The excess Gibbs energy can be written as

$$^{ex}G^{mix} = G^{ass} + G^{reg} \tag{16}$$

where G^{ass} is the Gibbs energy due to formation of the associate and G^{reg} is the Gibbs energy due interactions between associates. The G^{ass} might be defined as

$$G^{ass} = n_{AiBj}G^0_{AiBj} \tag{17}$$

where G^o_{AiBj} is the molar Gibbs energy of formation of the associate A_iB_j. The G^{reg} considers the interactions between components A,B and associate A_iB_j and can be written as

$$G^{reg} = G^{reg}_{A,B} \frac{n_{A1}n_{B1}}{n_{A1}+n_{B1}+n_{AiBj}} + G^{reg}_{A,AiBj} \frac{n_{A1}n_{AiBj}}{n_{A1}+n_{B1}+n_{AiBj}} + G^{reg}_{B,AiBj} \frac{n_{B1}n_{AiBj}}{n_{A1}+n_{B1}+n_{AiBj}} \tag{18}$$

where $G^{reg}_{A,B}$, $G^{reg}_{A,AiBj}$ and $G^{reg}_{B,AiBj}$ are the excess Gibbs energies of mixing of components or associates, and can be described using the Redlich-Kister polynomial shown in Equation (11).

With a similar procedure, the equations could be derived for ternary and higher order systems. [27,28,32]

3.1.3 Sublattice model

For crystalline solid phases, the sublattice model takes into account the possibility of atoms or ions occupying different lattices in the structure of the phase. [21,33] Instead of the overall composition x_i, site fraction y_i is used as the composition variable

$$y_i^S = \frac{n_i^S}{\sum_i^n n_i^S} \tag{19}$$

where n_i^S is the number of atoms in sublattice S. If there are vacancies on the sublattice, they are treated similarly to components. The overall composition in mole fractions related to site fractions will be given as

$$x_i = \frac{\sum_S N^S y_i^S}{\sum_S N^S(1-y_{Va}^S)} \tag{20}$$

where N^S is the total number of sites on sublattice S and the y^S_{Va} is the number of vacancies on sublattice S. The ideal Gibbs energy of mixing is

$$^{id}G = RT \sum_S N^S \sum_i y_i^S ln y_i^S \tag{21}$$

For the description of Gibbs energy, a frame of reference needs to be defined

$$G^{ref} = \sum_I P_I(Y) \cdot G_I^0 \tag{22}$$

where $P_I(Y)$ is a lxc matrix, where l is the number of sublattices and c is the number of compounds and G_I^0 is the Gibbs energy on compound I. The Gibbs energy of a phase determined with the sublattice model is obtained by combining Equations (21) and (22) with Equation (7)

$$G = \sum_I P_I(Y) \cdot G_I^0 + RT \sum_S N^S \sum_i y_i^S ln y_i^S + {}^{ex}G^{mix} \tag{23}$$

where the excess Gibbs energy of mixing ${}^{ex}G^{mix}$ includes the interactions between different components in the sublattice and could be described using the Redlich-Kister polynomial shown earlier in Equation (11).

3.2 Assessment procedure

The overall procedure of deriving a thermodynamic description for a system from experimental information is called assessment. The procedure includes steps from collecting the experimental information to evaluation of the created thermodynamic interaction data. The procedure is shown schematically in Figure 2.
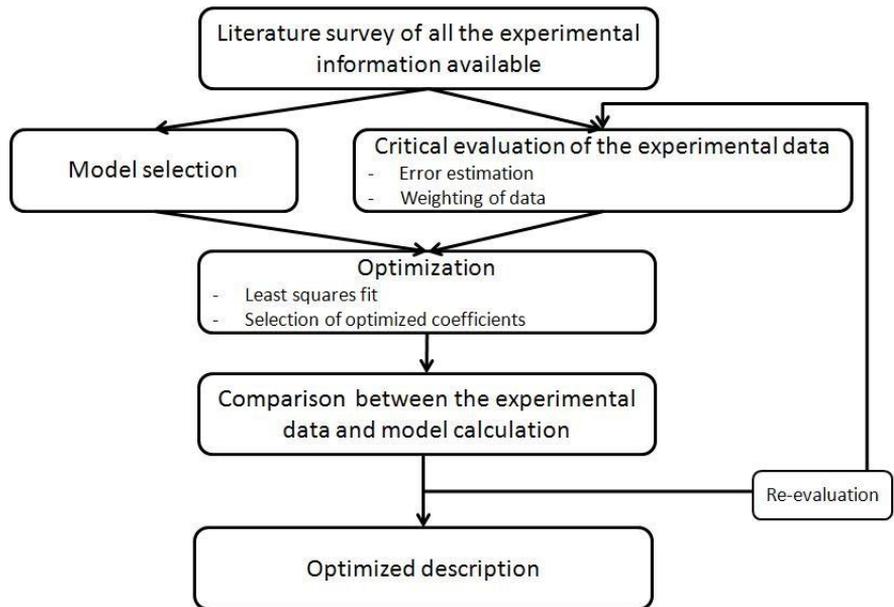
Figure 2 Schematic picture of assessment procedure steps.

The assessment starts with a literature survey and collection of the experimental information available. This is followed by critical analysis, where

the quality of the experimental information is evaluated together with an estimation of the errors of the experimental results, including systematic errors in the techniques utilized and possible impurities in the samples. Based on this evaluation, the experimental information used in the assessment is selected and the uncertainty of each experimental point is defined.

The next step in the assessment process is the selection of the thermodynamic excess Gibbs energy model used for each phase for the entire temperature and composition range. The selected models for each phase must also be compatible with each other and with higher order calculations as part of an extensive database. Part of this step also comprises the selection of reference state used and thermodynamic information for lower order systems needed in the assessment, which may include pure elements or compounds or binary systems. In this thesis, the SER reference state is used and UNARY data [22] for the thermodynamic description of pure elements and the MTOX database information for other compounds or systems.

The coefficients selected for optimization are fitted in this thesis using MTDATA software, versions 4.81, 5.03 and 5.10 [15]. The aim is to keep the number of optimized coefficients as low as possible while still producing good agreement with the experimental data. In the MTDATA software, the assessment module minimizes the weighted sum of squares of errors, where error is defined as the difference between calculated C_i and experimental E_i values of property i.

$$Sum\ of\ errors = \sum_i^n W_i \left(\frac{[C_i - E_i]}{U_i}\right)^2 \qquad (24)$$

where n is the number of properties considered in the optimization, U_i is the stated experimental uncertainty, and W_i is the weight factor assigned to property i. The weight factor was used to exclude and include experimental points in the calculation as well as to weight the value of certain experimental work.

As a result of the optimization, a thermodynamic dataset is created, which is then evaluated against the experimental information. If the level of agreement with the experimental data is not acceptable, optimization is continued with reassessment after the evaluation of optimized variables, including model selection, experimental data, and parameter selection. However, if the agreement is acceptable, the dataset can be evaluated against higher order systems in order to ensure the extrapolation behavior where the overall quality of the dataset can be ensured. If the results of this test are favorable, the optimized dataset can be used as a thermodynamic description of the system.

4. Results and discussion

The purpose of this thesis is to experimentally investigate selected sulfide impurity systems at elevated temperatures. As a result, phase diagrams showing the phase relations of these systems have been produced. For some of the experimentally studied systems, in addition a thermodynamic assessment has been performed to produce the thermodynamic description of the system with a larger temperature and composition range. The results obtained within this work are presented in Appendices [I-V], but a summary with discussion is given in this chapter. After summarizing the results of the binary and ternary systems studied, some industrial considerations of these results as well as recommendations for future work will be given.

4.1   Binary systems

In this thesis, altogether five binary or pseudobinary systems were investigated. From these, four were investigated experimentally and one covered only with thermodynamic assessment. Thermodynamic assessments were also created for two of the four experimentally investigated systems.

The phase diagram of the FeS-PbS system presented in [I] was previously investigated to some extent. The experimental study of this system was the first to be performed with the current experimental technique designed and utilized in this work. The results of the phase diagram study of the FeS-PbS system are in agreement with those previously reported [34-39], indicating that the experimental technique developed during work on this thesis can produce reliable results, as shown in Figure 3.
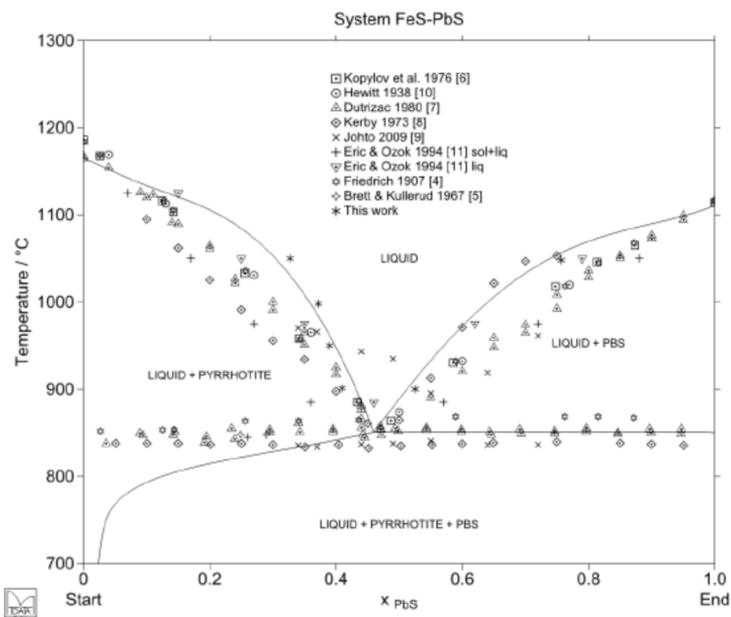
Figure 3 The calculated PbS-FeS phase diagram with the experimental result points. The figure is reproduced from [I].

The thermodynamic assessment of the molten phase in the FeS-PbS system was performed using the substitutional solution model of sulfide associates FeS and PbS. The calculated phase diagram indicates a simple eutectic system with the eutectic point at 851 ºC and at 46.0 mol. % PbS, which is in good agreement with the experimental results of this thesis, Dutrizac [38] and Eric [39].

The phase relations of the pseudobinary Cu_2S-PbS system were investigated experimentally at temperatures between 490 and 1000 ºC [II]. The system is based on the experimental results showing a simple eutectic system, with limited solid solubilities at both ends. With a temperature range of 490 to 515 ºC, a ternary compound with a composition $Cu_{16}Pb_2S_{10}$ was detected, which is close to the composition and temperature range also reported by [40,41]. The agreement between the results of this thesis and with previous liquidus line investigations [40,42] is good, as shown in Figure 4. The thermodynamic assessment of the pseudobinary system was performed as part of the ternary Cu-Pb-S, described in more detail later, with a good agreement between the experimental information in the pseudobinary system.

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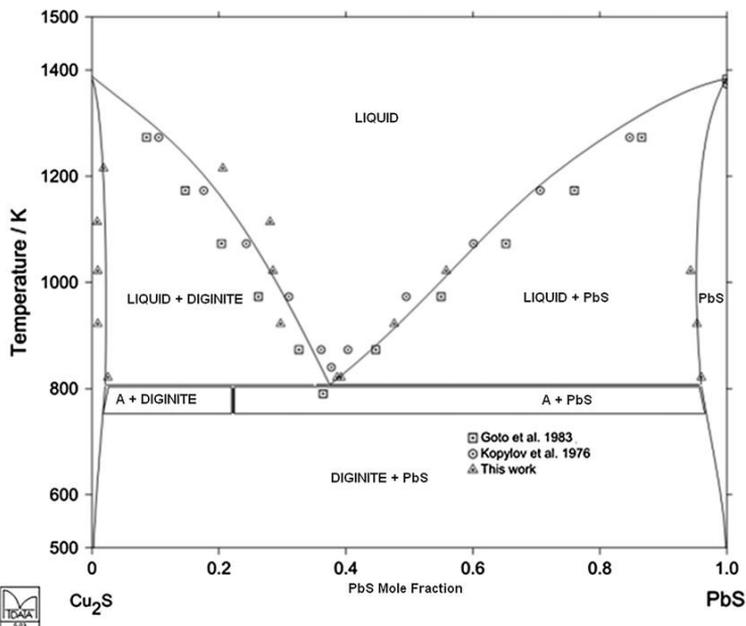
Figure 4 The calculated phase diagram of the pseudobinary system Cu_2S-PbS with the experimental results superimposed. Figure reproduced from [II].

A thermodynamic assessment of the PbS-ZnS system was performed using the substitutional solution model of sulfide associates PbS and ZnS in the liquid phase, based on selected literature data in publication [IV] in order to be able to perform a thermodynamic assessment of the ternary system Cu_2S-PbS-ZnS. No experiments of the authors were performed in this system. The described system is a simple eutectic with a eutectic temperature of 1051 °C and composition of 7.2 wt. % ZnS, and the liquidus line is in good agreement with the literature data [38,43].

The liquidus lines of the arsenic sulfide containing systems As_2S_3-Cu_2S and As_2S_3-PbS were also investigated experimentally at temperatures above 500 °C. The experimental results in both systems show deviations from previously reported data [44-46], indicating a higher solubility of arsenic sulfide into the liquid phase at PbS or Cu_2S saturations. The previous studies [45,46] had been performed using different experimental methods and the experiments had covered only lower temperatures. In the As_2S_3-Cu_2S system, the results show the liquidus line running steeply between 600 and 1000 °C at around 40 wt. % As_2S_3, while in the As_2S_3-PbS system similar behavior can be seen between 550 and 1000 °C at around 35 wt. % As_2S_3, as shown in Figures 5 and 6, respectively.
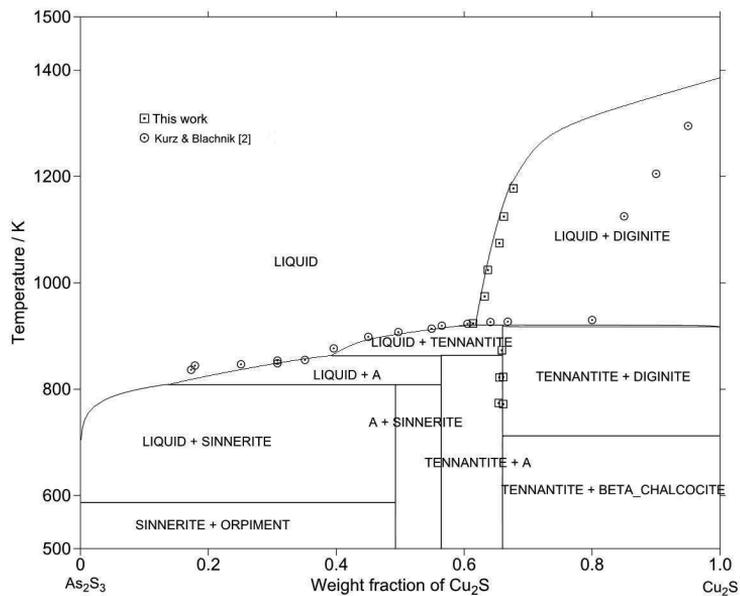
Figure 5 Estimated phase diagram of the As_2S_3-Cu_2S system together with experimental points. Reproduced from publication [V].
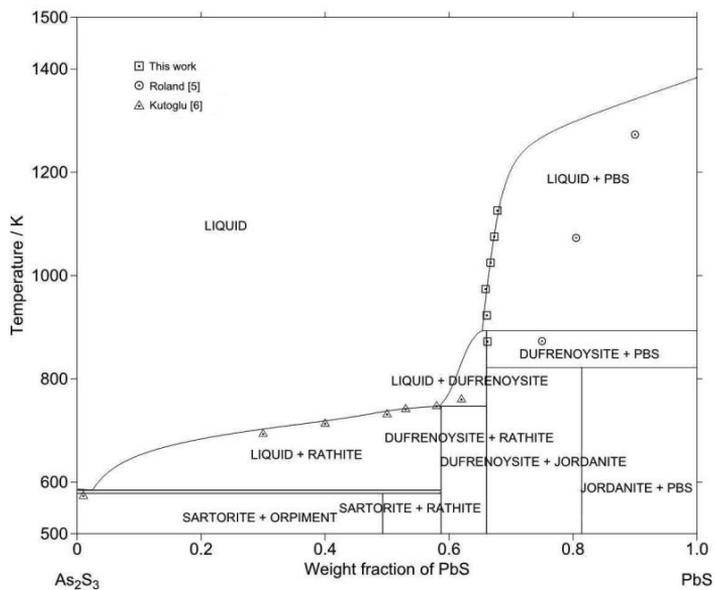
Figure 6 The estimated phase diagram of the As_2S_3-PbS system together with experimental points. Reproduction from publication [V].

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The studied binary phase diagrams are in good agreement with experimental work reported in the literature performed using a similar determination method. A large deviation, especially in the systems containing arsenic sulfide, shown in Figures 5 and 6, can be seen between the results in this thesis and the experimental results [45,46]. The main source of difference might be the evaporation of some compounds with high vapor pressure during experiments, which is an issue in thermal analysis in open sample holders used in references [45,46], but not in the method applied in this thesis.

4.2 Ternary systems

The ternary systems investigated experimentally in this thesis were Fe-O-S [III], Cu_2S-PbS-ZnS [IV] and As_2S_3-Cu_2S-PbS [V]. From these, the Fe-O-S system was investigated with different experimental technique, using an open system in a reactive substrate while the experiments in the Cu_2S-PbS-ZnS and As_2S_3-Cu_2S-PbS systems were performed in closed silica ampoules. Thermodynamic assessments were performed in this thesis for the ternary systems Cu-Pb-S in publication [II] and Cu_2S-PbS-ZnS in publication [IV].

The thermodynamic assessment of the Cu-Pb-S system was based on critically evaluated experimental information from the literature and this thesis, considering the pseudobinary Cu_2S-PbS system as reported in publication [II]. The entire system was evaluated for a temperature range of between 300 and 2000 °C and the liquid phase was described using the substitutional solution model of sulfide associates and pure elements. The agreement with experimental data is good [34,40-42,47-53] and the thermodynamic dataset that was created allows calculation of thermodynamic properties and phase relations in the whole temperature and composition range, including the distributions of components between phases. For example, the calculated polythermal ternary phase diagram indicating the behavior of the liquid miscibility gap is presented in Figure 7.
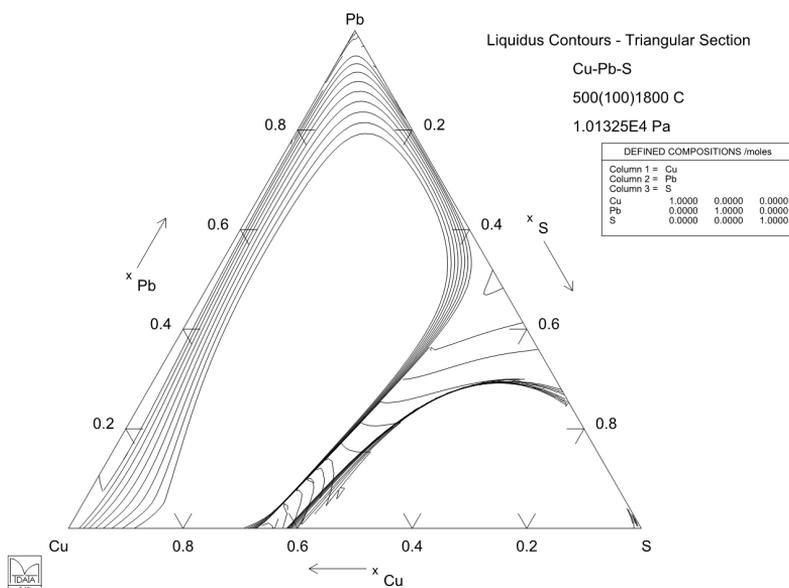
Figure 7 Calculated polythermal phase diagram of the ternary system Cu–Pb–S at 500-1800 °C. Calculation based on the thermodynamic dataset created in [II].

In publication [III], the Fe-O-S system was investigated experimentally. The location of the eutectic point of the system was determined to be between 915 and 920 °C by determination of stable phases in samples quenched at different annealing temperatures, while the previous investigations had reported the eutectic temperature to be between 915 and 922 °C [54,55]. Above the ternary eutectic temperature, the liquidus surface was investigated at 950 °C, 1000 °C and 1200 °C in metallic iron, wustite, and magnetite saturations. Based on the experimental results, the liquidus isotherms were estimated at different temperatures, as shown in Figure 8.

The current results of the liquidus line are in agreement with previous results [55-57] in metallic iron saturation. When considering univariant Fe/FeO points at different temperatures, the results of this study are in agreement with the results of Hilty and Crafts [56], while they differ widely from the results of more recent studies by Lee [57] and Ueda [55]. A large difference is also found in the results regarding wustite saturation between the results of this study and those of Lee [57] and Ueda [55]. The reason for the difference may be in the different experimental method used in [55,57], which includes inaccurate physical phase separation before chemical analysis. The results of publication [III] were derived using direct analysis by EPMA in the quenched samples, which eliminates the problem of phase separation. Therefore these results can

be considered to be more accurate and reliable than previously reported works, [55-57], especially in oxide saturation.
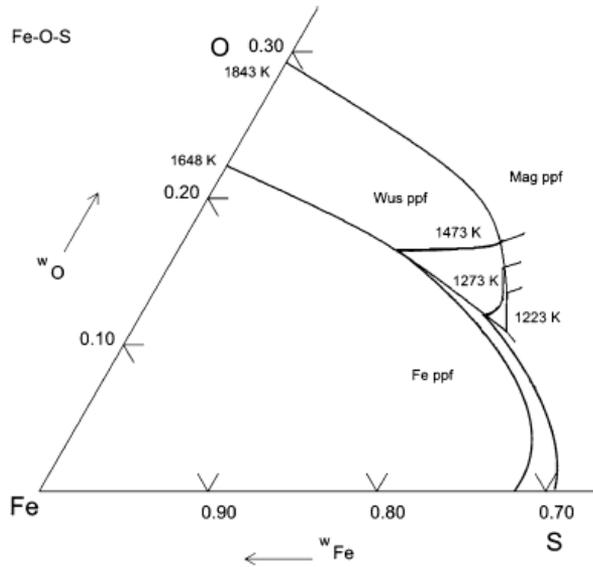
Figure 8 The estimated polythermal liquidus surface with primary phase fields. The figure is reproduced from publication [III].

Publication [IV] describes the phase diagram of the Cu_2S-PbS-ZnS system. The ternary system has been investigated at temperatures between 600 and 1000 °C and thermodynamic assessment has been performed at temperature range between 300 and 2000 °C. The assessed thermodynamic dataset agrees reasonably with the experimental results of this thesis at temperatures between 600 and 1000 °C, indicating a narrow liquid domain expanding from the Cu_2S-PbS join with limited ZnS solubility and with only minor temperature dependency, as shown in Figure 9. At 1200 °C, the calculated phase diagram indicates a ZnS primary phase field and a limited ZnS solubility into the liquid sulfide, of around 5 wt. %, as also reported by [58].
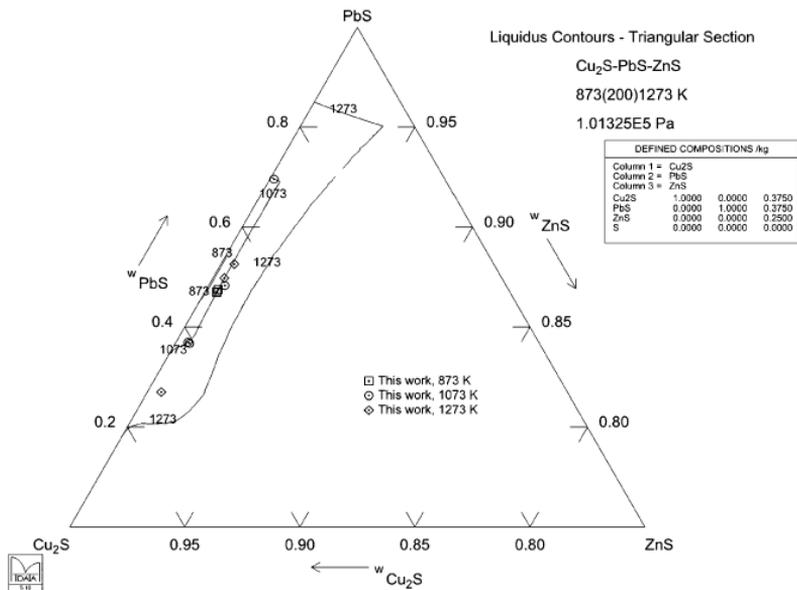
Figure 9 The calculated liquidus borders of the Cu_2S-PbS-ZnS system together with the experimental points, reproduced from publication [IV].

The phase relations of the ternary As_2S_3-Cu_2S-PbS system were investigated at temperatures between 600 and 900 °C and the results were reported in publication [V]. The phase relations of this system have not been reported previously in the literature. The experimental results indicate an expansion of the fully molten phase field from the Cu_2S-PbS join toward arsenic sulfide rich compositions, as shown in Figure 10. With arsenic sulfide additions of 10-20 wt. %, the results indicate a smaller fully molten area between the PbS and Cu_2S primary phase fields at all studied temperatures than with the arsenic-free system.
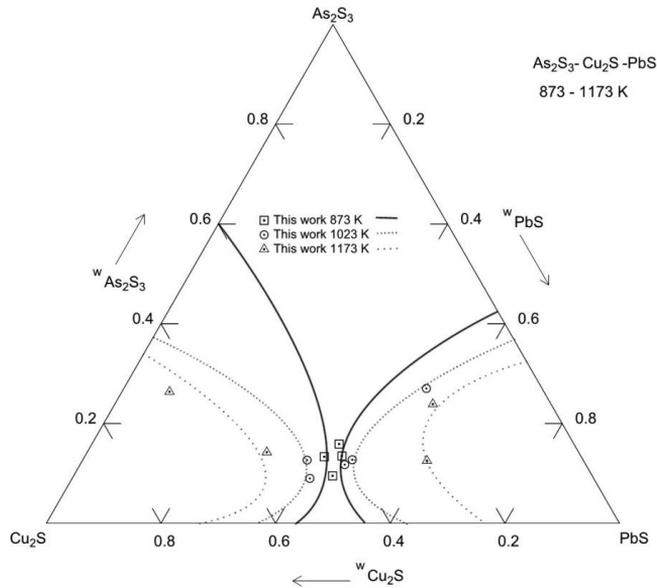
Figure 10 The estimated liquidus isotherms of the As₂S₃-Cu₂S-PbS system together with experimental points. The figure is reproduced from publication [V].

Three ternary or pseudoternary phase diagrams have been studied experimentally in this thesis. Two of them, the Fe-O-S [III] and Cu₂S-PbS-ZnS [IV] systems, had been investigated previously but this thesis provides more accurate results by using different experimental methods at a wider temperature range than in previous studies. The study on the As₂S₃-Cu₂S-PbS [V] system provides new information, since no previous data on the system are available. Consequently, a wider knowledge of the selected ternary sulfide systems has been created.

4.3   Industrial applications

One of the main industrial applications of this study is the treatment of impure zinc sulfide concentrates, where impurities like copper, lead, iron and arsenic have been suggested to be problematic when inducing the formation of a stable molten phase and to cause build-up formation, poor flowability and excessive calcine agglomeration in the roaster [6,8,9] in fluidized bed roasting operations.

On the basis of this thesis, at zinc roasting temperatures between 900 and 1000 °C, the formation of a molten sulfide phase is possible with mixtures of

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lead and iron sulfides [I] and with mixtures of lead and copper sulfides [II,IV]. For a mixture of copper, lead and zinc sulfides, the fraction of the liquid phase at 950 °C with an elemental composition of 3 wt. % of Cu+Pb can be calculated based on publications [II, IV] to be a maximum 3.5 wt. % of the total sulfide matrix, as shown in Figure 11. From industrial practice it is observed that this amount of Cu and Pb impurity is close to the maximum impurity level that roaster operations tolerate without serious problems in fluidized bed stability. The estimated phase diagram of As_2S_3-Cu_2S-PbS might suggest [V], on the other hand, that small amounts of arsenic sulfide, less than 5 wt.%, in zinc sulfide concentrate do not increase the amount of molten sulfide phase from the Cu_2S-PbS join and thus small amounts of arsenic sulfide in the feed mixture would not have an impact on roaster operation in this way. The effect of arsenic on zinc sulfide roaster operation and on the molten phase formation, thus, might lie in phase relations or phenomena not studied in this thesis.

In addition, the formation of a molten oxysulfide phase in the Fe-O-S system in zinc sulfide roasting conditions was found to be possible. The experimentally determined phase diagram shows a fully molten area at 950 °C [III], see Figure 8, which might, in addition to the sulfide melt, be the source of instabilities in zinc sulfide roasting, as indicated previously by [7].
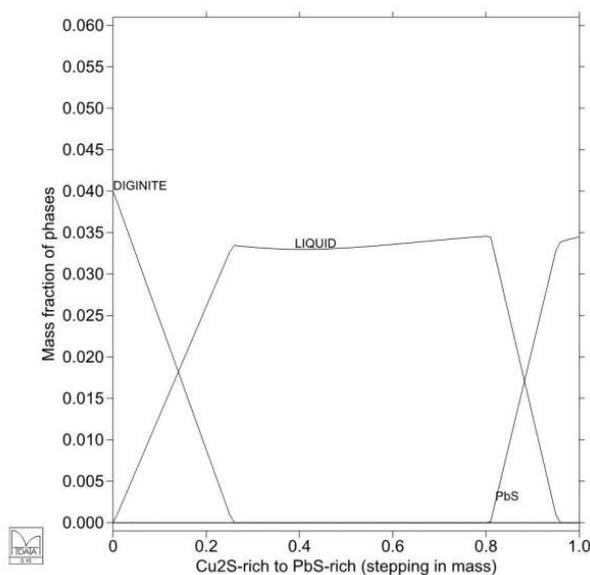
Figure 11 The calculated fraction of phases in the Cu_2S-PbS-ZnS system with a Cu+Pb content of around 3 wt. % at 950 °C, starting from a composition of 3.7 wt. % Cu_2S in ZnS and ending with a composition of 3.45 wt. % PbS in ZnS. The calculation is based on the thermodynamic dataset created in publications [II,IV].

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Removal of arsenic and other impurities from copper concentrates is the focus of growing industrial research interest, because more complex ore bodies have been utilized for processing. The removal of arsenic and other volatile heavy elements can be performed by sulfating roasting in fluidized bed reactors [11,59] or kiln furnaces [12]. For these processes and while developing novel processing techniques, the knowledge of phase equilibria between arsenic and copper sulfides is essential. Similar bed stability problems to those with zinc sulfide roasting have been detected in arsenic removal with fluidized bed roasting [11] and these problems might also be due to the formation of a molten sulfide phase.

Thermodynamic calculations can be used as an effective tool in process design and optimization in pyrometallurgical processes. In the course of this thesis work, several thermodynamic assessments have been performed [I,II,IV] and the created datasets have been included in a wider thermodynamic databank, MTOX [14,16,17]. The created thermodynamic datasets are not process- or technology-dependent and thus the information can be used widely in various contexts. With these datasets, better understanding of copper smelting can be achieved, including the possibility to calculate lead distributions between matte and blister copper [II] and to estimate zinc and sulfur behavior in copper matte with additions of lead [IV]. In zinc roasting, the created thermodynamic assessments can be used to evaluate molten phase formation, as shown previously.

In addition, better thermodynamic assessments can be performed with the more reliable experimental information provided in this thesis for slag-matte equilibria based on a better knowledge of the Fe-O-S system [III] and for arsenic behavior in sulfide mattes [V], to further improve the capability of utilizing thermodynamic calculations in high temperature sulfide processes.

4.4   Future work

This thesis has covered a small number of phase diagrams relevant to industrial application. Part of the studied systems has been assessed and the created thermodynamic datasets have been included in an extensive thermodynamic database, the MTOX [14,16,17]. The assessments of this thesis have covered lead but still more experimental and assessment work is needed to achieve a thermodynamic description of the behavior of lead in sulfide smelting.

As most of the systems studied in this thesis have covered only the "real" sulfide systems, experimental work should be extended towards metallic

compositions, creating a better understanding of the Cu-Pb-Zn-As-S system. This expansion would not only help the thermodynamic modelling of these systems and increase the coverage of the thermodynamic databases, but would also be important in terms of the knowledge of "speiss" phase behavior in many industrial applications like lead and copper smelting [60,61] as well as the behavior of different compounds during copper converter processes [62].

Publication [III] covers part of the Fe-O-S phase diagram, but the knowledge based on this publication is not complete while the liquidus line in FeS saturation remains unknown. Thus the liquidus line should be experimentally investigated at FeS saturation in order to achieve a more reliable established description of this system, which is important in numerous metallurgical applications.

5. Conclusions

In this thesis, the phase equilibria of selected sulfide impurity systems have been evaluated at temperatures above 500 °C. Phase diagram information has been produced about the FeS-PbS, Cu_2S-PbS, Fe-O-S, Cu_2S-PbS-ZnS, As_2S_3-Cu_2S, As_2S_3-PbS, and As_2S_3-Cu_2S-PbS systems using the isothermal equilibration-quenching technique. For this purpose, three different experimental set-ups were used, two of which were designed and built during this thesis. In addition, thermodynamic model descriptions for the phases of the FeS-PbS, Cu-Pb-S, PbS-ZnS and Cu_2S-PbS-ZnS systems have been derived using the CALPHAD method and MTDATA software.

Based on the experimentally measured phase compositions in equilibrium, the phase diagrams have been established for the studied systems. The experimental method used was selected as suitable for each studied system and experimental methods were developed and changed during work on the thesis. Differences in phase diagram information between the results of this thesis and literature information were found in the Fe-O-S, As_2S_3-Cu_2S and As_2S_3-PbS systems. However, the reason for the differences may be the different experimental or analytical method used. The new scientific information in this thesis consists of the descriptions of the phase equilibria of the As_2S_3-Cu_2S-PbS system, as no previous information was available. In other studied systems, information about the phase equilibria has been provided in wider temperature and composition areas with accurate measurement methods than those previously reported in the literature.

The thermodynamic assessments were performed for the phases of the FeS-PbS, Cu-Pb-S, PbS-ZnS and Cu_2S-PbS-ZnS systems based on the literature data and experimental results of this thesis in a wide temperature range using an association solution model for the liquid phase. The created datasets agree well with critically evaluated experimental information and the thermodynamic descriptions of the assessed systems can be used for calculations of various

high temperature multicomponent processes or phenomena as part of a wider thermodynamic database, the MTOX.

The phase equilibria information provided in this thesis may be used to evaluate and give more accurate knowledge of various pyrometallurgical processes, including zinc roasting and copper smelting, when selected low-order phase systems have been described in more detail.

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