

Modelling of chemical processes and materials by free energy minimisation

Additional constraints and work terms

Risto Pajarre



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Abstract

Chemical equilibrium thermodynamics has found numerous application areas in diverse fields such as pyrolysis and combustion, metallurgy, petrochemistry, the pulp and paper industry, the study of advanced inorganic materials, environmental science and biochemistry. As many of the cases of interest are not actually in equilibrium, there is a need for methods that extend the application area of multiphase chemical equilibrium solvers to non-equilibrium systems.

Likewise, there is a demand for efficient handling of systems that are described by thermodynamic parameters other than those most commonly associated with Gibbs energy, namely temperature, pressure and fixed elemental (and charge) balances.

In this thesis computational methods and related theory are presented that can be used with a standard Gibbs energy minimiser to solve advanced thermochemical problems. The extensions developed enable handling of systems with multiple kinds of thermodynamic work, systems with constrained reaction extents and other systems with linear constraints on composition. The actual calculations have been performed using the ChemSheet software, but the presentation has aimed to be generic and applicable with other thermochemical codes that allow the user to define thermodynamic data and the stoichiometries of the constituent species in the system.

The examples discussed include the electrochemical Donnan equilibrium (particularly applied to aqueous pulp suspension), surface and interfacial energies, systems affected by external magnetic fields and systems with time—dependent reaction extents. The greatest practical success has been achieved with the models that combine reaction kinetics with partial thermodynamic equilibrium calculation and ion exchange models based on Donnan equilibrium, both of which have been applied with success in real-life industrial design and development work with multicomponent, multiphase systems. The method has also been successfully applied to liquid surface energies in systems with multiple components and complex non-ideality data.

Keywords thermodynamic equilibrium, Gibbs free energy minimisation, surface energy, Donnan equilibrium, extent of reaction, nanoparticles

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Tekijä

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Väitöskirjan nimi

Kemiallisten prosessien ja materiaalien mallinnus vapaan energian minimoinnilla. Lisätyt rajoitukset ja työtermit

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Kemiallista tasapainotermodynamiikkaa hyödynnetään lukuisilla sovellusalueilla, kuten pyrolyysi- ja polttoreaktioissa, metallurgiassa, petrokemiassa, paperiteollisuudessa, kehittyneiden epäorgaanisten materiaalien tutkimuksessa, ympäristötieteissä ja biokemiassa. Koska tutkittavat systeemit eivät monesti kuitenkaan ole tasapainossa, on tarve metodeille, joilla monifaasisatapainoratkaisijoiden sovellusalueita voidaan laajentaa epätasapainosysteemeihin. Samaten pitäisi pystyä käsittelemään tehokkaasti systeemejä, joita ohjaavat muut termodynaamiset parametrit kuin Gibbsin vapaaseen energiaan useimmin yhdistetyt lämpötila, paine ja alkuaine- sekä varaustaset.

Väitöstyössä esitetään laskennallisia metodeja ja niihin liittyvä teoria jota voidaan käyttää tavanomaisissa Gibbsin energian minimointirutiineissa. Kehitetyt laajennukset mahdollistavat sellaisten systeemien käsittelyn, joihin liittyy erilaisia termodynaamisia työtermejä, joissa on rajoitettuja reaktion etenemisasteita ja joihin kohdistuu muita systeemin koostumukseen vaikuttavia lineaarisia rajoitteita. Työhön liittyvät mallit on toteutettu käyttäen ChemSheet-ohjelmaa, mutta esityksessä on pyritty yleisyyteen ja sovellettavuuteen myös muissa termodynaamisissa ohjelmistoissa, jotka sallivat käyttäjän määrittellä systeemiin liittyvän termodynaamisen datan ja sen osaslajien stoikiometrian.

Käsiteltäviä esimerkkejä ovat sähkökemiallinen Donnanin tasapaino (sovellusalueena kuituvesisuspensiot), rajapintaenergiat, ulkoisen magneettikentän alaiset systeemit sekä systeemit, joita ohjaavat ajasta riippuvat reaktioiden etenemisasteet. Suurin käytännön arvo on saavutettu malleilla, jotka yhdistävät reaktiokinetiikan osittaiseen tasapainolaskentaan, ja Donnanin tasapainoon perustuvilla ioninvaihtomalleilla. Molempia on sovellettu käytännön kehitys- ja suunnittelutyöhön monikomponentti- ja monifaasisysteemeille. Menetelmää on myös onnistuneesti käytetty nestepintojen pintaenergian mallinnukseen epäideaalisille monikomponenttisysteemeille.

Avainsanat termodynaaminen tasapaino, Gibbsin vapaa energia, pintaenergia, Donnanin tasapaino, reaktion etenemisaste, nanopartikkelit

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Preface

This work was carried out while I worked among the thermodynamic modellers at VTT Technical Research Centre of Finland during the years 2004-2016.

I wish to thank my supervising Professor Kari Laasonen, and Professor Emeritus Simo Liukkonen for their support and interest in my work.

My thesis advisor, Professor Pertti Koukkari, has been leading the work in chemical thermodynamics at VTT for about twenty years. As he brought the area of research to VTT and later hired me, he is probably more responsible than I am that I ended up writing this thesis.

I wish to thank my many co-workers over the years. Special thanks to Karri Penttilä, who introduced me to the software tools most of this work has been done with, and who has assisted me in numerous ways in doing computations and process modelling. I thank Lea Räsänen for all the experimental work (and its explanations) directly or indirectly related to this thesis and for managing to endure a shared office space with me for over a decade.

Many thanks to my co-authors, Petteri Kangas for helping to bring renewed interest to modelling dynamic reactive systems, Erkki Räsänen, who was instrumental in development of the ion-exchange model, and Professors Toshihiro Tanaka and Joonho Lee for their support in the interfacial modelling. I also specifically wish to thank Professor Tanaka for being such a generous host during my stays in Japan.

The staff of GTT technologies, especially Gunnar Eriksson, Klaus Hack and Stephan Petersen, have provided immeasurable help for the work by their instructions in applying ChemApp software and by the software updates necessary for some of the features developed during this work to properly run.

Because of the length of the time period this work was done, it is practically impossible to properly list all the companies working in chemistry, paper and pulp making, metallurgy or engineering that have financially helped to make it happen. The financial support of VTT Technical Research Centre of Finland Ltd, Tekes – the Finnish Funding Agency for Innovation, and FIMECC - Finnish Metals and Engineering Competence Cluster is specifically gratefully acknowledged.

Loving thanks and apologies for my family for the time it took to finish this work. I realise I would not have them, had I never started it.

October 2016, Helsinki
Risto Pajarre.

List of publications

This thesis is based on the following original publications which are referred to in the text as I–V. The publications are reproduced with kind permission from the publishers.

- I Pertti Koukkari, Risto Pajarre, Calculation of constrained equilibria by Gibbs energy minimization, CALPHAD, 30(2), (2006), 18-26.
doi: 10.1016/j.calphad.2005.11.007
- II Risto Pajarre, Pertti Koukkari, Toshihiro Tanaka, Joonho Lee, Computing surface tensions of binary and ternary alloy systems with the Gibbsian method, CALPHAD, 30(2), (2006), 196-200.
doi: 10.1016/j.calphad.2005.08.003
- III Risto Pajarre, Pertti Koukkari, Erkki Räsänen, Inclusion of the Donnan effect in Gibbs energy minimization, Journal of Molecular Liquids, 125(1), (2006), 58-61. doi: 10.1016/j.molliq.2005.11.016
- IV Risto Pajarre, Pertti Koukkari, Toshihiro Tanka, Surface tension of a liquid metal-oxygen system using a multilayer free energy model, International Journal of Materials Research, 104(8), (2013), 736-747.
doi: 10.3139/146.110921
- V Risto Pajarre, Pertti Koukkari, Petteri Kangas, Constrained and extended free energy minimisation for modelling of processes and materials. Chemical Engineering Science, 146, (2016), 244-258.
doi: 10.1016/j.ces.2016.02.033

Author's contributions

Publication I: "Calculation of constrained equilibria by Gibbs energy minimization"

The paper contains initial general formulation of the Constrained Free Energy (CFE) method with applications to reaction kinetics, monolayer surface model and Donnan ion-exchange systems. The author made the most of the development for the physically descriptive equations (i.e., roughly those that do not have Lagrangian function L or the multipliers λ_j explicitly present) and did the modelling work for the section on ion-exchange systems and supported the writing of the other parts of the manuscript, corresponding to half of the total work done.

Publication II: "Computing surface tensions of binary and ternary alloy systems with the Gibbsian method" presents a monolayer surface tension model applied to metal alloys. The author formulated the CFE model for the systems and wrote the paper. The co-authors helped with collecting the data, participated in discussions during the model development and helped to refine the final text.

Publication III: "Inclusion of the Donnan effect in Gibbs energy minimization" contains a description for aqueous pulp suspensions where the ion exchange phenomena between the pulp fibres can be modelled together with the external non-ideal aqueous solution, solid precipitates and gas atmosphere. The author formulated the CFE model compatible with the Donnan equilibrium theory with osmotic pressure effect and wrote the paper. The co-authors helped with collecting the data and refining the final text. The paper was an extended version of a conference presentation given by the author in the International Conference on Chemical Thermodynamics in 2004 (ICCT-2004).

Publication IV: "Surface tension of a liquid metal-oxygen system using a multilayer free energy model" extends the monolayer surface tension model to multiple interacting layers in a surface or interfacial system. The author formulated the thermodynamic model, made the computer implementation and wrote the paper. The co-authors participated in discussions during early development and helped to refine the final paper.

Publication V: "Constrained and extended free energy minimisation for modelling of processes and materials" updates the general formulation of the theory. New application areas discussed include nanoparticle melting behaviour and the effect of magnetic fields to phase equilibria. The theory for reaction constraints is refined. Both the outline and contents of this dissertation largely follow those of Publication V. The author wrote the paper. Section 4.6 was based on an advanced draft text and model by Dr. Petteri Kangas. The co-authors helped with refining the final text.

Contents

Preface	1
List of publications	2
Author's contributions	3
Contents	5
List of symbols	7
1. Introduction	11
2. Thermodynamic basis	13
2.1 Definitions	13
2.1.1 Phase	13
2.1.2 Component	14
2.1.3 Species	14
2.2 Minimum free energy as an equilibrium condition	14
2.3 Systems with constant work coordinates	17
2.4 Systems with constant chemical potentials	18
2.5 Systems with other than work coordinate constraints	19
3. Use of a free energy minimiser	21
3.1 Traditional problem statement	21
3.2 Additional work coefficients	23
3.3 Addition of new components to computational systems	24
3.4 Applying additional components for calculations with additional non-zero constant work coefficients L_h	26
4. Application examples and results	27
4.1 Surface and interfacial energy	30
4.2 Volume-constrained system	33
4.3 Nanoparticles with a combined area and volume constraint	33
4.4 Donnan equilibrium	35
4.5 Systems with an external magnetic field	37
4.6 Constrained reaction extents and mass transfer	38

5. Conclusions.....	43
6. Discussion.....	45
References	47

List of symbols

A	$(M \times N)$ matrix of stoichiometric coefficients
A	surface or interfacial area (m^2)
A_i	Affinity of reaction i ($\text{J} \cdot \text{mol}^{-1}$)
a_i	activity of species i
a_{j,i}	stoichiometric coefficient between component j and species i ; matrix element of A
B	magnetic flux density ($\text{T} = \text{V} \cdot \text{s} \cdot \text{m}^{-2}$)
b	$(M \times 1)$ column vector of molar amounts of components (<i>mol</i>)
b_k	molar amount of component k (<i>mol</i>)
C	number of added constraints in a matrix of stoichiometric coefficients,
E	electric field ($\text{N} \cdot \text{C}^{-1}$)
F	Helmholtz free energy (J)
F	Faraday constant ($\approx 96485 \text{ J} \cdot \text{mol}^{-1} \cdot \text{V}^{-1}$)
G	Gibbs free energy (J)
G'	free energy function (other than G) matching system specific constraints (J)
G	free energy function as calculated by a free energy minimiser (J)
G'	modified minimised free energy function in a free energy minimiser (J)
H	enthalpy (J)
L	Lagrangian function
L_j	thermodynamic work coefficient j
L_jⁱ	thermodynamic work coefficient j for a species i as pure phase (such as surface energy σ_i)

l_j	thermodynamic work coordinate j
$l_{j,i}$	molar contribution to the thermodynamic work coordinate j by species i
M	number of components in the system
\mathbf{m}	magnetic moment ($\text{J} \cdot \text{T}^{-1}$)
N	number of species in the system
NR	number of reactions
\mathbf{n}	$(N \times 1)$ column vector of molar amount of species (mol)
n_i	molar amount of species (mol)
P	pressure ($\text{Pa} = \text{N} \cdot \text{m}^{-2}$)
\mathbf{p}	electric dipole moment ($\text{C} \cdot \text{m}$)
Q	heat (J)
q	charge (C)
R	gas constant ($\approx 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
S	entropy ($\text{J} \cdot \text{K}^{-1}$)
T	temperature (K)
U	internal energy (J)
V	volume (m^3)
v_i, w_i	stoichiometric coefficient of species i in a reaction
Y_i	mole ratio of i to reference metal
ϕ	electric potential (V)
γ_i	activity coefficient of species
λ_j	Lagrange multiplier related to component j
μ_i	chemical potential of species i ($\text{J} \cdot \text{mol}^{-1}$)
ξ	$(R \times 1)$ column vector of extents of R reactions
ξ_r	extent of reaction r (mol)
$\Omega_{i,j}$	interaction energy between i and j
π_k	chemical potential of component k ($\text{J} \cdot \text{mol}^{-1}$)
σ	surface energy ($\text{J} \cdot \text{m}^{-2}$)
σ_i	surface energy of pure substance i ($\text{J} \cdot \text{m}^{-2} \cdot \text{mol}$)

χ_i molar magnetic susceptibility of i ($\text{J} \cdot \text{T}^{-2} \cdot \text{mol}^{-1}$)

Subscript and superscript related terminology (X is a generic Roman or Greek character)

X_i where i can be also be j, k or l . Partial molar quantity corresponding to the integral quantity X of the whole system (unless X_i is explicitly given in the preceding list)

$d_i X, d_e X$ change in X due to processes that are internal to the system or those that are interactions with its surroundings respectively

X^α, X^β part or value of the quantity X related to the part α or β only

X_i^0 value of the quantity X for pure substance i

\mathbf{X}^T transpose of matrix \mathbf{X}

1. Introduction

Computational methods in chemical equilibrium thermodynamics have found numerous application areas in diverse fields such as pyrolysis and combustion, metallurgy, petrochemistry, the pulp and paper industry, the study of advanced inorganic materials, environmental science and biochemistry (Alberty, 2003; Gmehling, Kolbe, Kleiber, & Rarey, 2012; Hack, 2008; Jäntschi & Bolboacă, 2014; Kangas, 2015; Letcher, 2004). This is not surprising considering the general applicability of thermodynamic relations, theoretical and data development over a century and finally the rapid improvements in computational methods during the last few decades. Also a large number of computer codes and programmes have been developed for accurate handling of thermochemical systems and effective, robust and practical determination of the equilibrium state based on the minimisation of the Gibbs free energy of the system.

As many of the cases of interest are not in actual equilibrium, there is a need for methods that extend the application area of chemical equilibrium solvers to non-equilibrium systems. Likewise there is a need for efficient computational methods for thermochemical systems that are described by parameters other than those most commonly associated with Gibbs energy, namely temperature, pressure and fixed elemental (and charge) balances.

The purpose of this work has been to explore, develop and collect a systematic set of computational methods that can be used with a standard Gibbs energy minimiser for solving advanced thermochemical problems. The actual calculations have been made using the ChemSheet or ChemApp software (Koukkari, Penttilä, Hack, & Petersen, 2000), but the presentation has aimed to be generic and applicable with other thermochemical codes that allow the user to define thermodynamic data and the stoichiometries of the constituent species in the system. The algorithmic functioning of those codes, such as finding the global free energy minimum reliably and computationally efficiently in systems containing multiple components (dozens, if required), and potentially multiple non-ideal mixture phases has not been considered a part of this work. The idea has been to extract as much as possible useful information regarding the system by applying the regular bulk thermodynamic data (assumed well established) by involving as few additional assumptions or parameters as possible.

The first version of this work published in **Paper I**, used the term Constrained Free Energy (CFE) method as a descriptions of the extensions done to standard

Gibbs energy minimisation models. In **Paper V**, additional constraints and energy terms were treated in more systematic fashion applying the term Constrained and Extended Free Energy Minimisation.

2. Thermodynamic basis

In this work it is assumed that the system considered is either isotropic, having the same values for T , chemical potentials, P and other work-coefficients throughout the system, or that it can be divided into a finite number of such parts. If not explicitly stated otherwise, the model equations are written for one isotropic part. The presentation of the thermodynamic theory in this chapter aims to be sufficient for understanding the concepts presented in the work, not complete in other respects.

2.1 Definitions

A computational system in chemistry can be divided from one hand to phases and their constituent species, and from the other hand to components that form the species according to their stoichiometries. While the same definitions are also understood to apply for real systems, there is some level of abstraction with each of them. With phases regarding their assumed uniformity, with components regarding the time scale used to study and what processes can be considered in equilibrium within it. Different kinds of speciations within a mixture phase and related excess energy models can be used to derive within practical accuracy same actual measurable properties of the system.

2.1.1 Phase

A *phase* in thermodynamics is typically defined as a region of a system with a uniform composition, temperature and physical state (Clarke, Hastie, Kihlberg, Metselaar, & Thackeray, 1994; Pitzer, 1995; Prigogine, Defay, & Everett, 1954). In his work, Guggenheim stated that systems with for example compositional gradients should be considered to be composed of infinite number of infinitesimal phases (Guggenheim, 1967). In this work, it has been assumed the system can, with sufficient accuracy, be divided to a finite number of such parts with phases of uniform composition within each part. In a computational system, a predefined set of possible phases exists from which the free energy minimiser selects the ones leading to the free energy minimum.

2.1.2 Component

The number of independent *components* in a thermochemical system refers to the number of substances constituting the system amounts of which can be independently set. In this work, the definition used by e.g. Pitzer (1995) is followed where the word component always refers to such independent components. In free energy minimiser programmes and related databases the stoichiometry of the various species or constituents is given in terms of some basic building blocks, most often elements and electrical charge that are typically denoted as ‘components’ or ‘system components’. In most cases their number would equal the number thermodynamic components referred above. In some cases when, for example, the number of species present is less than the number of such ‘system components’, the stoichiometries would need to be redefined within the calculation routine (Eriksson & Hack, 1990) to correspond to the proper thermodynamic number of components.

2.1.3 Species

Each phase of the system is considered to be made of one or more *species*, or constituents (the two words are used interchangeably in this work, though in some texts difference is made between the two (Hillert, 2007)). They are typically molecular entities that can be transferred from one phase to another (though for example with charged species this is not necessarily true). In a computational system each phase definition contains one (when the phase has fixed stoichiometry) or more species (with their typically temperature- and pressure-dependent standard state chemical potentials) that may be present in the phase. This speciation together with the corresponding non-ideality model defines the equilibrium thermodynamic properties of the computational system.

2.2 Minimum free energy as an equilibrium condition

The change in internal energy of a system can be given (Haase, 1990) by the Eq. (1)

$$dU = TdS + \sum_j L_j \cdot dl_j + \sum_k \mu_k dn_k \quad (1)$$

while the corresponding Euler form for internal energy is

$$U = TS + \sum_j L_j \cdot l_j + \sum_k \mu_k n_k \quad (2)$$

where L_j is the generalised work coefficient with intensive character and l_j is the corresponding generalised work coordinate with extensive character. Example cases have been listed in Table 1. While the expression of the generalised work

[Eq. (1)] has been adapted from the comprehensive treatment of Haase (1990), the nomenclature mostly follows Alberty (2001).

Table 1. Common examples of thermodynamic work coefficients and coordinates

work coefficient L_j	work coordinate l_j
$-P$ (pressure)	V (volume)
σ (surface energy)	A (surface area)
ϕ^α (electric potential)	q_j (charge)
\mathbf{E} (electric field)	\mathbf{p} (electric dipole moment)
\mathbf{B} (magnetic flux density)	\mathbf{m} (magnetic moment)

For the internal energy U , the natural variables are S , l_i and n_k , meaning that if U is known as a function of those extensive variables, all the other thermodynamic properties of the system can be derived (Alberty, 2001).

Common definitions (Haase, 1990) for enthalpy (H), Helmholtz (F) and Gibbs (G) free energy are given by (Eqs. (3)-(5))

$$H \equiv U - \sum_j L_j \cdot l_j \quad (3)$$

$$F \equiv U - ST \quad (4)$$

$$G \equiv U - ST - \sum_j L_j \cdot l_j \quad (5)$$

In this work the extensive work coordinates l_j are divided into partial molar contributions from each species following Eq.(6)

$$l_{j,i} \equiv \left(\frac{\partial l_j}{\partial n_i} \right)_{T,L_k,n_{n \neq i}} \quad (6)$$

so that

$$l_j = \sum_i l_{j,i} n_i \quad (7)$$

For the practical applicability with a Gibbs energy minimiser, in the present work it has been further assumed that the partial molar properties expressed by Eq. (6) are not functions of phase composition.

Energy function expressions on molar basis are given by Eqs. (8)-(10)

$$H_i \equiv U_i - \sum_j L_j \cdot l_{j,i} \quad (8)$$

$$F_i \equiv U_i - S_i T \quad (9)$$

$$G_i \equiv U - S_i T - \sum_j L_j \cdot l_{j,i} = \mu_i \quad (10)$$

Based on the first law of thermodynamics the change in internal energy of a system can also be stated as

$$\begin{aligned} dU &= dQ + \sum_j L_j \cdot dl_j + \sum_k U_k d_e n_k - \sum_k \sum_j L_j l_{j,k} d_e n_k \\ &= dQ + \sum_j L_j \cdot dl_j + \sum_k H_k d_e n_k \end{aligned} \quad (11)$$

Changes in (molar) amounts of substances have been divided here to those due to mass transfer between the system and the surroundings and those due to chemical reactions within the system.

$$dn_k = d_e n_k + d_i n_k \quad (12)$$

Likewise, the entropy change in the system can be divided into those caused by internal processes ($d_i S$) and those caused by interactions of the system and its surroundings ($d_e S$)

$$dS = d_i S + d_e S \quad (13)$$

with

$$T d_e S = dQ + T \sum_k S_k d_e n_k \quad (14)$$

so that

$$dQ = -T \sum_k S_k d_e n_k + T dS - T d_i S \quad (15)$$

and

$$dU = T dS - T d_i S + \sum_j L_j \cdot dl_j + \sum_k \mu_k d_e n_k \quad (16)$$

According to one of the formulations of the second law of thermodynamics (Kondepudi & Prigogine, 1998), internal processes in any system always increase the entropy, so any internal changes in the system always increase the value given by expressions (17)-(20) towards its maximum value.

$$T d_i S = -dU + T dS + \sum_j L_j \cdot dl_j + \sum_j \mu_j d_e n_j \geq 0 \quad (17)$$

$$Td_iS = -dH + TdS - \sum_j l_j \cdot dL_j + \sum_j \mu_j d_e n_j \geq 0 \quad (18)$$

$$Td_iS = -dF - SdT + \sum_j L_j \cdot dl_j + \sum_j \mu_j d_e n_j \geq 0 \quad (19)$$

$$Td_iS = -dG - SdT - \sum_j l_j \cdot dL_j + \sum_j \mu_j d_e n_j \geq 0 \quad (20)$$

For a closed system with constant temperature and l_j (including V) the requirement that $d_iS \geq 0$ leads to $dF \leq 0$, with constant temperature and L_j (such as P) is the corresponding condition $dG \leq 0$. For an adiabatic system, $dS \geq 0$.

2.3 Systems with constant work coordinates

In cases in which some of the work coordinates (and not the corresponding work coefficients) are constant, a corresponding free energy function can be defined (Alberty, 2001)

$$G' \equiv G + \sum_h L_h \cdot l_h = \sum_i \mu_i n_i + \sum_h L_h \cdot l_h \quad (21)$$

where the summation is over the constant values of l_h so that

$$Td_iS = -dG' - SdT - \sum_{j \neq h} l_j \cdot dL_j + \sum_h L_h \cdot dl_h + \sum_k \mu_k d_e n_k \geq 0 \quad (22)$$

or

$$Td_iS = -dG' \quad (23)$$

when temperature and pressure and each of the L_j and l_h s are kept constant in a closed system. A corresponding molar free energy, $\mu_i'^{\alpha}$ in this work¹ that includes a contribution to the work coordinate amount specific to the species i can be defined as

$$\begin{aligned} \mu_i'^{\alpha} &\equiv \left(\frac{\partial G'}{\partial n_i^{\alpha}} \right)_{T, L_j, n_{k \neq i}, n_m^{\beta}} = \mu_i + \left(\frac{\partial G'}{\partial l_h} \right)_{T, L_j, n_k} \left(\frac{\partial l_h}{\partial n_i^{\alpha}} \right)_{T, L_j, n_{k \neq i}} \\ &= \mu_i + L_h l_{h,i}^{\alpha} \end{aligned} \quad (24)$$

Eq. (24) applied to pure phase gives the standard state free energy with the additional work coordinate contribution as

¹ Here the superscript α is used to denote a specific phase or part of the system in which the work coefficient of interest applies. When superscripts α and β are used, the species that n_i^{α} and n_i^{β} or μ_i^{α} and μ_i^{β} refer to are the same in different parts or phases of the system.

$$\mu_i^{\prime,\alpha,0} = \mu_i^0 + L_h l_{h,i}^\alpha \quad (25)$$

For simplicity, the Eqs. (24) and (25) are written for the case where only one work coordinate h is kept constant. In the constrained equilibrium, i.e., the minimum of G' , the chemical potential is still, as a state variable, the quantity that is phase independent, i.e., equal throughout the system.

$$\mu_i^\alpha = \mu_i^\beta = \mu_i \quad (26)$$

In terms of activities the chemical potential can be expressed as:

$$\mu_i = \mu_i^{\prime,\alpha} - L_h l_{h,i}^\alpha = \mu_i^{\prime,\alpha,0} + RT \ln a_i - L_h l_{h,i}^\alpha \quad (27)$$

2.4 Systems with constant chemical potentials

With regard to systems in chemical equilibrium, Eq. (22) can be written in terms of independent variables, so that the species in the system are replaced by components, whose number is less than the number of species assuming chemical reactions or mass transfer between phases are taking place.

$$Td_iS = -dG - SdT - \sum_j l_j \cdot dL_j + \sum_k \pi_k d_e b_k \quad (28)$$

The chemical potential of a component k in this work has been denoted by the symbol π_k , and its molar amount by b_k to make them easier to distinguish from the chemical potential μ_i and molar amount n_i of a *species* i .

A suitable free energy function when some component chemical potentials are kept at a constant value by material bath is given by

$$G' \equiv G - \sum_h \pi_h b_h \quad (29)$$

where the summation is over the non-constant values of b_h

$$Td_iS = -dG' - SdT - \sum_j l_j \cdot dL_j - \sum_h b_h d\pi_h - \sum_h \pi_h d_i b_h + \sum_{k \neq h} \pi_k d_e b_k \quad (30)$$

with Eq. (23) following, so that when temperature, work coordinates L_j and each of the π_h and $b_{k \neq h}$ are kept constant, G' is minimised.

Mathematically Eqs. (21) and (29) represent Legendre transforms of the free energy function to a new one with a new set of independent variables (Alberty, 2001). The transforms allow solving of the equilibrium state and all its thermodynamic functions specified by the natural variables, where the natural variables can be freely chosen from the conjugate pairs of molar amounts and chemical potentials; temperature and entropy as well as work coordinates and work coefficients.

2.5 Systems with other than work coordinate constraints

If other constraints (e.g. due to slow reaction rates) that are not related to an additional work term ($L_j \cdot l_j$) apply to the system, the form of the energy functions [Eqs. (2)-(5)] is not altered. The free energy corresponding to any specific composition remains unchanged. However, the possible states of the system are reduced and the equilibrium is generally shifted to some state with higher free energy than without the constraint. When the states of the system are constrained by a relation or relations that can be expressed as linear combinations of amounts of species, the effective number of components in the system is increased, as was first noted by J. W. Gibbs, who called these kinds of constraints "passive resistances" (Gibbs, 1876; Koukkari, Pajarre, & Hack, 2008).

3. Use of a free energy minimiser

3.1 Traditional problem statement

The problems to be solved with a typical free energy minimiser are of the type:
Find the minimum of function \mathbb{G} :

$$\mathbb{G} = \sum_{\alpha} \sum_i \mathbb{G}_i^{\alpha}(x_j^{\alpha}, T, P) n_i^{\alpha} \quad (31)$$

subject to constraints

$$n_i^{\alpha} \geq 0 \quad \forall i \quad (32)$$

and

$$\mathbf{A}\mathbf{n} - \mathbf{b} = \mathbf{0} \quad (33)$$

where matrix element a_{ji} of matrix \mathbf{A} is the stoichiometric coefficient between component j and species i , vector element n_i the molar amount of species i and vector element b_j the (fixed) molar amount of component j in the system. The \mathbb{G} in Eq. (31) is the free energy of the system, either G (Gibbs energy) or G' as defined by Eq. (5) or (21), depending on whether additional work co-ordinate constraints have been applied. When \mathbb{G} equals G , the molar quantity \mathbb{G}_i equals the chemical potential μ_i .

In the minimum free energy (\mathbb{G}) state, the derivatives of the Lagrangian function L (Smith & Missen, 1991)

$$L = \mathbb{G} - \boldsymbol{\lambda}^T(\mathbf{A}\mathbf{n} - \mathbf{b}) \quad (34)$$

(where $\boldsymbol{\lambda}$ is a vector of Lagrange multipliers) with respect to molar amounts and individual Lagrange multipliers must be zero, so that

$$\frac{\partial L}{\partial n_i} = \frac{\partial \mathbb{G}}{\partial n_i} - \sum_j \lambda_j a_{j,i} = \mathbb{G}_i - \sum_j \lambda_j a_{j,i} = 0 \quad (35)$$

The chemical potential or molar Gibbs energy of a species in the calculation is expressed in the following or equivalent form:

$$\mu_i = \mu_i^0(T, P) + RT \ln a_i \quad (36)$$

Most often the activities are calculated based on activity coefficients on a mole fraction based scale

$$a_i \equiv \gamma_i x_i \quad (37)$$

so that the standard state value $\mu_i^0(T, P)$ in Eq. (36) refers to the chemical potential of the pure substance in given conditions, but also other activity scales are used. The activity coefficients γ_i for a free energy minimiser are given as functions of phase composition, temperature, and possibly pressure. The pressure dependency of μ_i^0 is formally given by

$$\frac{\partial \mu_i^0}{\partial P} = V_i^0 \quad (38)$$

For gaseous species the ideal gas law is often applied leading to

$$\mu_i^0(T, P) = \mu_i^0(T, P^0) + RT \ln \left(\frac{P}{P^0} \right) \quad (39)$$

while for condensed phases the pressure dependency is often ignored, effectively assuming that V_i is small enough that it can be considered zero.

The Lagrange multiplier for a component can be equated with its chemical potential as

$$\pi_j \equiv \left(\frac{\partial \mathbb{G}}{\partial b_j} \right)_{T, P, b_{k \neq j}} = \lambda_j \quad (40)$$

both when \mathbb{G} equals G and when it equals G' . Eq. (35) can also be applied to species that are not present in the equilibrium, allowing the calculation of molar free energy for a species that is not present in the equilibrium state and for which Eq. (36) is not directly applicable (Eriksson, 1975).

Equilibrium solvers typically allow solving of problems where the equilibrium chemical potential of certain species is fixed while the corresponding feed amount is allowed to vary. After redefining system stoichiometry so that the species of interest equals one of the system components, the problem equals the one described by Eq. (29). Computationally it can be solved (Cheluget, Missen, & Smith, 1987; Norval, Phillips, Missen, & Smith, 1991) by normal numerical routines by noting that (here summation index h goes over the components whose chemical potentials are held constant)

$$\begin{aligned} \mathbb{G}' &\equiv \sum_i \mu_i n_i - \sum_h \pi_h b_h = \sum_i (\mu_i^0 + RT \ln a_i) n_i - \sum_i \pi_h a_{h,i} n_i \\ &= \sum_i \left(\left(\mu_i^0 - \sum_h \pi_h a_{h,i} \right) + RT \ln a_i \right) n_i \end{aligned} \quad (41)$$

This means that the correct free energy function is minimised if the standard state values of those species containing the components with fixed chemical potentials are adjusted according to Eq. (42)

$$\mu_i^{i,0} \equiv \mu_i^0 - \sum_h \pi_h a_{h,i} \quad (42)$$

Additionally the mass balance constraints (33) related to components h need to be relaxed (the components are removed from matrix \mathbf{A}).

3.2 Additional work coefficients

In most cases with chemical equilibrium problems, the thermodynamic data is not given as a function of any other work coefficients than pressure, that is, any other work coefficients are assumed to be zero. According to the Eqs. (10) and (20) the Gibbs energy is also the minimised free energy function for non-zero constant values of L_j . The Gibbs energy is then given by (from Eqs. (1) and (5))

$$\left(\frac{\partial G}{\partial L_j} \right)_{T, L_{k \neq j}, n_i} = -l_j \quad (43)$$

$$G(T, P, L_j) = G(T, P, L_j = 0) - \int l_j \cdot dL_j \quad (44)$$

while the change in chemical potential is given by

$$\left(\frac{\partial \mu_i}{\partial L_j} \right)_{T, L_{k \neq j}, n_k} = - \left(\frac{\partial l_j}{\partial n_i} \right)_{T, L_k, n_{k \neq i}} = -l_{j,i} \quad (45)$$

and therefore standard state value corresponding to constant non-zero L_j is

$$\mu_i^0(T, P, L_j) = \mu_i^0(T, P, L_j = 0) - \int l_{j,i} dL_j \quad (46)$$

In order to avoid handling vector components separately it is assumed for Eq. (46) that $L_h \cdot l_{h,i}$ can be replaced with $L_h l_{h,i}$ (L_h and $l_{h,i}$ are either scalars or they are aligned).

As an example, for a ferromagnetic material as a pure phase when the magnetisation is assumed to be constant

$$\mu_i^0(T, P, B) = \mu_i^0(T, P, B = 0) - m_i B \quad (47)$$

and for paramagnetic material, if magnetisation is directly proportional to the external field

$$\mu_i^0(T, P, B) = \mu_i^0(T, P, B = 0) - 0.5 \chi_i B^2 \quad (48)$$

The chemical potential for a mixture phase is then given by

$$\mu_i(T, P, L_j) = \mu_i^0(T, P, L_j) + RT \ln \gamma_i x_i \quad (49)$$

The practical applicability of Eq. (49) is greatest when the dependency of the activity coefficients on L_j can be ignored.

3.3 Addition of new components to computational systems

The addition of a new component/constraint to a computational system adds a new row to matrix \mathbf{A} and new elements to the vectors $\boldsymbol{\lambda}$, \mathbf{n} and \mathbf{b} in Eq. (34). The resulting Lagrangian function L is identical to one defined for a system with the original components, but with adjusted free energy function G' defined by

$$\begin{aligned} G' &\equiv G - \lambda_r \left(\sum_i a_{r,i} n_i - b_r \right) = \sum_i \mu_i n_i - \lambda_r \left(\sum_i a_{r,i} n_i - b_r \right) \\ &= \sum_i (\mu_i - \lambda_r a_{r,i}) n_i + \lambda_r b_r \end{aligned} \quad (50)$$

so that the adjusted free energy function is one where the molar contributions have been augmented by the factor $-\lambda_r a_{r,i}$

$$\mu'_i = \mu_i - \lambda_r a_{r,i} \equiv \mu_i - \pi_r a_{r,i} \quad (51)$$

while the free energy function includes an additional term

$$\lambda_r b_r = \pi_r b_r \quad (52)$$

The minimum energy condition corresponding to Eq. (35), together with the original mass balance constraints, is now

$$\mu_i'^0 + RT \ln a_i - \pi_r a_{r,i} = \sum_{j \neq r} \pi_j a_{j,i} \quad (53)$$

The quantity on the left side of Eq. (53), marked with μ'_i in (51), replaces the original chemical potential expression ($\mu_i^0 + RT \ln a_i$) as the quantity that must be equal in phases and parts of the system that are in equilibrium with each other, that is, it is the chemical potential in the system. The comma in $\mu_i'^0$ is used to denote, that the standard state value may have been adjusted from the value used in the unconstrained system if new work coordinate has been applied, in concurrence with Eq. (24)

$$\mu_i'^0 = \mu_i^0 + L_h^{i,\alpha} l_{h,i}^\alpha \quad (54)$$

Here $L_h^{i,\alpha}$ is the work coefficient for pure species i in phase or system part α . In the example cases discussed in this work, it is zero except with surface energy-related calculations, where it equals the surface energy of the pure substance (it can also be applied to the case of an external magnetic field as an alternative to a field-related new component (section 4.5)).

Comparing Eq. (53) with Eq. (27) we have, for cases where the constraint can be equated with a fixed work co-ordinate, the equality

$$L_h l_{h,i}^\alpha = \pi_r a_{r,i}^\alpha \quad (55)$$

For the practical applicability with Gibbs energy minimisers, it is also required here that $a_{r,i}$ is not a function of π_r . Therefore, it is assumed that $l_{h,i}^\alpha$ can be factored into two parts, separating the possible dependency on L_j from the dependency on i .

$$l_{j,i} = l_j'(L_j) l_{j,i}'' \quad (56)$$

(Subscript α omitted from the equation for clarity as a continuously repeating element) Provided that Eq. (56) is valid, the stoichiometric coefficient $a_{r,i}$ can be defined by

$$a_{r,i} = \frac{l_{j,i}''}{l_j^0} \quad (57)$$

and the corresponding work coefficient as

$$L_j = \frac{\pi_r}{l_j^0 l_j'} \quad (58)$$

In Eqs. (57)-(58), l_j^0 is a normalisation constant with the same units as $l_{j,i}''$ and an arbitrary yet fixed numerical value.

Formally then, if a work coordinate related stoichiometric coefficient can be deduced on physical basis, the $\min(G)$ procedure can incorporate such factors in a multiphase calculation. According to Eq. (55) the respective component potentials become solved as additional Lagrange multipliers within the minimisation.

If the applied constraint cannot be equated with a work co-ordinate, the corresponding term does not enter Eq. (5), so for example for the case of system with a constant temperature, (external) pressure and a non-work constraint the Gibbs energy remains

$$G \equiv U - ST + PV = \sum_i \mu_i n_i \quad (59)$$

In terms of original components the minimised free energy nevertheless has an additional term as expressed by Eq. (50). With a molar free energy defined as

$$G_i' = \left(\frac{\partial G'}{\partial n_i} \right)_{T,P,n_j \neq i,b_r} \quad (60)$$

we have from Eq. (53) an equality that is also valid for rate constrained systems.

$$G_i' = \mu_i^0 + RT \ln a_i - \pi_r a_{r,i} = \sum_{j \neq r} \pi_j a_{j,i} \quad (61)$$

3.4 Applying additional components for calculations with additional non-zero constant work coefficients L_h

In principle, the application of Eq. (46) to adjusted standard state values is sufficient for calculations when the value of new work coefficient instead of the corresponding work coordinate is specified (it is assumed here that the activity coefficients are not explicit functions of L_h). However, one often wants to perform repeated calculations with many different values of L_h while the databases used and free energy minimiser programmes do not necessarily readily support this. An alternative is to define a new component for the stoichiometry of the relevant species and adjust the chemical potential of that component.

From Eqs. (41) and (46)

$$-\int l_{j,i} dL_j = -\pi_h a_{h,i} \quad (62)$$

As before, it is assumed here that $\int l_{j,i} dL_j$ can be factored to two parts, separating the possible dependency on L_j from the dependency on i as shown by Eq. (63) (If this is not possible, more than one added component with fixed potentials should be applied in the model system)

$$l_{j,i} \equiv l'_j(L_j) l''_{j,i} \quad (63)$$

so that

$$\int l_{j,i} dL_j = l''_{j,i} \int l'_j dL_j \quad (64)$$

Applying Eqs. (62) and (64) one can again set a definition for the stoichiometric coefficient

$$a_{r,i} = \frac{l''_{j,i}}{l_j^0} \quad (65)$$

The value of the corresponding chemical potential is consequently given by

$$\pi_r = \frac{l''_{j,i}}{a_{r,i}} \int l'_j dL_j = l_j^0 \int l'_j dL_j \quad (66)$$

If $l_{j,i}$ is not a function of L_j , the preceding Eqs. simplify to

$$a_{r,i} = \frac{l_{j,i}}{l_j^0} \quad (67)$$

$$\pi_r = L_j l_j^0 \quad (68)$$

4. Application examples and results

A collection of various example systems and their properties are presented in Table 2. Given are the minimised Free energy functions (G or G'), work coefficients and coordinates, the adjusted standard state values for pure phases as given by Eqs. (54) (for systems with constant work coordinates) or (46) (for a case of constant work coefficient and the equipotential between species of same stoichiometry² in different phases or parts of the system (typically called chemical potential). Also given are the expressions for the stoichiometric coefficients related to the new constraints and the constraint equations.

Example systems where the applied constraint and the corresponding chemical potential do not form a work coefficient and coordinate pair are listed in Table 3. Given are the formulas for stoichiometric coefficients related to the constraining components and the chemical potentials of those components. The coefficients and chemical potentials are largely analogous to the work coefficients and coordinates of the previous examples.

² 'Same stoichiometry' refers to here to the regular components of the system, excluding the added component related to the new constraint and/or work coordinate. Amounts of those components used to limit chemical reactions in the system are still required to be same.

Table 2. Applications of the free energy method (2 pages)

System	Minimised free energy G or G'	Work coefficient	Work coordinate
Generic (constant work coordinate j)	$G' = \sum_i \mu_i n_i + L_j l_{j,i} n_i$	L_j	$l_j = \sum_i l_{j,i} n_i$
Generic (constant work coefficient j)	$G = \sum_i \mu_i n_i$		
Surface	$G' = \sum_i \mu_i n_i + \sum_k \sum_i \sigma^k A_i^k n_i^k$	σ surface energy (contribution from individual layer)	$A = \sum_i A_i n_i$ area
Donnan equilibrium	$G' = \sum_i \mu_i n_i - \sum_i \Delta\phi^\alpha F z_i n_i^\alpha$	$\Delta\phi^\alpha$ electrochemical potential difference	$-q^\alpha = -\sum_i F z_i n_i^\alpha$ charge
Constrained volume	$G' = \sum_i \mu_i n_i - \Delta P \sum_i V_i n_i$	ΔP^α (osmotic) pressure difference	$V^\alpha = -\sum_i V_i n_i^\alpha$
Magnetised	$G = \sum_i \mu_i n_i$	B magnetic flux density	$m = \sum_i m_i n_i$ magnetic moment

Adjusted standard state	Equipotential (between species of the same stoichiometry in different phases or parts of a system)	Stoichiometric coefficient	Constraint
$\mu_i^0 = \left(\frac{\partial G'}{\partial n_i} \right)_{T,P,L_h} = \mu_i^0 + L_j^0 l_{j,i}^{\alpha}$	$\mu_i^{\alpha} - L_j l_{j,i}^{\alpha}$ $\mu_i = \mu_i^0 + RT \ln a_i^{\alpha} - L_j l_{j,i}^{\alpha}$ <p>chemical potential</p>	$a_{r,i} = l_{j,i}^{\alpha} / l_j^0$ <p>when</p> $l_{j,i} \equiv l_j(L_j) \cdot l_{j,i}'$	$\sum_i a_{r,i} n_i - b_r = 0$
$\mu_i^0(T, P, L)$ $= \mu_i^0(T, P, L = 0) - \int l_{j,i} dL$	μ_i <p>chemical potential</p>	not required	not applicable
$\mu_i^{\delta,0}(T, P, \sigma_i) = \mu_i^0(T, P) + \sigma_i A_i$ <p>(for the topmost surface layer)</p>	$\mu_i = \mu_i' - \sigma^{\alpha} A_i^{\alpha}$ $= \mu_i^0 + RT \ln a_i^{\alpha} - \sigma^{\alpha} A_i^{\alpha}$	$a_{r,i} = A_i / A_0$	$\sum_i A_i n_i - A = 0$
$\mu_i^0(T, P, \phi^{\alpha}) = \mu_i^0(T, P)$ $(L_j^0 = 0)$	$\mu_i' = \mu_i^0 + RT \ln a_i + \Delta \phi F z_i$ <p>(electro)chemical potential</p>	$a_{r,i} = z_i / z_0$	$\sum_i z_i n_i = 0$
$\mu_i^0(T, P^{\beta})$ <p>($\Delta P^{\alpha} = 0$ in a single species system)</p>	$\mu_i' = \mu_i^0(T, P^{\beta}) + RT \ln a_i + \Delta P^{\alpha} V_i$	$a_{r,i} = V_i / V_0$ <p>(V_i assumed to be independent of pressure)</p>	$\sum_i V_i n_i - V = 0$
$\mu_i^0(T, P, B)$ $= \mu_i^0(T, P, B = 0) - \int m_{j,i} dB$	$\mu_i^{\alpha} = \mu_i$	$a_{r,i} = m_i' / m_0$ <p>when</p> $m_i \equiv m'(B) \cdot m_i''$	not applicable

Table 3. Example system with additional components that are not directly linked to a work coordinate.

System	Stoichiometric coefficient for the constraint	component chemical potential
Spherical nanoparticle	$\left(A_i - \frac{2V_i}{r}\right) \frac{1}{A_0}$ (geometric constraint)	$\sigma_i A_0$ surface energy · normalisation constant
Reaction extent or affinity constrained system	$\xi_r = \sum_i a_{r,i} n_i$ extent of reaction r	$-A_r$ affinity of reaction r

In these cases when the component amount is constrained, the minimised free energy function is the Gibbs energy of the system as defined by equation (59). The energy and entropy terms (and therefore chemical potentials) may still contain added work coefficient-dependent terms (as they do in the nanoparticle case).

4.1 Surface and interfacial energy

The model application for surface and interfacial systems has been discussed in detail in **Papers II** and **IV**. **Paper II** describes a monolayer model of a liquid surface, where the single surface layer is modelled as a separate phase, whose constituents interact only with each other. In **Paper IV** a multilayer model that includes non-ideal interactions between different layers is developed for metal-oxide surface, and tested for liquid-liquid metal alloy interfaces.

In a system with a liquid-vapour surface or liquid-liquid interface the derivative of the free energy with respect to interfacial area is the surface or interfacial energy

$$\frac{\partial G}{\partial A} = \sigma \equiv L_h \quad (69)$$

In the current work the surface or interface has been modelled with a finite number, one or more, individual monomolecular layers. With the simplifying assumption that the molar surface areas of individual constituents are independent from system composition

$$\frac{\partial A_i}{\partial x_j} = 0 \quad (70)$$

the contribution of an individual interfacial layer k can be included in the free energy equation as

$$\mu_i^k = \sum_{j=1}^M a_{j,i} \pi_j + \sigma^k A_i = \sum_{j=1}^M a_{j,i} \pi_j + a_{ji} \pi_{M+k} \quad (71)$$

with the following relations based on Eqs. (57) and (58).

$$a_{k+M,i} = \frac{A_i}{A_0} \quad (72)$$

$$\sigma^k = \frac{\pi_{M+k}}{A_0} \quad (73)$$

where the normalisation constant A_0 has the units of $m^2 mol^{-1}$. For the bulk phase(s) the molar surface/interfacial areas A_i are zero, as there is no surface area associated with them. The interfacial energy contribution of an individual layer is denoted by σ^k while the physical interfacial energy given by summation over all NL layers.

$$\sigma = \sum_{k=1}^{NL} \sigma^k \quad (74)$$

The μ_i^k in Eq. (71) is the molar free energy of constituent i on the layer k , as stated in Eq. (24). For the bulk phases in the models described in both **Papers II and IV**, it was assumed that the direct energetic effects related to the surface were restricted to the top most atomic or molecular layer of the surface. With that convention applied, following Eqs. (27) and (54) the chemical potential was expressed on the layer closest to the surface by equation (superscripts s and b denote the surface layer and bulk respectively)

$$\begin{aligned} \mu_i^s &= \mu_i^{s,0} + RT \ln a_i^s - \sigma A_i = \mu_i^{b,0} + \sigma_i A_i + RT \ln a_i^s - \sigma A_i = \mu_i^b \\ &= \mu_i \end{aligned} \quad (75)$$

and on other interfacial layers by (superscript α denotes the interfacial layer)

$$\mu_i^\alpha = \mu_i^{b,0} + RT \ln a_i^\alpha - \sigma A_i = \mu_i^b = \mu_i \quad (76)$$

The molar free energies for the surface and interfacial species, as defined by Eq. (24), were in **Papers II and IV** defined implicitly via excess energies using the Redlich-Kister model. In **Paper IV** the excess energies were evaluated considering both the compositions of the individual layer in question and its nearest neighbours using the equation

$$\begin{aligned}
G^{ex,k} = n^k \sum_i \sum_j & \left(\frac{1}{2} (1 - m^0) \Omega_{ij}^k x_i^k x_j^k \right. \\
& + \frac{1}{2} m^0 \left(-\frac{1}{2} \Omega_{ij}^{k+1} x_i^{k+1} x_j^{k+1} - \frac{1}{2} \Omega_{ij}^{k-1} x_i^{k-1} x_j^{k-1} \right. \\
& \left. \left. + \Omega_{ij}^{k,k+1} x_i^k x_j^{k+1} + \Omega_{ij}^{k,k-1} x_i^k x_j^{k-1} \right) \right) \quad (77)
\end{aligned}$$

for the excess free energy for an individual layer k , where Ω_{ij}^k , $\Omega_{ij}^{k,k+1}$ and $\Omega_{ij}^{k,k-1}$ are composition dependent interaction energies within layer k and between it and its nearest neighbours and m^0 is a geometric parameter expressing the factor of nearest neighbours of a species that are in one of the adjacent layers in a compositionally uniform system. For the derivation of thermodynamically consistent relations it was necessary for the multilayer system to add further constraint(s) that kept the composition of the interfacial layer closest to the bulk equal to that of the bulk, the interfacial energy contribution of the additional constraints approaching zero with an increasing number of layers. Example results for calculations in metal alloy and metal-oxygen systems are shown in Fig. 1.

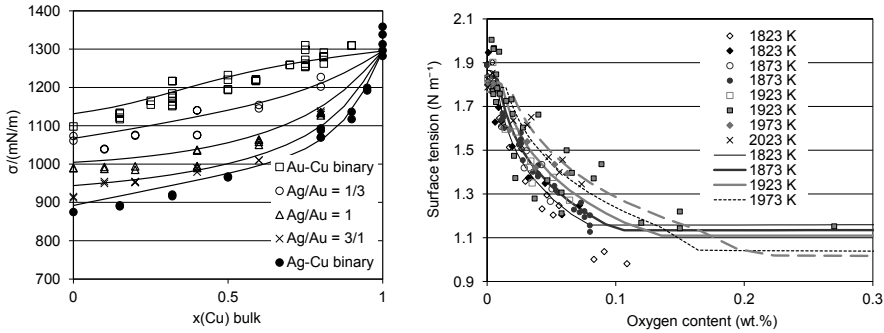


Figure 1. Surface tension in Ag-Au-Cu metal alloys system (left) and iron-oxygen system (right). The model and experimental data for Ag-Au-Cu alloy as presented in **Paper II** and for Fe-O system as in **Paper IV**.

In the surface monolayer model the assumption of no interactions between the surface layer and the bulk make the model elegantly simple as a mathematical construction. It is also obvious that is not physically reasonable to assume it to be strictly accurate. However, as a practical tool it has found wide use (Egry, Ricci, Novakovic, & Ozawa, 2010; Tanaka, Hack, Iida, & Hara, 1996) and has been shown to work reasonably accurately for especially metallic systems. The analogy of the surface ‘phase’ in a monolayer model to regular bulk phase equilibria has also been explored by Kang (2015a, 2015b). Additional assumptions, which are validated only insofar as the resulting model gives reasonable predictions com-

pared with experimental data, are needed for the monolayer or multilayer excess energies.

4.2 Volume-constrained system

In a system in which the volume of part of the system is constrained, an additional pressure component affecting its chemical potential applies to that part. For straightforward application of the current method, it is necessary that the partial molar volumes are not functions of phase composition, although they could be functions of pressure. In the ion-exchange system of **Paper III**, a constraint on the water volume is an essential feature of the model. Only the molar volume of the water itself (assumed to be incompressible) is considered. The free energy from Eq. (21) can then be stated as

$$G' = \sum_i \mu_i n_i - \Delta P \cdot V_{H_2O} n_{H_2O}^\alpha = G - \Delta P V^\alpha = G^\beta + F^\alpha + V^\alpha P^\beta \quad (78)$$

where the last term is constant. The stoichiometric coefficient related to the constraining component is directly proportional to the molar volume.

$$a_{r,i} = \frac{V_{H_2O}}{V_j^0} \quad (79)$$

The osmotic pressure difference is consequently obtained as

$$\Delta P = -\pi_r V_j^0 \quad (80)$$

In principle it could be expected to be possible to predict, e.g., the swelling behaviour of fibres (application area in **Paper III**) applying the calculated osmotic pressure together with the modelled charge state and a model for the fibre wall elasticity, but even a semi quantitative model has been found to be elusive.

4.3 Nanoparticles with a combined area and volume constraint

A model for small-scale systems can have volume and surface that area inter-linked. Considering the simplest case of a spherical particle, the changes in volume and area are connected by the equation

$$dA = \frac{2dV}{r} \quad (81)$$

Therefore, the balance equation for surface area related to molar area and volume can be written as

$$\sum_a \sum_i dn_i^\alpha \left(A_i^\alpha - \frac{2V_i^\alpha}{r} \right) = 0 \quad (82)$$

If the change in total volume (and therefore radius) is relatively small, the value in brackets in Eq. (82) can be taken as a constant similarly to molar volumes and areas in the previous sections. In **Paper V** a model for a melting nanoparticle was developed based on the idea that the limiting phase transition would be the formation of a liquid surface on a solid core.

The Euler equation for internal energy of a fully solid or liquid particle is given following Eq. (2)

$$U = TS - P^0V + \sigma_{Me(\alpha)}A + \mu_{Me(\alpha)}(P^0)n_{Me} \quad (83)$$

where (α) denotes the physical state (solid or liquid) and P^0 is used to emphasise that the standard state value is the one based on the external pressure of the system. The minimised free energy when there is no external constraint on the surface energy or surface area³ is given by

$$G' \equiv U - ST + P^0V = \mu_{Me}(P^0)n_{Me} + \sigma_{Me(\alpha)}A \quad (84)$$

Correspondingly, the standard states for the core and the second layer can be given by

$$\mu_{Me(\alpha)}^{',c,0} = \mu_{Me(\alpha)}^{',z,0} = \mu_{Me(\alpha)}^0(P^0) \quad (85)$$

and for the solid surface by

$$\mu_{Me(s)}^{',1,0} = \mu_{Me(s)}^0 + \sigma_{Me}^s A_{Me}^s \quad (86)$$

and for a liquid surface on a solid core

$$\mu_{Me(l)}^{',1,0} = \mu_{Me(l)}^0 + \sigma_{Me}^l A_{Me}^l + \sigma_{Me}^{sl} A_{Me}^l \frac{A^2}{A^1} \quad (87)$$

The ratio of the area of the interface between the first and second atomic layers, A^2 , and the surface area, A^1 in Eq. (87) can be estimated based on liquid metal molar area and volume by

$$\frac{A^2}{A^1} = \left(1 - \frac{3V_{Me(l)}}{A_{Me(l)}r}\right)^{\frac{2}{3}} \quad (88)$$

The chemical potential of the component Me , π_{Me} is the chemical potential of the macroscopic unconstrained substance Me in the system. With the definitions used, it is given for one chemical component fully solid or liquid system by Eq. (89) (superscript α refers to either a solid or liquid state).

$$\pi_{Me} = \mu_{Me}^{0,\alpha} + \frac{2V_{Me}^\alpha}{rA_0} \pi_{AConstraint} = \mu_{Me}^{0,s} + \frac{2V_{Me}^\alpha}{r} \sigma_{Me}^\alpha \quad (89)$$

³ The added constraint in the stoichiometry in Table 4 (or equation (82)) is really for particle sphericity and the assumption that the number of spherical particles is not changed. While not discussed here, with orientation dependencies ignored, the spherical form is the one corresponding to minimum energy.

The differences in chemical potential in the particle and a macroscopic phase in a same state can be related to the differences in vapour pressures. The familiar Kelvin equation directly follows from Eq. (89).

$$\pi_{Me} - \mu_{Me}^{0,\alpha} = RT \ln \frac{P_{Me}}{P_{Me}^{0,\alpha}} = \frac{2V_{Me}}{r} \sigma_{Me}^s \quad (90)$$

The graphs in Fig. 2 for melting of tin and silver nanoparticles have been calculated assuming that the interfacial energy between the solid and liquid follows the perfect wetting condition (Eustathopoulos, 1983) and applying the experimental solid and liquid surface energies, molar volumes and free energies of melting as referenced in **Paper V**.

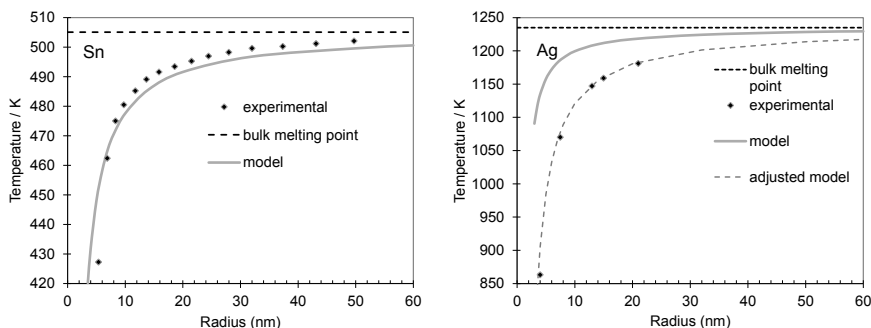


Figure 2. Melting temperature of metallic nanoparticles. From **Paper V**.

In Fig. 2. the model calculations are compared with experimental data from literature for Sn (left) and Ag (right). While a reasonably good match between the basic model (solid curve) and the experimental data was found with Sn, an agreement with Ag data could be reached only assuming (following Sim & Lee (2014)) that the effective solid surface energy (taking into account as adjustable correction factor the effect of surface strain and anisotropic nature particle surface) was higher by a factor of 1.17 than the tabulated one.

It was noted in **Paper V** that the model used closely matches the one for which the melting point of the particle is calculated based on equal chemical potential (not free energy) such as the one used in e.g. Lee et al. (2007), Sim & Lee (2014) and Sopousek et al. (2014).

4.4 Donnan equilibrium

Ion-exchange model with Donnan equilibrium was described in detail in **Papers I and III** with comparison to lab results. Process simulation work based on the thermodynamic this model has been published several papers and presentations (Kalliola, Pajarre, Koukkari, Hakala, & Kukkamäki, 2012; Kangas, Pajarre, Nappa, & Koukkari, 2012; Koukkari et al., 2007; Pajarre, Koukkari, & Penttilä, 2008).

For a system in which the electrochemical Donnan equilibrium is present, a new component needs to be defined for the electrical charge for each additional sub-volume present. The related new constraint equation is

$$\sum_i n_i^\alpha z_i = 0 \quad (91)$$

The potential difference in a Donnan equilibrium system is caused by electrically charged species that are not freely mobile. The electrical work related to them can be stated (taking into account Eq. (91)) as

$$dW = \sum_i \Delta\phi^\alpha F z_i dn_{i(\text{immobile})}^\alpha = - \sum_i \Delta\phi^\alpha F z_i dn_{i(\text{mobile})}^\alpha \quad (92)$$

A Donnan equilibrium free energy problem requires at least two additional components related to the charged species: at least one constraining the immobile species, the amount of which in the pulp suspension models was a fixed quantity (bound, carboxylic or sulfonic acid groups), and whose chemical potential was without practical interest, and one for the overall charge balance. Based on Eq. (92), the work term common to all the charged species is

$$L_j l_{j,i} n_i = -\Delta\phi^\alpha F z_i n_i \quad (93)$$

Setting $a_{ri} \equiv z_i$ the Donnan potential difference is obtained as

$$\Delta\phi^\alpha \equiv (\phi^\alpha - \phi^\beta) = -\frac{\pi_r}{F} \quad (94)$$

The equipotential, commonly called the electrochemical potential, that is same in both aqueous phases for mobile ions is following Eq. (27) given by

$$\mu_i = \mu_i^{\prime 0} + RT \ln a_i + \Delta\phi^\alpha F z_i = \mu_i^0 + RT \ln a_i + \Delta\phi^\alpha F z_i \quad (95)$$

The μ_i in Eq. (95), rather than merely the ‘chemical’ part it ($\mu_i^0 + RT \ln a_i$), is the chemical potential of the species i as defined by Eq. (1) and other fundamental relationships in thermodynamics. As pointed out by for example, Guggenheim (1967), the ‘chemical’ and ‘electrical’ parts of it are not experimentally measurable and have questionable meaning as physical entities. For the purposes of computational thermodynamics it is useful to define individual ion activities and activity coefficients that are compatible with well-definable and measurable activities and activity coefficients of neutral combinations of them. The models used by the authors have in common that the aqueous solution has been modelled applying the Pitzer non-ideality model (Harvie, Møller, & Weare, 1984) while the multicomponent model has also included solid precipitates, and when applicable, a gas phase exchanging carbon dioxide with the solution. The specifics of the individual ion activity coefficients and the corresponding implicit pH scale have been discussed e.g. by Harvie et al. (1984).

An example of the Donnan theory applied to a laboratory system is presented in Fig. 3. All the calculation results for each pH are from a single multi-component

equilibrium calculation, just as the various metal amounts were determined from a single sample.

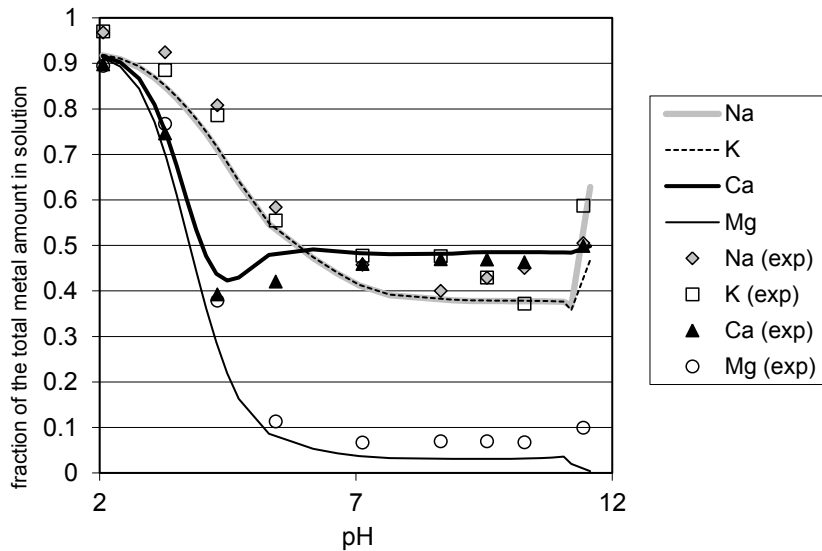


Figure 3. Experimental and modelled concentrations in an aqueous solution in a multicomponent and multiphase system with ion exchange, complexation and precipitation. Adapted from **Paper III**.

The Donnan equilibrium model application for pulp suspensions has been found to be valuable to predict the chemical phenomena and process behaviour in pulping, bleaching and paper machines (Kalliola et al., 2012; Kuitunen, 2014), while the assumed non-specific nature of ion-exchange interactions is known to face limitations with di- and multivalent ions, especially in systems with high ionic strengths (Kangas et al., 2012; Sundman, Persson, & Öhman, 2010; Sundman, 2008).

4.5 Systems with an external magnetic field

The chemical system for a free energy minimiser can be defined either following Eq. (46) and modifying the standard states for the given field strength (without defining any additional components), or by applying one or more additional components whose chemical potentials are set following Eq. (66) based on the field strength-dependent magnetisation properties of the substance. The second method has been found by the authors to be more readily applicable to calculations that are repeated with multiple field strengths. The applicable equations in this case are

$$a_{r,i} = \frac{m_i''}{m_j^0} \quad (96)$$

for the stoichiometric coefficient, and

$$\pi_r = m^0 \int m' dB \quad (97)$$

when the molar magnetic moment can be factorised (Eq. (98))

$$m_i \equiv m'(B)m_i'' \quad (98)$$

Example cases of equilibrium in external magnetic field were discussed in **Paper V**.

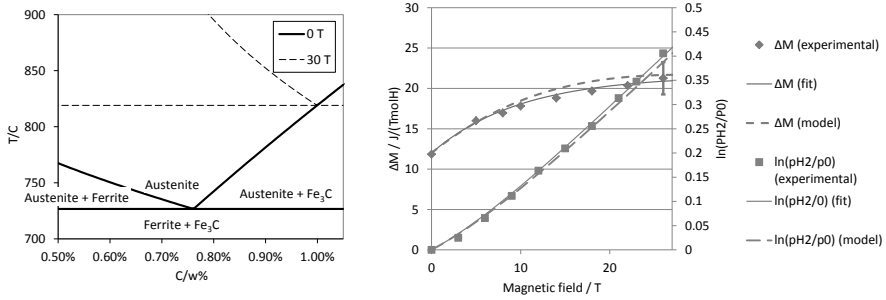


Figure 4. Left: Effect of magnetic field on the equilibrium phase diagram in the Fe-C system. Right; Equilibrium hydrogen pressure and magnetic moment as a function of magnetic field strength with a LaCo₅-H system. Experimental data points shown with a smoothed fit together with a model curve for both equilibrium pressure and magnetisation based on measured magnetic moment and pressure values respectively. Adapted from **Paper V**.

4.6 Constrained reaction extents and mass transfer

In a system where a single reaction of the form



or

$$\sum_i v_i n_i = 0 \quad (99)$$

where v_i equals w_i for products and $-w_i$ for reactants, the extent of the reaction is defined as

$$d\xi = \frac{dn_i}{v_i} \quad (100)$$

In a system with multiple possible reactions, it is in general impossible to define the change in the extent of any individual reaction $d\xi_r$, based on the change in

system composition unless the other linearly independent reactions forming a basis spanning the reaction space are first defined. When they are, the equation (101) for $\mathbf{d}\xi$ can be solved

$$\mathbf{d}\mathbf{n} = \mathbf{v}\mathbf{d}\xi \quad (101)$$

where $\mathbf{d}\mathbf{n}$ is the vector of changes of molar amounts of the N constituents in the system, $\mathbf{d}\xi$ a vector of changes in extents of the NR specified reactions, and \mathbf{v} a $N \times NR$ matrix of stoichiometric coefficients of the reaction vectors spanning the reaction space.

For an equilibrium system, the matrix equation

$$\mathbf{A}\mathbf{v} = \mathbf{0} \quad (102)$$

where \mathbf{A} is an $M \times N$ matrix of stoichiometric coefficients between the N constituents and M components ($M = \text{rank}(\mathbf{v})$) that forms a link between the system stoichiometry and the reactions allowed by it (Alberty, 1989, 1991; Keck & Gillespie, 1971; Keck, 1990; Koukkari & Pajarre, 2006; Smith & Missen, 1991).

Any kinetic restrictions in the possible reactions that cause the system to develop towards some other state than full equilibrium will lead to a new matrix equation

$$\mathbf{A}'\mathbf{v}' = \mathbf{0} \quad (103)$$

where \mathbf{v}' is an $N \times NR'$ matrix ($NR' < NR$) made of the reduced reaction set and \mathbf{A}' is the corresponding $M' \times N$ matrix ($M' = M + NR - NR' \equiv M + C$, where C is the number of added constraints) of stoichiometric coefficients for the new augmented matrix of stoichiometric coefficients.

Each linearly independent restriction on the set of reactions allowed to freely equilibrate corresponds to an additional stoichiometric constraint, or a row in the \mathbf{A} matrix that is linearly independent of the existing component balances or previously defined reaction kinetic constraints. A practical way of defining a restricted reaction in a multispecies constrained equilibrium system is by Eq. (104)

$$d\xi_j \equiv \sum_i a_{M+j,i} dn_i = db_{M+j} \quad (104)$$

where $a_{M+j,i}$ is a matrix element in the augmented matrix \mathbf{A}' , where the $M + j^{\text{th}}$ row defines the constraint related to the reaction and db_{M+j} the change in the value of the corresponding element in the augmented component vector. The matrix form corresponding to Eq. (104) is

$$\mathbf{d}\xi = \mathbf{A}''\mathbf{d}\mathbf{n} = \mathbf{d}\mathbf{b}'' \quad (105)$$

where \mathbf{A}'' is the $C \times N$ submatrix forming the lower part of \mathbf{A}' .

If the number of restricted reactions (constraints) defined equals NR , so that no unrestricted linearly independent reactions remain, \mathbf{A}'' in Eq. (105) can be replaced with \mathbf{A}' , and $\mathbf{d}\xi$ with $\mathbf{d}\xi'$, where the first $N - NR$ components of the $\mathbf{d}\xi'$ vector equal zero, and the last NR components are the same as in $\mathbf{d}\xi$.

$$d\xi' = A' dn \quad (106)$$

As matrix A' has linearly independent rows it is invertible. Matrix $(A')^{-1}$ contains in its columns coefficients for reaction like transformations for the set of species, so that in each transformation the amount of one of the components is increased by one, while the amounts of other components are kept constant. In matrix form this can be stated as.

$$(A')^{-1}A' = I \quad (107)$$

Multiplying the Eq. (106) by $(A')^{-1}$ one obtains

$$(A')^{-1}d\xi' = dn \quad (108)$$

The first M transformations are not allowed as they violate the normal component balances, and the corresponding values in the change of advancement vector $d\xi'$ are zero, while the remaining reactions are the constrained ones defined by Eq. (105), so that the last NR columns of matrix $(A')^{-1}$ equal matrix ν and the last NR values of $d\xi'$ equal vector $d\xi$ in Eq. (105). The definition in Eq. (105) thus becomes equivalent to the one in Eq. (101).

As a schematic example, one can consider a system with the following species H_2 , CH_4 , C_2H_4 , C_2H_6 and C_3H_8 . $N = 5$ and $M = 2$, so that it is possible to define a maximum of three independent constrained reactions using the formalism of Eq. (104) corresponding to, for example to the following A' matrix where the first two rows refer to the elements C and H and the last three to the added constraints:

$$A' = \begin{matrix} & \begin{matrix} H_2 & CH_4 & C_2H_4 & C_2H_6 & C_3H_8 \end{matrix} \\ \begin{matrix} 0 \\ 2 \\ 0 \\ 1 \\ 0 \end{matrix} & \begin{bmatrix} 1 & 2 & 2 & 3 \\ 4 & 4 & 6 & 8 \\ 0 & 0 & 0 & 1 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \end{matrix} \quad (109)$$

The constraints set here are of arbitrary nature for the schematic example although the first and third of them are fairly intuitive (both restricting the amount of an individual species). By inspection or by linear algebra one can derive

$$(A')^{-1} = \begin{matrix} \begin{matrix} H_2 \\ CH_4 \\ C_2H_4 \\ C_2H_6 \\ C_3H_8 \end{matrix} & \begin{bmatrix} 2 & -0.5 & -2 & 2 & -1 \\ -3 & 1 & 1 & -2 & 0 \\ 2 & -0.5 & -2 & 1 & -1 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix} \end{matrix} \quad (110)$$

where the last three columns give in the traditional reaction equation format the following three rate constrained reactions compatible with both Eqs. (101) and (105).



However, the three reaction constraints given by matrix (109) are also unambiguously defined individually, while the reaction equation format (II-IV) is properly defined only for a full set of independent equilibrium or non-equilibrium reactions.

With the reaction equations defined by the added components, many of the mathematical relationships defined in earlier sections can also be applied. The affinity of a restricted reaction j , \mathbb{A}_j , in a constrained equilibrium system is directly related to the chemical potential of the corresponding component.

$$\mathbb{A}_j = -\left(\frac{\partial G}{\partial \xi_j}\right)_{T,P,b_i,\xi_{k \neq j}} = -\left(\frac{\partial G}{\partial b_{j+M}}\right)_{T,P,b_i,\xi_{k \neq j}} = -\pi_{j+M} \quad (111)$$

where b_i is the amount of any of the components $b_1 \dots b_M$ in the system. For any chemical reaction that is not one of those defined by Eq. (104), the affinity is obtained as a linear combination of them and equilibrium reactions

$$\begin{aligned} \mathbb{A}_j &= -\sum_i v_{i,j'} \mu_i = -\sum_i v_{i,j'} \sum_{k=1}^{M+C} a_{ki} \pi_k = -\sum_i v_{i,j'} \sum_{k=M+1}^{M+C} a_{ki} \pi_k \\ &= -\sum_{k=M+1}^{M+C} a_{k,j} \pi_k \end{aligned} \quad (112)$$

where $v_{kj'}$ is the stoichiometric coefficient between the reaction j' and component k .

It is possible that in a system where the extent of one or more reactions are constrained, the modelled time behaviour of the system approaches a state where the affinity or affinities are zero without the state in question being the actual equilibrium state of the system. Such a state would be a local, but not global free energy minimum of the system with respect to the specified reaction extents. Provided that the applied reaction rates give a sufficiently accurate description of the real reactions taking place in the system, such a local minimum state corresponds to a real long term metastable state. In such cases constrained chemical potential (affinity) could not be reasonably used as an alternative to constrained reaction extent for specifying the state of the system.

Corresponding to Eq. (53) it is possible to form a relationship between chemical potentials in a rate constrained system

$$\mu_i^0 + RT \ln a_i - \sum_r \pi_r a_{r,i} = \mu_i^0 + RT \ln a_i + \sum_r \mathbb{A}_r a_{r,i} \quad (113)$$

By setting the affinity (corresponding to the component chemical potential π_j) to a constant value, it can be used to calculate restricted equilibrium states with a

fixed affinity (deviation from equilibrium), or when affinity is set to zero, equilibrium (in respect to the specified reaction) without redefining the system stoichiometry. A standard state value for species for a system with given T , P and A_r could be defined following Eq. (29) by relation (114)

$$\mu_i^0(T, P, A_r) = \mu_i^0(T, P, A_r = 0) + A_r a_{r,i} \quad (114)$$

but typically applying the fixed chemical potential condition via the added component is more practical.

Reaction constrained free energy models have been presented for e.g., industrial production of precipitated calcium carbonate (PCC) (Koukkari, Pajarre, & Blomberg, 2011) high temperature oxidation of $TiCl_4$ to TiO_2 (Koukkari et al., 2008), calcination of TiO_2 from an oxyhydrate slurry (Koukkari & Pajarre, 2006) and in studies of biomass gasification (Kangas, Hannula, Koukkari, & Hupa, 2014; Kangas, Koukkari, & Hupa, 2014; Kangas, 2015; Yakaboylu, Harinck, Smit, & de Jong, 2015). Application of the current model to NO emissions was also presented in **Paper V**.

The fundamental guiding principle of work related to reaction constraints has been to strive towards a model containing only the necessary amount of kinetic complexity while applying the constrained equilibrium thermodynamics as much as possible. Highly complex reaction kinetic models have been criticised in the area of gas phase chemistry on the basis that because of uncertainties related to modelling parameters, the increased complexity is unlikely to bring additional value to the results (Keck, 2008). With multiphase processes and kinetics the uncertainties will probably tend to be even greater. Therefore, it has been considered valid in the work regarding reaction-constrained systems to aim at system descriptions that capture the most essential parts of the rate-dependent processes with only a few constrained reactions. Such descriptions are of course only an approximation of the physical system; shortcomings of the approach are probably more likely to become apparent when behaviour of complex systems is studied over moderate temperatures and short time intervals (Kangas, 2015).

From the computational point of view, a mass transfer process between two phases is a reaction where the species i in phase α is transformed to same species (or a species of equal stoichiometry) in another phase. Therefore, the reaction rate and affinity equations derived earlier apply equally to such mass transfer processes. As a specific example one can consider metallurgical paraequilibrium where new phases are formed with the same alloy composition as the parent phase but substitutional element like carbon can equilibrate between them. The resulting constraints are of the form (Pelton, Koukkari, Pajarre, & Eriksson, 2014)

$$\sum_i (Y_{Me} a_{Me,i}^\alpha - a_{Fe,i}^\alpha) n_i^\alpha = 0 \quad (115)$$

where Y_{Me} is the mole ratio of iron (or other reference metal chosen for the system) and metal Me in the parent phase.

5. Conclusions

The topic of this work has been to extend the application area of traditional Gibbs energy minimisers for systems of theoretical and practical interest. The aim has been to develop, within the possibilities offered by the minimisers, as generic as possible methods for both increased understanding the thermodynamic relationships in the systems and for easier future application of the method for systems that are not handled in present work

The application area of standard Gibbs energy minimisers has been extended, for the most part using existing published phase models with supplementary data and stoichiometry definitions.

Chemical problems worked with have included reaction rate constrained systems, surface and interfacial tension in molten systems, Donnan equilibrium as a part of multiphase model, and systems affected by external magnetic fields.

The greatest practical success has been achieved with the models that combine reaction kinetics with partial thermodynamic equilibrium calculation and ion exchange models based on Donnan equilibrium, that both have been applied with success in real-life industrial design and development work with multicomponent, multiphase systems. Applied to liquid surface energies the method has been successful in handling systems with multiple components and complex non-equilibrium data.

6. Discussion

Thermodynamic data for bulk phases in this work has been generally accepted as it has been found in literature or databases. The charge parameterization required for the Donnan model for pulp systems could be set based on titration experiment independent of the ion exchange model itself. Effects of adjusting the interaction or interfacial energies for better fit have been discussed with nanoparticles (section 4.3) and with surface tension model in section 3.1 of **Paper IV**.

A fundamental guiding principle of the modelling work has been to keep the number of parameters not directly related to known bulk thermodynamics as low as possible. This has been done both to avoid overparametrised models with seemingly good fits but little predictive power and to keep the models easier to work with and results clearer to interpret.

The surface and interfacial energy models have required 1-2 geometric parameters for the excess energies. Same parameter values have been used for similar systems. The Donnan model requires an estimate of the bound aqueous volume, which could be tied to the measurable water retention value. The model results are not very sensitive to exact value chosen and (regarding pulp suspensions) in the work by the author, co-authors and other researches, quite similar values have been used. The models with reaction kinetics require literature-derived or fitted rate equation for each constrained linearly independent reaction. The benefit of applying the Constrained Free Energy method is naturally greatest here when the number of reactions proceeding to equilibrium is great and the multiphase chemistry of the system is complex, while the number of kinetic constraints required for modelling the time development for sufficient accuracy is small. Need for more complex handling of reaction kinetics will generally increase when studies are done over moderate temperatures (especially not in aqueous/liquid solutions) over and short time intervals as noted in section 4.6. For systems in a magnetic field, the magnetisation as a function of field strength had to be known or be fitted to the model.

Restrictions on the applicability of the present method include the assumption that the stoichiometric coefficients between species and components are constant when calculating the equilibrium for a specified set of conditions; especially, that they are not functions of system or phase composition. This applies for example to the molar surface or interfacial areas in the interfacial models. This is expected to

be less of a problem with the metallic or oxide systems discussed in **Papers II and IV** than for example aqueous solutions. The requirement for constant stoichiometric coefficients also makes it necessary that the possible dependency of the molar contributions to work coordinates from the work coefficients can be separated by factorization from any dependency from identity of the species themselves. These are requirements related to the software tools applied.

Additional assumptions are applied to keep the models structurally simple. As discussed in section 4.1, for the surface monolayer model the assumption of no interactions between the surface layer and the bulk is made, making the model surface layer formally equivalent to a proper phase. Thermodynamics of systems where this is not an applicable approximation are discussed in **Paper IV** with a more complex model where the similar assumption is then made only for the layer closest to the bulk in a multilayer model. Implicit assumption in the ion-exchange models presented is that the non-specific Donnan equilibrium concept is sufficient to describe the interactions between the bound and solute ions with acceptable accuracy. As noted in section 4.4, this is not necessarily always true even with pulp suspensions. Inclusion of specific interactions to the model via complexation would be straightforward in theory, but has not been applied by the author due to increased complexity of the parameterisation. Again, regarding reaction rate constrained systems the model construction in practice has started with the equilibrium system with reaction rate constraints and equations added only up to the level where sufficient accuracy compared to experimental results has been obtained. Considering the large uncertainties in the known reaction kinetic parameters, this approach of minimum kinetics is regarded justified (with the limitations mentioned earlier).

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Calculation of constrained equilibria by Gibbs energy minimization

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Abstract

The Gibbs energy minimization encompasses active use of the chemical potentials (partial molar Gibbs energies) of the constituents of the system. Usually, these appear at their equilibrium values as a result of the minimization calculation, the mass balance constraints being the necessary subsidiary conditions. Yet, there are several such physico-chemical circumstances where the system is also constrained by other factors, such as surface effects, potential fields or even by chemical reaction kinetics. In this paper a particular method is presented by which constrained chemical potentials can be applied in a multi-phase Gibbs energy minimization. The constrained potentials arise typically from work-related thermodynamic displacements in the system. When Gibbs energy minimization is performed by the Lagrange method, these constraints appear as additional Lagrangian multipliers. Examples of the constrained potential method are presented in terms of the electrochemical Donnan equilibria in aqueous systems containing semi-permeable interfaces, the phase formation in surface-energy controlled systems and in systems with affinities controlled by chemical reaction kinetics. The methods have been applied successfully in calculating distribution coefficients for metal ions together with pH-values in pulp suspensions, in the calculation of surface tension of alloys, and in thermochemical process modeling involving chemical reaction rates.

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1. Introduction

With the improving numerical capacity of present day computers, Gibbs energy minimization has gained increasing interest not only in the calculation of complex chemical equilibria and phase diagrams, but also in performing complicated process simulations. The advantage of the thermodynamic method is that it avails a common basis for complex chemical problems in multi-phase systems with various proportions and conditions. Both industrial processes and small scale laboratory systems can be calculated successfully with the Gibbs energy method.

However, the multi-phase Gibbs energy minimization technique has not been applicable to more complicated problems where the thermodynamic system is subjected to a displacement caused by a generalized work coefficient or when the chemical or phase change is constrained by slow reaction kinetics. Such problems are often encountered in practical materials science and in the simulation of processes, notably including such topics as membrane separated electrochemical equilibrium systems, complex surface energy equilibria and

finally time-dependent systems controlled with chemical reaction rates. A common feature of all these phenomena is that the total Gibbs energy is affected by an additional physical constraint, which is due to a work-related thermodynamic displacement, including the affinity of kinetically controlled chemical reactions.

In the conventional Gibbs energy minimization calculation, the system is subjected to the mass balance constraints which are deduced from the input amounts of the components of the equilibrium system. The Gibbs free energy minimum is often solved by using the Lagrange method of undetermined multipliers with the mass balances of the system components as the necessary subsidiary constraints. The chemical potentials of the constituents of the multi-component system can then be solved in terms of the elements of the mass conservation (stoichiometric) matrix and the Lagrange multipliers. As the elements of the matrix are dimensionless factors, the Lagrange multipliers represent chemical potentials of the system components. By extension of the matrix, one may introduce additional constraints for a desired set of constituents and thus take into account additional Gibbs energy terms due to the surface tension, electrochemical potential or affinity of a kinetically controlled reaction. In what follows, we present a

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Lagrangian method, which allows a number of such phenomena to be calculated with Gibbs energy minimization.

2. Theory

2.1. Overview of the Lagrangian method

The Gibbs energy of the multicomponent system is written in terms of the chemical potentials as follows

$$G = \sum_{\alpha} \sum_k n_k^{\alpha} \mu_k^{\alpha} \quad (1)$$

where $\mu_k^{\alpha} = \mu_k^{\alpha}(T, p, n_k^{\alpha})$ is the chemical potential of the species (k) in the respective phase α and n_k^{α} is its molar amount. The Gibbs energy is an extensive state variable and the chemical potential μ_k^{α} is the partial molar Gibbs energy of the constituent k .

For the Lagrangian method, the mass balance equations are needed as follows [1,2]:

$$\phi_j = b_j - \sum_{\alpha=1}^{\Psi} \sum_{k=1}^{N_{\alpha}} a_{kj}^{\alpha} n_k^{\alpha} = 0 \quad (j = 1, 2, \dots, l) \quad (2)$$

where b_j is the total input amount of a system component and a_{kj}^{α} refers to the stoichiometric number of component j in constituent k , in its respective phase α . The number of phases is denoted by Ψ , and N_{α} is used for the number of constituents in phase α . A system component is typically, but not necessarily, a chemical element. The total number of system components is l . The individual mass balances are denoted for brevity as ϕ_j . The Lagrangian function is then written in terms of the Gibbs energy and the mass balance conditions:

$$L = G - \sum_{j=1}^l \lambda_j \phi_j \quad (3)$$

where the λ_j s are the undetermined multipliers of the Lagrange method. The minimum condition of the Gibbs energy is the same as this condition for the Lagrangian function (L), and is received at constant temperature and pressure by finding the extremum points for the respective partial derivatives:

$$\left(\frac{\partial L}{\partial n_k} \right)_{i \neq k} = \mu_k - \sum_{j=1}^l a_{kj} \lambda_j = 0 \quad (k = 1, 2, \dots, N) \quad (4)$$

Conditions (2) and (4) together give a set of $N + l$ equations with an equal number of unknowns to be solved (N is the total number of constituents). The solution gives the molar amounts (n_k s) at equilibrium for the closed system when temperature and pressure are held constant. In addition, the undetermined multipliers (λ_j) become solved. By definition of (3), they connect the mass balances of each system component to the Gibbs energy. In fact, the solution of the undetermined multipliers produces each λ_j as representing the chemical potential of the respective system component j . To emphasize, we denote this potential by π_j and get, for the chemical potentials of any constituent k :

$$\mu_k = \sum_{j=1}^l a_{kj} \pi_j \quad (k = 1, 2, \dots, N) \quad (5)$$

Eq. (5) gives the chemical potential of any constituent k as a linear combination of the respective potentials of the system components [1]. The respective ($N \times l$) conservation matrix is

$$\mathbf{A} = \begin{pmatrix} a_{1,1}^{(1)} & \cdots & a_{1,l}^{(1)} \\ \vdots & \ddots & \vdots \\ a_{N_1,1}^{(1)} & \cdots & a_{N_1,l}^{(1)} \\ a_{N_1+1,1}^{(2)} & \cdots & a_{N_1+1,l}^{(2)} \\ \vdots & \ddots & \vdots \\ a_{N,1}^{(\Psi)} & \cdots & a_{N,l}^{(\Psi)} \end{pmatrix} \quad (6)$$

In the conventional CALPHAD methods, the system components represent stoichiometric building blocks of the constituents and the matrix elements a_{kj} are the respective stoichiometric coefficients. For example, the chemical potential of carbon dioxide (CO_2) in an equilibrium system with the elements carbon (C) and oxygen (O) as system components will be given in terms of their potentials. Carbon dioxide consists of one unit of carbon and two units of oxygen, and the chemical potential is accordingly $\mu_{\text{CO}_2} = \pi_{\text{C}} + 2\pi_{\text{O}}$. The condition is equivalent to the requirement that the affinity of all possible chemical reactions is zero at equilibrium.

The independent components of the system may be chosen to represent stoichiometric entities other than chemical elements. These include, for example, chemical substances, ions and electronic charge, which characteristically may occur as independent components of a phase constituent. The stoichiometric coefficients given in the transformed matrix must be consistent with the conservation of mass in the system, which is defined in terms of the total mass (m_{tot}) as $\sum_{j=1}^l b_j M_j = m_{\text{tot}}$. Here, M_j is the molecular mass of the system component j .

2.2. Setting additional constraints with the conservation matrix

The conservation matrix \mathbf{A} has a row for each species and a column for each independent conservation equation [1,3]. The conservation matrix is thus made up of the coefficients of the conservation equations valid in the system. As stated above, in chemical reactions, atoms of elements and electric charge are conserved. Sometimes, additional conservation equations are required, for example to denote conserved molecular groups [4]. The new constraint appears as an additional column in the conservation matrix:

$$\mathbf{A} = \begin{pmatrix} a_{1,1}^{(1)} & \cdots & a_{1,l}^{(1)} & a_{1,l+1}^{(1)} \\ \vdots & \ddots & \vdots & \vdots \\ a_{N_1,1}^{(1)} & \cdots & a_{N_1,l}^{(1)} & a_{N_1,l+1}^{(1)} \\ a_{N_1+1,1}^{(2)} & \cdots & a_{N_1+1,l}^{(2)} & a_{N_1+1,l+1}^{(2)} \\ \vdots & \ddots & \vdots & \vdots \\ a_{N,1}^{(\Psi)} & \cdots & a_{N,l}^{(\Psi)} & a_{N,l+1}^{(\Psi)} \end{pmatrix} \quad (7)$$

Here the matrix elements for the phase constituents remain equivalent to those in Eq. (6), but the additional column with

subscript $l + 1$ represents the new conservation equation. Thus, the element $a_{k,l+1}^\alpha = 0$ for all those constituents k which are not affected by the additional constraint, whereas $a_{k,l+1}^\alpha$ is *not zero* for those constituents which are affected by the said constraint. Thus, for example, the number of aromatic groups to be conserved in each aromatic compound can be attached to the Gibbs energy calculation by the new pseudoelement [4]. It is obvious that the mass balance of the total system is not affected if the molecular mass of the pseudoelement M_{l+1} is chosen to be zero.

The additional constraint affects the chemical potential of the phase constituents through Eq. (5). As the elements of the matrix are dimensionless factors, the Lagrangian multipliers represent additive contributions to the chemical potentials of the constituents. Applying this property, one may introduce additional conditions for a desired set of constituents, thus generalizing the conservation matrix to applicable physical constraints of the system. Such constraints may be set for the electroneutrality condition of phases [5], or for an affinity related metastable or kinetically conserved species [6,7]. Further, a constraint set for the surface area of the system is similarly linked to the surface energy of the system and it can be used to predict the surface tension and surface compositions of multi-component mixtures [8]. In what follows, three simple examples are presented to detail the use of the additional constraint when calculating surface tensions of multi-component alloys, to determine Donnan equilibria in membrane-separated multi-phase aqueous systems, and to conserve the affinity of a kinetically conserved chemical reaction in a multi-phase system.

3. Calculation examples

3.1. Computation of surface tension

Surface energy can appear as an additional factor in the Gibbs energy function of a multi-component system. If the (flat) surface layer is assumed to be one monolayer thick, the total Gibbs energy of the system is:

$$G = \sum_{k=1}^{N_b} \mu_k^b n_k^b + \sum_{k=1}^{N_s} \mu_k^s n_k^s + \sigma \sum_{k=1}^{N_s} A_k n_k^s \quad (8)$$

Here superscripts and subscripts b and s have been used for the bulk and surface phases, respectively. As the same species can be assumed to be present both in the bulk and in the surface, with N being the total number of species, we have $N_b = N_s = N/2$ and the same subscript denotes the same chemical species in both the bulk and the surface phase. The surface tension is a function of temperature and composition, $\sigma = \sigma(T, x_k)$. Each constituent of the surface phase occupies a characteristic molar surface area A_k . The total surface area is assumed to be constant at equilibrium:

$$\sum_{k=1}^N A_k n_k^s = A \quad (9)$$

Considering the two phases, Eq. (9) may also be written as

$$A/A_0 - \sum_{\alpha} \sum_{k=1}^N (A_k^\alpha/A_0) n_k^\alpha = 0 \quad (10)$$

where the molar surface for any species in the bulk phase is zero. The area terms are divided by a normalization constant A_0 with dimensions of m^2/mol . This equation then shows the constraint of constant surface area, in analogy to the mass balance conditions of Eq. (2). It is then mathematically possible to consider Eq. (10) as an additional constraint of a multi-component system, where the surface layer is introduced as a separate phase and the surface area as an additional system component [6].

Using (8) and (3) and by applying (2) and (10), the Lagrangian function of the multi-component surface system becomes

$$L = \sum_{k=1}^{N_b} \mu_k^b n_k^b + \sum_{k=1}^{N_s} \mu_k^s n_k^s + \sigma \sum_{k=1}^{N_s} A_k n_k^s - \sum_{j=1}^{l+1} \lambda_j \left(b_j - \left(\sum_k a_{kj}^b n_k^b + \sum_k a_{kj}^s n_k^s \right) \right) \quad (11)$$

Here, summation of the constraints extend over all system components, that is, $j = 1, 2, \dots, l, l + 1$, where the last constraint is the one deduced from the surface area, with $b_{l+1} = A/A_0$, and $a_{k,l+1}^s = A_k/A_0$. From Eqs. (4) and (11), the partial derivative conditions become:

$$\left(\frac{\partial L}{\partial n_k^b} \right)_{i \neq k} = \mu_k^b - \sum_{j=1}^l a_{kj}^b \lambda_j = 0 \quad (12)$$

$$\left(\frac{\partial L}{\partial n_k^s} \right)_{i \neq k} = \mu_k^s + A_k \sigma - \sum_{j=1}^{l+1} a_{kj}^s \lambda_j = 0 \quad (13)$$

At equilibrium, the chemical potential of each species is independent of phase, that is, $\mu_k^b = \mu_k^s = \mu_k$. From Eqs. (12) and (13), it follows that the surface tension of the mixture is obtained as the additional Lagrange multiplier:

$$\sigma \cdot A_0 = \pi_{l+1} \quad (14)$$

The numerical value of the constant A_0 can be chosen arbitrarily, but for practical calculation reasons it can be advantageous if the ratio A_k/A_0 is a value close to unity, being of the same order of magnitude as the stoichiometric coefficients appearing in the conservation matrix.

To perform the calculations with a Gibbs energy minimizing program, such as ChemApp [9], the input data must be arranged in terms of the standard state and excess Gibbs energy data of chemical potentials of the system constituents. It is sufficient here to state that the chemical potentials of species k in the bulk and surface phases can be written in terms of the respective activities as follows:

$$\mu_k^b = \mu_k^0 + RT \ln a_k^b \quad (15)$$

$$\mu_k^s = \mu_k^{0,s} + RT \ln a_k^s - A_k \sigma \quad (16)$$

where the superscript 0 refers to the standard state, and a_k^b and a_k^s are the activities of the constituent k in the bulk phase and

Table 1
Stoichiometric matrix for the Fe–FeO system

		Fe	FeO	Area
Bulk	Fe	1	0	0
	FeO	0	1	0
Surface	Fe	1	0	3.7187
	FeO	0	1	5.8782

The molar surface areas for Fe and FeO at 1973 K are 37 187 m²/mol and 58 782 m²/mol, respectively [10].

surface phases, respectively. By applying Eqs. (15) and (16) for the case of a pure one-component system, a relationship between the standard states of the bulk and surface phase can be derived:

$$\mu_k^{0,s} = \mu_k^0 + A_k \sigma_k \quad (17)$$

Eqs. (15)–(17) then indicate that the necessary input for a Gibbsian surface energy model must include not only standard state and activity (excess Gibbs energy) data for the constituents of the bulk and surface phases, but also the data for surface tensions of the pure substances (σ_k) as well as their molar surface areas (A_k). The numerical calculation technique is described in detail elsewhere [6]. In Table 1, the extended matrix of an FeO/Fe binary system is given. Respective calculation results at 1970 K are presented in Fig. 1 (the mole fraction of FeO in the surface phase vs. that in the bulk (left) and surface tension of the mixture (right)). The molar surface area, pure substance surface tension values and Gibbs excess energy are taken from Tanaka and Hara [10]. The calculated results for the FeO/Fe binary also agree with those presented in [10].

The obvious advantage of the Gibbsian method is in the direct calculation of surface tensions in multi-component mixtures. An example of a simple ternary system was given earlier in [6].

3.2. Ion exchange equilibria in aqueous multi-phase systems

When two aqueous solutions at the same temperature (and pressure) are separated with a membrane that is permeable to some ions but not to others nor to the solvent, a distribution known as Donnan equilibrium. Donnan equilibrium is formed in the system of the two compartments [11,12]. The system consists of two aqueous phases with water as the solvent and mobile and immobile ions as solute species. In a multi-phase system, gas as well as precipitating solids may be present. Both compartments containing the aqueous solutions remain electrically neutral. The essential feature of the Donnan equilibrium is that, due to the macroscopic charge balance in the separate compartments, immobility of some of the ions will cause an uneven distribution for the mobile ions too. This distribution strongly depends on the acidity (pH) of the system in such cases where dissociating molecules in one of the compartments may release mobile hydrogen ions, while their respective (large or bound) counter anions remain immobile due to the separating membrane. By applying the electroneutrality condition together with other physical conditions of the membrane system, the constrained potential method allows the

calculation of the multi-phase Donnan equilibrium with Gibbs energy minimization. Thus, the distribution of ions in the two compartments, together with formation of precipitating phases for example, can be calculated.

In Table 2 an example of the stoichiometric matrix for a two-compartment Donnan system is presented. For the two solution phases present, notations ' and '' have been used. The constancy of the amount of water in the second compartment is ascertained by setting the respective matrix element to unity. As there is no molecular mass assigned for this system component, the mass for the constituent H₂O in the second solution volume (solvent'') is obtained from the respective system components O (for oxygen) and H (for hydrogen). The electronic charge of aqueous ions is introduced to both aqueous phases in terms of the negative charge numbers, and an additional electroneutrality condition has been set for the secondary aqueous phase, denoted in the matrix as q'' . The immobile anion (Anion_a) has been positioned as a constituent for the secondary aqueous phase''. For clarity, just values different from zero are shown.

With the given matrix conditions, by using Eq. (5) for the chemical potentials of charged species at equilibrium, we have

$$\begin{aligned} \mu_k'' &= \mu_k^{0''} + RT \ln a_k'' \\ &= \mu_k' + z_k \pi_{q''} = \mu_k^{0'} + RT \ln a_k' + z_k \pi_{q''} \end{aligned} \quad (18)$$

where the chemical potentials of the primary and secondary aqueous phases have been written in terms of their respective activities (a_k' and a_k''). The additional term ($z_k \pi_{q''}$) deduced from Eq. (5) is due to the supplementary electroneutrality constraint set for the secondary aqueous phase. Eq. (18) is comparable to the general form of electrochemical equilibrium of charged species [11]:

$$\mu_k^{0''} + RT \ln a_k'' = \mu_k^{0'} + RT \ln a_k' + z_k F \Delta \varphi \quad (19)$$

where F is the Faraday constant and $\Delta \varphi$ is the electrical potential difference between the primary and secondary aqueous phases. It follows that the solution of the Gibbsian problem with the additional electroneutrality constraint gives this potential difference as the Lagrange multiplier $\pi_{q''}$:

$$F \Delta \varphi = \pi_{q''} \quad (20)$$

Similarly, from Eq. (5) one may deduce the chemical potential of water in the two aqueous phases in terms of the Lagrangian multipliers. Obviously, these two chemical potentials are not equal, but differ by the Lagrange multiplier $\pi_{\text{solvent}''}$. This is because the Gibbs energy model does not include the effect of the contractive forces of the membrane system, which prevent the transport of water from the primary compartment to the secondary volume. Yet the model can be applied to determine the activity difference of the two aqueous phases and thus to define the expected pressure difference in various membrane systems [12,13]. Assuming incompressibility, i.e. that the partial molar volume of water is constant in the moderate pressure range of the membrane systems, we have

$$-\pi_{\text{solvent}''} = (p'' - p') V_{\text{solvent}}^m = RT \ln \left(\frac{a'_{\text{solvent}}}{a''_{\text{solvent}}} \right) \quad (21)$$

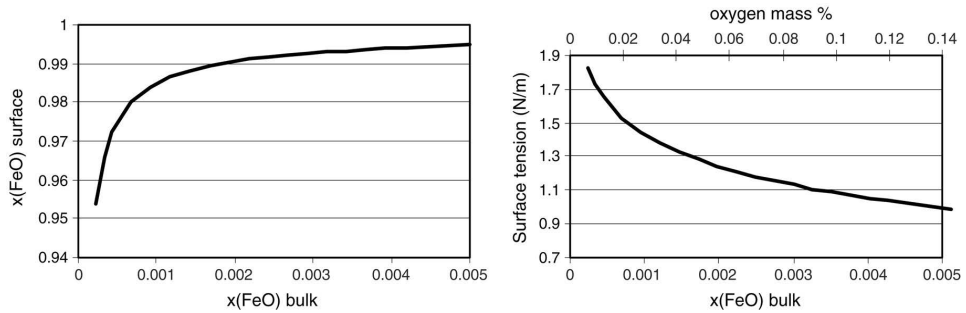


Fig. 1. Surface composition and surface tension as a function of bulk composition in a Fe-FeO mixture at 1970 K.

Table 2

Example of the stoichiometric matrix for a Donnan equilibrium system with two membrane-separated compartments containing ionic solutions

	O	H	Na	C	Ca	Solvent ^m	Anion _a	e ⁻	q ^m
1. Solution volume	H ₂ O	1	2						
	H ⁺		1					-1	
	OH ⁻	1	1					1	
	Na ⁺			1				-1	
	CO ₂	2			1				
	HCO ₃ ⁻	3	1		1			1	
	CO ₃ ²⁻	3			1			2	
Ca ²⁺					1		-2		
2. Solution volume	H ₂ O	1	2			1			
	H ⁺		1					-1	1
	OH ⁻	1	1					1	-1
	Na ⁺			1				-1	1
	CO ₂	2			1				
	HCO ₃ ⁻	3	1		1			1	-1
	CO ₃ ²⁻	3			1			2	-2
Ca ²⁺					1		-2	2	
Anion _a							1	1	-1
CaCO ₃	CaCO ₃	3		1	1				

The partial molar volume of the solvent (water) is denoted by V_{solvent}^m . The constraining factor π_{solvent^m} emerges as the potential difference due to the different activities of solvent water in the two different compartments. Thus, the pressure drop across the membrane ($p'' - p'$) can be calculated on the basis of either the activities of the solvent in the two volumes or the potential π_{solvent^m} .

An example calculation of the above described Donnan equilibrium system is a pulp fiber suspension where the fibers absorb both water and solute ions. Fibers contain carboxylic acid groups of hemicellulose and phenolic groups of the lignines. The anions of these groups are generally bound to the fiber, but the protons of these acidic functional groups can be dissolved and transferred through the fiber to an external bulk solution. Charge neutrality prevails both within the fiber structure and in the external solution, and thus the dissociation of the functional groups may lead to ion exchange between the cell structure of the fiber and the bulk solution. The stoichiometric Donnan equilibrium theory has been used already by Neale (1929) and Farrar and Neale (1952) to characterize electrolyte interactions with cellulose

fibers [14,15]. In 1996 Towers and Scallan published their Donnan model, which could be used to calculate the ionic distribution of mixtures of mono- and divalent cations and monovalent anions in pulp suspensions [16]. The solution model was further extended by Räsänen et al. to include the presence of multivalent anions as well as the formation of hydroxyl complexes and ligands [17]. The multi-phase Gibbs energy model of the fiber suspension, introduced by Koukkari, Pajarre and Pakarinen (2002), enables the calculation of the solution equilibria (including the distribution of the charged species) while precipitating solids and the dissolution of gaseous constituents are also taken into account [5].

The Gibbs energy model of the fiber suspension is essentially based on the electrochemical theory described above, the fibers representing the secondary aqueous phase containing both mobile and immobile ions. The basic input data of the multi-phase Donnan model is similar to any characteristic aqueous solution model, requiring the incoming amounts of substances and equilibrium temperature and pressure. The water content of pulp fibers is based on experimental water retention values and given as additional model input.

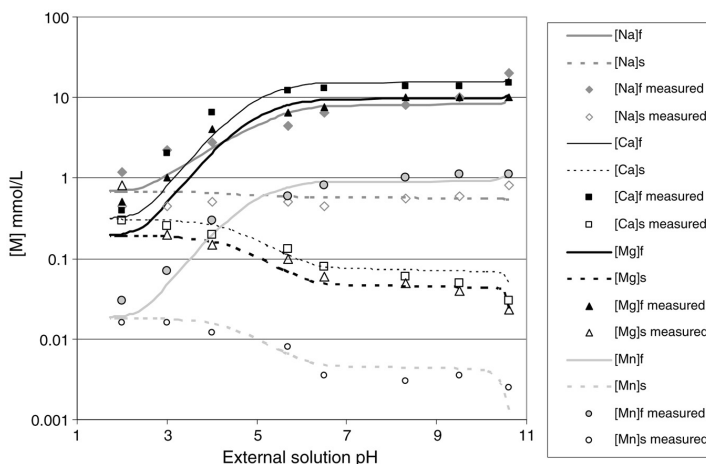


Fig. 2. Measured and modeled concentrations of Na, Ca, Mg, and Mn ions bound by the fibers (f) and in the surrounding solution (s). Experimental results are taken from Ref. [16]. Low concentrations in the surrounding solutions at pH values above 10 are due to precipitation of hydroxides.

Furthermore, to characterize the immobile anionic species in the fiber phase, their amounts and Gibbs energy data must be specified. Unlike the mobile ions and neutral solutes, the bound acidic groups are included only in the fiber phase. As no reactions that would change the total amount of these groups is assumed to take place, the chemical potential of the undissociated forms of these groups can be set to zero, while the chemical potential of the anionic forms can be calculated based on the thermodynamic relation

$$\Delta G_i = -RT \ln K_i \quad (22)$$

where the acidic dissociation constants (K_i) and the corresponding molar amounts are determined experimentally by potentiometric or conductometric titration. This data is sufficient to perform the equilibrium calculations, and the chemical structure of the acids needs not to be known. It has been found quite customarily that both the K_i -values and amount of charge are characteristic to a given form of cellulose or pulp with a known treatment history. Consequently, this data appears comparable with standard Gibbs energy data of known substances [18,19]. In Fig. 2, typical ionic distributions and phase formation in terms of changing pH in various pulp suspensions have been calculated from thermodynamic equilibrium data and compared with the experimental results of Towers and Scallan [16]. The input amounts (Table 3) are from the same source. At low pH of the external solution, the acidic groups within the fiber phase remain undissociated, their anionic charge is small and the cations, such as Ca^{2+} , Mg^{2+} , Na^+ and K^+ typically, are evenly distributed between the fiber and the external solution. With decreasing acidity, the pH in the external solution is raised and the acid groups in the fiber are dissociated. This feature triggers the ion exchange between the two aqueous phases, the protons are transported to the external solution and the corresponding charge in the fiber phase becomes compensated with the metal cations. At high enough pH, precipitating carbonates and hydroxides are formed

Table 3
Input amounts used for pulp suspension model calculations

H_2O	89.12 kg
H_2O_f	1.4 kg
Bound acid (pK = 4)	0.085 mol
$\text{Ca}(\text{OH})_2$	0.0282 mol
$\text{Mg}(\text{OH})_2$	0.0174 mol
$\text{Mn}(\text{OH})_2$	0.00166 mol
NaOH	0.0615 mol
HCl	varied for pH control

H_2O_f denotes the water inside the fibers, H_2O the amount of the rest of the aqueous solution (corresponding to the 1. solution volume in Table 2).

as solid phases. The practical perspective of the multi-phase equilibria in pulp suspensions lies in the improved control of pH buffering of paper machines and in metal management of pulp bleaching solutions [18].

3.3. Reaction rate controlled systems

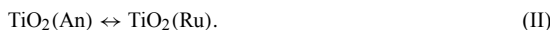
The conventional method in studies of reaction mechanisms is to distinguish between the fast (equilibrium) reactions and the slow (rate controlled) reactions. This has been a viable approach when applying the stoichiometric method with explicit reaction equations, with the equilibrium constant data easily available for the reactions between thermodynamically well-defined substances and the reaction rate constants usually deduced from experiment. A similar technique, when applied with the Gibbsian multi-phase method, would avail a flexible route to calculate reaction rate controlled systems in terms of their thermochemical properties. An early approach in combining reaction rates with multi-phase calculations was the extension of the stoichiometric matrix of a Gibbsian multi-component system by the inert image component [20]. The image method was proven successful in many cases where the driving force of a single reaction is sufficient for reaching 100% conversion from reactants to products. The introduction

Table 4
Thermodynamic and kinetic data for TiO(OH)₂ calcination reactions

Reaction	$\Delta H(1000^\circ\text{C})$ (kJ mol ⁻¹)	$\Delta G(1000^\circ\text{C})$ (kJ mol ⁻¹)	Reaction rate equation	E_a (kJ mol ⁻¹)	A (h ⁻¹)
TiO(OH) ₂ ↔ TiO ₂ (An) + H ₂ O ↑	43.5	-83.6	-	-	-
TiO ₂ (An) ↔ TiO ₂ (Ru)	-6.6	-5.9	$\xi = 1 - (1 - kt)^3$	441.99	1.80E+17

of conservable groups as additional system components to the stoichiometric matrix in the Lagrangian method of Gibbs energy minimization was originally used by Alberty [4] to preserve aromatic rings in a benzene flame model. With a further matrix extension, this technique was shown to be applicable to kinetically conserved species [6] and could be applied to several related problems [7]. In what follows, the method is shown to include the characteristics of the potential constraint technique, in the sense that it conserves the (non-zero) affinity of the rate controlled reactions step as the additional Lagrange multiplier.

As a simple example, calcination of titanium oxyhydrate (TiO(OH)₂) slurry is considered, referring to the formation of titanium dioxide powder in a calciner. The feed consists of (wet) titanium oxyhydrate slurry, the chemical composition being approximated as TiO(OH)₂ * nH₂O. During calcination, the slurry is dried and finally the hydrate decomposes, leaving the product titanium dioxide in the bed. From the oxyhydrate, at relatively low temperatures (ca. 200 °C) the crystalline form anatase, TiO₂(An), is formed first, and only in the high temperature zone of the furnace end, the thermodynamically stable rutile form TiO₂(Ru) appears as the desired product. The reactions are as follows:



Rutile is the thermodynamically more stable form of these two titanium dioxide species (Table 4). Thus a thermodynamic calculation, such as Gibbs free energy minimization, would at all temperatures result in rutile and water. This would lead to a 100% rutilisation of the titania already at temperatures where the Ti-oxyhydrate is all but calcined by reaction (I). Yet it is well known from practical experience that the rutilisation reaction (II) is slow and only takes place with a finite rate at elevated temperatures (above 850 °C). The simulation of the calcination reactions must take this feature into account [21].

In Table 5, the stoichiometry of the calcination system is presented. The three first columns with system components oxygen (O), hydrogen (H) and titanium (Ti) show the elemental abundance-constrained stoichiometry of the equilibrium system. The additional column (R) represents the additional kinetic constraint, affecting the conservation of rutile content in each Gibbsian calculation sequence.

The formation of the Lagrangian function from Eq. (3) by using the equilibrium matrix is straightforward, as well as the solution of the (zero) affinities for the stoichiometric reactions (I) and (II) from the equilibrium condition in Eq. (4). (For simplicity, the Ti-oxyhydrate has been written without the bound water molecules.) When the additional constraint is

Table 5
Stoichiometric matrix for TiO(OH)₂ calcination with kinetically constrained rutilisation

Index (<i>k</i>)	Species	O	H	Ti	R
1	O ₂ -gas	2	0	0	0
2	H ₂ O-gas	1	2	0	0
3	TiO(OH) ₂	3	2	1	0
4	TiO ₂ (An)	2	0	1	0
5	TiO ₂ (Ru)	2	0	1	1

Substance index (*k*) is shown in the left-hand column.

taken into account, the Lagrangian function becomes:

$$L(n) = \sum_{k=1}^2 n_k \left(\mu_k^0 + \ln \frac{n_k}{n_1 + n_2} \right) + \sum_{k=3}^{N=5} n_k \mu_k - \sum_{j=1}^{l^*=4} \pi_j \left(b_j - \sum_{k=1}^{N=5} a_{kj} n_k \right) \quad (23)$$

where the first term on the right is the chemical potentials of the two gaseous species in terms of their partial pressures, the second is formed from the three condensed species, and the last term is deduced from the mass balances (a single ascending value has been used for the constituent index *k*). The total number of mass balance constraints is $l^* = 4$, including the additional zero-mass ‘rutility’ of the formed titanium dioxide. From (4) and (23), the following conditions are obtained:

$$\mu_4 + \left(\mu_2^0 + \ln \frac{n_2}{n_1 + n_2} \right) - \mu_3 = 0 \quad (24)$$

$$\mu_4 - \mu_5 = \pi_4. \quad (25)$$

Eq. (24) is the equilibrium condition for the fast reaction (I) which forms anatase and water from the oxyhydrate at elevated temperatures. Condition (25) gives the additional Lagrange multiplier as the affinity of reaction (II) and is dependent on the value of the constraint b_4 . In a sequential computation, the kinetic constraint is defined as a function of the extent of such a given reaction [$b_R = f(\xi_R)$] and is set as the input of the Gibbsian calculation. The reaction rate parameters of the rutilisation example are given in Table 4, where the reaction kinetics are deduced from the experimental study of McKenzie [22] (model of contracting spheres). The integrated reaction rate is obtained as a dimensionless ‘degree of rutilisation’, which equals the extent of reaction (II). At each sequence of calculation, the constraint $b_4 = \xi \times$ (number of TiO(OH)₂ moles in the input). As ξ is dimensionless, the unit of b_R is moles.

With the procedure described above, the kinetically constrained Gibbs energy calculation can be performed in a sequential procedure, provided that there is a means to define the value of the additional system component (b_R) as

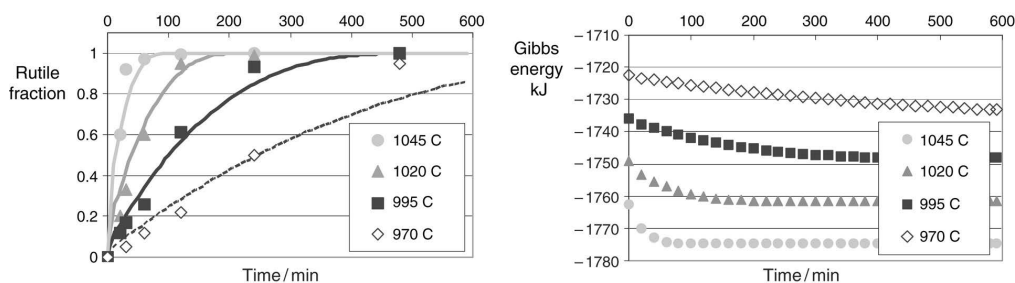


Fig. 3. Measured points and model curves for the rutile fractions are presented at four temperatures (left). The respective Gibbs energies of the system at the same temperatures are calculated as monotonically descending curves (right).

program input. For the ChemApp program, which applies the Lagrange method and is hence suitable for the calculation of the constrained problems, we have developed a more indirect procedure, which allows for the control of a kinetically constrained reaction either in its forward or reverse mode [7,9,23].

The thermodynamic (Gibbs energy) data for the species are from standard sources [26], yet the estimates for the standard enthalpy, entropy and heat capacity of $\text{TiO}(\text{OH})_2$ were used as in [24]. The kinetic calculation is then performed in 60 steps with 10 min intervals to cover the experimental data of McKenzie, ranging up to 10 h at 995 °C. For each step, the Gibbs energy of the system is minimized and, as a result, the composition and the Gibbs energy of the system are calculated. The calculation method has been described in more detail in [23]. The results are shown in Fig. 3. The rutile fraction rises from zero to one according to the given reaction rate. It is worth noticing that, with the Gibbsian approach, the thermodynamic properties of the system also become calculated for each sequential step. The Gibbs energy of the reactive system is a monotonically descending curve at any constant temperature. As the anatase-rutile transformation is an exothermic reaction, it is of practical interest to also follow the enthalpy change of the system during the gradual process.

Additional constraints may be set to include a more complex reaction mechanism. Each kinetically conserved species will then be annexed to a rate constraint [23]. It seems viable that a systematic approach, which embeds the necessary reaction rates as source terms to the multi-phase Gibbsian calculation, can be developed on the basis of the additional constraints. It is emphasized, however, that the method provides a technique to connect the experimentally found reaction rates with the thermodynamic calculation, but includes no attempt to predict reaction rates from thermochemical theory.

4. Summary

The method of constrained potentials provides an extension of the applicability of the Gibbs energy minimization method to a variety of problems encountered in chemical thermodynamics. A common feature of all these problems is that there is a conservation factor additional to that of mass balance. Above, we have presented three examples, where

Table 6

Potential constraints for surface energy, electro-chemical and reaction rate systems

System	Constraint	Potential equation
Surface	$\sum_k A_k n_k^s = A$	$\sigma \cdot A_0 = \pi_{\text{surface}}$
Electro-chemical	$\sum_{k=1}^{N_\alpha} z_k n_k = 0$	$F\varphi_\alpha = \pi_{q-\alpha}$
Kinetic	$\sum_k \nu_{kr} n_k = b_r$	$\sum_{\text{Reactants}} \nu_{kr} \mu_{kr} - \sum_{\text{Products}} \nu_{kr} \mu_{kr} = \pi_R$

the additional conservation clause follows from surface area, electroneutrality or due to reaction rate. The respective Gibbs energy factor is then surface energy, electrochemical potential and affinity of the kinetically constrained reaction. This potential becomes solved during the Gibbs energy minimization as the additional Lagrange multiplier. A summary of the three examples with the additional constraints and the respective potential factors is given in Table 6.

For the equilibrium systems in Table 6, i.e. the surface energy and electrochemical systems, the equations relating the Lagrange multiplier and the respective physical quantity seem to be unambiguous in the form presented. For those systems, generally one single constraint is necessary. As for systems constrained by reaction rate, the equation presented in Table 6 is valid for a single stoichiometric reaction, with the constraint set for one of the reaction products as was given in the example of anatase-rutile transformation. When considering a mechanism with more than one linearly independent rate controlled reaction, an equal number of constraints needs to be defined into the Gibbsian system, and the respective relation between the affinities of these reactions and the constrained potentials (π_r) in terms of their stoichiometric coefficients is then applicable [23].

The method of constrained potentials avails the possibility for quantitative Gibbs energy calculations of several new phenomena with a wide scope of practical applications. From the examples presented above, the surface tension of metals and alloys, including that of steel, can be deduced in various conditions. As the surface energy becomes more dominant for material properties with decreasing particle/grain size, an interesting application is the phase behavior and properties of nano-size particles [25]. As for electrochemistry, the approach of constrained potentials has enabled the pH-dependent solubility and ion exchange models for pulp

suspensions and other membrane separated systems (e.g. [18]). One may expect similar applications in related electrochemical problems. The constraining of reaction rate-dependent affinities in the Gibbsian calculation extends the applicability of the thermodynamic method to process simulations in systems where it is essential to follow both chemical and energy changes and their interdependence. Finally, as there are many analogous phenomena in chemical thermodynamics where an additional displacement factor affects the chemical potential of one or several species, we expect that the method presented will also find applications other than those mentioned in this text.

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Computing surface tensions of binary and ternary alloy systems with the Gibbsian method

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Abstract

The surface tension in metallic alloy systems is modelled by applying a direct Gibbs energy minimisation technique to the surface monolayer model. The model results are compared with previously published experimental values for the Bi–Sn system as well as surface tension values determined by the authors using the sessile drop method for the ternary Ag–Au–Cu system.

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Keywords: Surface tension; Gibbs energy minimisation; Metal alloys

1. Introduction

Information about the surface tension of metal alloy systems is essential for understanding and prediction of things such as wettability, crystal growth or phase properties of nanoscale particles. A commonly used assumption is that the surface can be modelled as a single monolayer. The purpose of this work is to show how the monolayer model can be handled by normal thermodynamic equilibrium programs based on the minimisation of the total Gibbs energy of the system. The model results are compared with experimental data in two example cases.

2. Experimental

Experimental surface tension values for the Ag–Au–Cu system were determined by the sessile drop method at 1381 K. The shape of metal alloy drops of about 6–8 mm in equatorial diameter and 4–6 mm in height was determined using a CCD camera and image analysis software and the drop shape was

used to calculate the surface tension of the alloy. A detailed description of the experimental procedure can be found in Ref. [1].

3. Theory

3.1. Basic thermodynamic relations

If a system containing a surface is considered as being comprised of two parts (phases), a surface layer (*s*) and an isotropic bulk (*b*), the total Gibbs energy of the system can be written as

$$G = \sum_i n_i^b \mu_i + A\sigma = \sum_i n_i^b \mu_i + \sum_i n_i^s \mu_i + A\sigma \quad (1)$$

where n_i is the molar amount and μ_i the chemical potential of species *i*, σ the surface tension in the system and *A* the surface area. If the surface phase is considered to be of a monolayer thickness, Eq. (1) can be rewritten in a form

$$G = \sum_i n_i^b \mu_i + \sum_i n_i^s (\mu_i + A_i \sigma) \quad (2)$$

where A_i is the molar surface area of the species *i*. The chemical potential of species *i* in the bulk phase can be written as

$$\mu_i = \mu_i^0 + RT \ln a_i^b \quad (3)$$

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Table 1
Presentation in a matrix form of stoichiometries in a system with a bulk phase and a surface phase, N species and M components

		Component (1)	Component (2)	...	Component (M)	Area
Bulk	Species (1)	v_{11}	v_{12}	...	v_{1M}	0
	Species (2)	v_{21}	v_{22}	...	v_{2M}	0
	⋮	⋮	⋮	⋮	⋮	⋮
	Species (N)	v_{N1}	v_{N2}	...	v_{NM}	0
Surface	Species (1)	v_{11}	v_{12}	...	v_{1M}	A_1/A_0
	Species (2)	v_{21}	v_{22}	...	v_{2M}	A_2/A_0
	⋮	⋮	⋮	⋮	⋮	⋮
	Species (N)	v_{N1}	v_{N2}	...	v_{NM}	A_N/A_0

and in the surface phase as

$$\mu_i = \mu_i^{0,s} + RT \ln a_i^s - A_i \sigma. \quad (4)$$

By applying Eqs. (3) and (4) for the case of a pure one-component system, a relationship between the standard states of the bulk and surface phase can be derived:

$$\mu_i^{0,s} = \mu_i^0 + A_i \sigma_i. \quad (5)$$

By combining Eqs. (1), (3) and (4), the total Gibbs energy of the system can be given in a simple form that does not explicitly include the surface tension term:

$$G = \sum_i n_i^b (\mu_i^0 + RT \ln a_i^b) + \sum_i n_i^s (\mu_i^{0,s} + RT \ln a_i^s) \quad (6)$$

while from Eqs. (3)–(5) one obtains

$$\begin{aligned} \mu_i^0 + A_i \sigma_i + RT \ln a_i^s - A_i \sigma &= \mu_i^0 + RT \ln a_i^b \\ \Rightarrow \sigma &= \sigma_i + \frac{RT}{A_i} \ln \frac{a_i^s}{a_i^b} \end{aligned} \quad (7)$$

an equation first derived by Butler [2], and used extensively in calculating surface tension in various mixtures, including metal alloy systems [3].

3.2. Use of Gibbs energy minimiser for surface equilibria calculations

When a Gibbs energy minimiser is used to solve chemical equilibrium states, the total Gibbs energy is usually calculated as

$$G = \sum_{\alpha} \sum_i n_i^{\alpha} \mu_i \quad (\text{over all phases } (\alpha) \text{ and species } (i) \text{ present in the system}) \quad (8)$$

where the chemical potentials of the species are calculated from supplied thermodynamic data using an equation of the type or equivalent to

$$\mu_i^{\alpha} = \mu_i^{0,\alpha}(T, p) + RT \ln x_i^{\alpha} \gamma_i^{\alpha}. \quad (9)$$

Comparing Eqs. (2), (4) and (9), one can see that the chemical potential for a species in the surface phase as calculated by a Gibbs energy minimiser would really be the total molar Gibbs energy of the surface species, marked here with μ_i^* :

$$\mu_i^* \equiv \mu_i + A_i \sigma. \quad (10)$$

For a traditional chemical equilibrium calculation the mass balance relations restricting the possible states can be given in the form

$$\sum_{\alpha} \sum_i v_{ik} n_i^{\alpha} - b_k = 0 \quad (\text{for all components } k) \quad (11)$$

where b_k is the total molar amount of component k and v_{ik} the stoichiometric coefficient between species i and component k . The condition of constant total surface area can be stated in a similar form as

$$\sum_i A_i n_i^s - A = 0 \quad (12)$$

or alternatively as

$$\sum_{\alpha} \sum_i A_i^{\alpha} n_i^{\alpha} - A = 0 \quad (13)$$

where the molar surface for any species in any non-surface phase α is zero. A is the total surface area of the system. As the constant surface area condition (Eq. (13)) is of the same form as the traditional mass balances (Eq. (11)), it can for the mathematical handling of the system be combined with them by considering the surface area as a new component in the system. In the Table 1 this is presented in a matrix form; the species in the system are presented as rows and the conserved components as columns.

In Table 1 A_0 is a normalisation constant with dimensions of m^2/mol . The numerical value of A_0 is in principle arbitrary, but for the best numerical performance of Gibbs energy minimisers it is generally best to choose the value so that the resulting A_i/A_0 values are fairly near to unity.

In a chemical equilibrium state, in addition to species and phases, chemical potentials can also be defined for the different components in the system [4]. The chemical potential of individual species are related to the chemical potentials of the components by Eq. (14)

$$\mu_i = \sum_k v_{ik} \pi_k \quad (14)$$

where π_k is the chemical potential of the component k , and v_{ik} the stoichiometric coefficient between species i and component k .

Table 2

Required data for calculations in Bi–Sn binary system from Refs. [4,5]

V_{Bi} (m ³ /mol) = 0.0000208 * (1 + 0.000117 * (T/K - 544)) [5]
V_{Sn} (m ³ /mol) = 0.000017 * (1 + 0.00087 * (T/K - 505)) [5]
σ_{Bi} (N/m) = 0.378 - 0.00007 * (T/K - 544) [5]
σ_{Sn} (N/m) = 0.56 - 0.00009 * (T/K - 544) [5]
G^{Excess} (J/mol) = $x_{\text{Bi}}x_{\text{Sn}}L$ [6]
L (J/mol) = 490 + 0.97T + (x _{Bi} - x _{Sn})(-30 - 0.235T)

Applied to the surface system, Eq. (14) can be stated for a bulk species as

$$\mu_i = \sum_{k=1}^{M+1} v_{ik}\pi_k = \sum_{k=1}^M v_{ik}\pi_k \quad (15)$$

and for the surface species as

$$\mu_i^* = \sum_{k=1}^{M+1} v_{ik}\pi_k = \sum_{k=1}^M v_{ik}\pi_k + \frac{A_i}{A_0}\pi_{\text{area}} \quad (16)$$

where π_{area} is the chemical potential of the new component defined to fix the total surface area of the system.

Finally, from Eqs. (15), (10) and (16) we have the equalities

$$\pi_{\text{area}}/A_0 = (\mu_i^* - \mu_i)/A_i = \sigma. \quad (17)$$

The chemical potential (divided by the normalisation constant A_0) of the new 'area' component is equal to the surface tension of the system.

4. Results

As examples we consider a binary and a ternary alloy system in the liquid state. The method described above is applied to calculate the surface tension and composition of Bi–Sn and Ag–Au–Cu melts in temperatures where experimental surface tension data are available for these mixtures.

4.1. Bi–Sn liquid binary system at 608 K

The thermodynamic and other physical data required to make the calculations in the Bi–Sn system are presented in Table 2.

The molar surface areas are calculated from the molar volume data using Eq. (18) where N_a is Avogadro's number.

$$A_i = 1.091 \cdot N_a^{1/3} V_i^{2/3}. \quad (18)$$

The resulting surface areas at 608 K are $A_{\text{Bi}} = 70\,028$ m²/mol and $A_{\text{Sn}} = 64\,499$ m²/mol. By choosing the value 10 000 m²/mol for the normalisation factor A_0 the stoichiometric definitions for the system at 608 K are as presented in Table 3.

Normal standard state values can be used for the bulk phase (although for the purpose of calculating surface tension and equilibrium composition they could also be set to zero), while the standard state values for the surface phase need to be adjusted using Eq. (5). The excess Gibbs energy for the bulk

Table 3

Stoichiometry of the Bi–Sn system at 608 K

		Bi	Sn	Area
Bulk	Bi(l)	1	0	0
	Sn(l)	0	1	0
Surface	Bi(l)	1	0	7.0028
	Sn(l)	0	1	6.4499

Table 4

Calculated chemical potentials of the surface component and the surface tensions as a function of Sn content of the Bi–Sn binary alloy

X(Sn)	π_{area} (J/mol)	$\pi_{\text{area}}/A_0 = \sigma$ (N/m)
0	3736.71	0.3737
0.05	3769.70	0.3770
0.1	3803.93	0.3804
0.15	3839.54	0.3840
0.2	3876.66	0.3877
0.25	3915.50	0.3915
0.3	3956.28	0.3956
0.35	3999.33	0.3999
0.4	4045.01	0.4045
0.45	4093.82	0.4094
0.5	4146.41	0.4146
0.55	4203.61	0.4204
0.6	4266.53	0.4267
0.65	4336.72	0.4337
0.7	4416.33	0.4416
0.75	4508.53	0.4509
0.8	4618.17	0.4618
0.85	4753.25	0.4753
0.9	4928.10	0.4928
0.95	5171.49	0.5171
1	5542.38	0.5542

Table 5

Molar volume and surface tension data for the Ag–Au–Cu system

V_{Au} (m ³ /mol) = 11.3 * (1 + 0.8/10 000 * (T/K - 1337.33))/1000 000 [5]
V_{Ag} (m ³ /mol) = 11.6 * (1 + 0.98/10 000 * (T/K - 1234.93))/1000 000 [9]
V_{Cu} (m ³ /mol) = 7.94 * (1 + 1/10 000 * (T/K - 1357.77))/1000 000 [9]
σ_{Au} (N/m) = 1.33 - 0.00014 * T/K [5]
σ_{Ag} (N/m) = 1.207 - 0.000228 * T/K [9]
σ_{Cu} (N/m) = 1.585 - 0.00021 * T/K [9]

is calculated as given in Table 2, but the excess energy for the surface phase is modified by using Eq. (19):

$$G_{\text{surface}}^{\text{Excess}} = \beta \cdot x_{\text{Bi}}^s x_{\text{Sn}}^s L \quad (19)$$

where the factor β with a numerical value of 0.83 [3] is used to approximate the effect that the reduced coordination number of metal atoms on the surface as well as that of reconfiguration has on the excess Gibbs energy.

The calculation results for the example system are as shown in Table 4 and in Fig. 1. The calculations were made using the ChemSheet program [7] that is based on the ChemApp [7] thermodynamic program library.

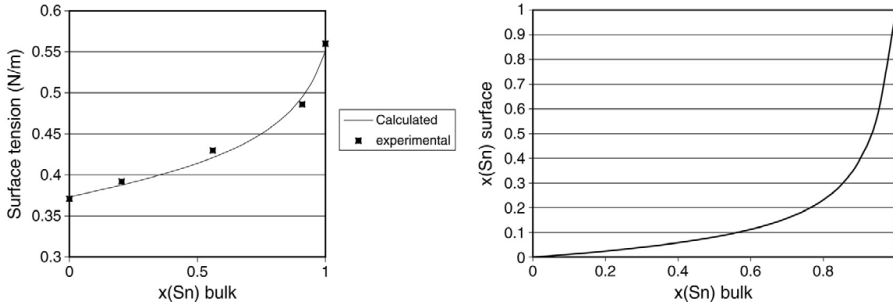


Fig. 1. Calculated surface tension values (left) and surface layer composition (right) as a function of bulk composition in the Bi-Sn system. Experimental surface tension values are from Ref. [8].

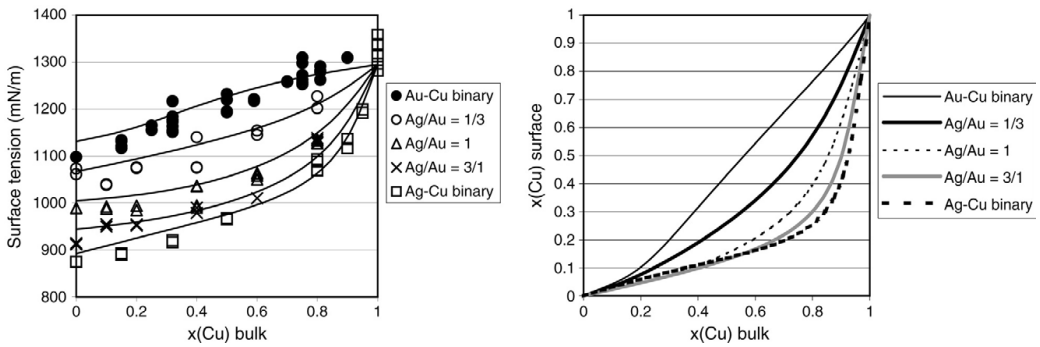


Fig. 2. Calculated surface tension values compared to experimental values measured by the authors (left) and the dependency of the surface molar fraction of copper from bulk composition (right) in the Ag-Au-Cu ternary system.

Table 6
Interaction parameters for the Ag-Au-Cu system

${}^0L_{\text{Ag,Au}} = -16402 + 1.14T/K$ [11]	${}^1L_{\text{Ag,Cu}} = 1660.74 - 2.31516T/K$ [10]	${}^2L_{\text{Au,Cu}} = 3500 + 3.57T/K$ [12]
${}^0L_{\text{Ag,Cu}} = 17384.37 - 4.46438T/K$ [10]	${}^1L_{\text{Au,Cu}} = 4730$ [12]	${}^2L_{\text{Ag,Au,Cu}} = -1000$ [10]
${}^0L_{\text{Au,Cu}} = -27900 - T/K$ [12]	${}^1L_{\text{Ag,Au,Cu}} = -105000 + 30T/K$ [10]	
${}^0L_{\text{Ag,Au,Cu}} = 10000$ [10]		

4.2. Ag-Au-Cu liquid ternary system at 1381 K

Molar volume and surface tension data required for the calculations in the Au-Ag-Cu system are presented in Table 5.

The excess Gibbs energy values for the bulk phase are calculated using Eq. (20) [10]:

$$G^{\text{Excess}} \text{ (J/mol)} = \sum_i \sum_{j>i} x_i x_j L_{i,j} + x_i x_j x_k L_{i,j,k} \quad (20)$$

The binary and ternary interaction parameters have a Redlich-Kister type dependency on the composition (Eqs. (21) and (22)):

$$L_{i,j} = \sum_v (x_i - x_j)^v {}^v L_{i,j} \quad (21)$$

$$L_{i,j,k} = x_i {}^0 L_{i,j,k} + x_j {}^1 L_{i,j,k} + x_k {}^2 L_{i,j,k} \quad (22)$$

The interaction parameters are listed in Table 6.

For the surface phase the excess Gibbs energy is modified as in previous example by multiplying the excess energy

expression with $\beta = 0.83$. Modelled surface tension values are compared with experimental results in Fig. 2. There is a fairly large amount of scatter in the experimental surface tension results. More precise measurements are currently being conducted in Osaka University using the constrained drop method [13]. Also modelled dependencies of surface mole fraction of copper from the bulk fraction are shown for different Ag/Au ratios.

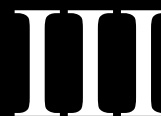
5. Conclusions

The stoichiometric conservation matrix of a Gibbs energy minimising program can be extended to include a surface monolayer as a separate phase while the constraint of constant surface area is included by adding a new component in the system. A single equilibrium calculation then results in the equilibrium composition of the bulk and surface phases. The surface tension of the mixture is received from the chemical potential

of the new area component. The model is consistent with the Butler monolayer model for surfaces while the use of a general Gibbs energy minimiser makes it easier to handle systems with multiple components and complex non-ideal mixing energies. The example cases considered in the paper are metal alloy systems with a particularly simple relation between the expressions of excess Gibbs energies in the bulk and in the surface, but the method is also directly extendable to other systems where more complex relations for Gibbs excess energies for the surface layer have been derived, such as ionic melts [14].

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Inclusion of the Donnan effect in Gibbs energy minimization

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Abstract

Donnan equilibrium based models can be used to predict ion-exchange related phenomena within many application fields. In this paper, a method for doing Donnan equilibrium calculations using Gibbs energy minimization is presented. With this approach, it is possible to solve Donnan equilibrium systems with complex solution or multiphase chemistry using Gibbs energy minimizing programs.

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Keywords: Donnan equilibrium; Ion-exchange; Gibbs energy minimization

1. Introduction

Donnan equilibrium based models have been used to model ion exchange phenomena in industrial pulp and papermaking processes [1], in basic research of polyelectrolytes [2] and membrane equilibrium with ionic drugs [3]. In some of these situations, the overall chemistry of the system can be quite complex with multiple components and phases and non-ideal interactions in solutions. As advanced computer programs and databases have been developed for solving multi-component and multi-phase equilibria problems, it has been the purpose of this work to show how a general purpose Gibbs energy minimizing program can be used for equilibrium calculations in systems where the Donnan equilibrium applies.

2. Theory

2.1. Donnan equilibrium

Electrochemical systems consisting of two parts where one or more charged species are restricted to one part of the system by a semi-permeable membrane were first investigated by Donnan in early 20th century [4]. It has been later shown that the same basic relations can also often be applied to model systems where the confinement of some ionic species is caused, not by a membrane, but by chemical bonding to a macromolecular structure. The

essential feature of Donnan equilibrium is that because all macroscopic parts of the system must remain electrically neutral, the binding of some of the ions into one part of the system will cause an uneven distribution also for the freely mobile ions. The equilibrium distributions between different solution volumes will be defined by their electrochemical potentials

$$\begin{aligned} \mu_i^{*'} &= \mu_i^{0'} + RT \ln a_i' + z_i F \psi' \\ &= \mu_i^{*''} = \mu_i^{0''} + RT \ln a_i'' + z_i F \psi'' \end{aligned} \quad (1)$$

where μ_i^* is the electrochemical potential, μ_i^0 the standard state chemical potential, a_i the activity and z_i the charge of species i , F Faraday's constant and ψ the electrical potential. Superscripts ' and '' denote the two solution volumes. Rearranging Eq. (1), a relation for the equilibrium activities of solutes in the two solution volumes is reached:

$$\frac{a_i''}{a_i'} = \exp\left(\frac{\mu_i^{0'} - \mu_i^{0''} + z_i F(\psi' - \psi'')}{RT}\right) \quad (2)$$

With the equality of standard state chemical potentials, Eq. (2) can be simplified further

$$\begin{aligned} \frac{a_i''}{a_i'} &= \exp\left(\frac{z_i F(\psi' - \psi'')}{RT}\right) \\ &= \left(\exp\left(\frac{F(\psi' - \psi'')}{RT}\right)\right)^{z_i} \equiv \lambda^{z_i} \end{aligned} \quad (3)$$

where the characteristic constant λ is the same for all mobile solute species for any given state of the system.

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Table 1
A representation of a simple chemical system consisting of an aqueous solution and a solid precipitate

		O	H	Na	C	Ca	N	e ⁻
Aqueous solution	H ₂ O	1	2					
	H ⁺		1					-1
	OH ⁻	1	1					1
	N ₂						2	
	O ₂	2						
	Na ⁺			1				-1
	CO ₂	2			1			
	HCO ₃ ⁻	3	1		1			1
	CO ₃ ²⁻	3			1			2
Ca ²⁺					1		-2	
CaCO ₃	CaCO ₃	3			1	1		

2.2. Gibbs energy minimization

Computer programs that can calculate the equilibrium state of a chemically reactive system by minimizing its overall Gibbs energy have been in active use since the 1950's. For such programs, two kinds of data are needed for calculations: a listing of phases and their constituent species together with their stoichiometries with respect to the chemical elements or other fundamental components they can be considered to be formed of, and functions for calculating the chemical potentials (molar Gibbs energies) of each species as a function of temperature, pressure and phase composition. The stoichiometric data for the system can be presented in a matrix format, an example of which is given in Table 1.

The equilibrium composition of a system defined in this way (with *N* possible species and *M* elements or other components) can be derived by solving the nonlinear optimization problem of finding the minimum of the total Gibbs energy of the system:

$$G = \sum_{i=1}^N n_i \mu_i \tag{4}$$

Table 2
The chemical system of Table 1 divided to two volumes with an added ion (Anion_a) that cannot be transferred from the second sub-volume to the first one

		O	H	Na	C	Ca	solvent ₂	Anion _a	e ⁻	charge ₂
(1) Solution volume	H ₂ O	1	2							
	H ⁺		1						-1	
	OH ⁻	1	1						1	
	Na ⁺			1					-1	
	CO ₂	2			1					
	HCO ₃ ⁻	3	1		1				1	
	CO ₃ ²⁻	3			1				2	
	Ca ²⁺					1			-2	
(2) Solution volume	H ₂ O	1	2				1			
	H ⁺		1						-1	1
	OH ⁻	1	1						1	-1
	Na ⁺			1					-1	1
	CO ₂	2			1					
	HCO ₃ ⁻	3	1		1				1	-1
	CO ₃ ²⁻	3			1				2	-2
	Ca ²⁺					1			-2	2
Anion _a ⁻							1	1	-1	
CaCO ₃	CaCO ₃	3			1	1				

subject to the constraints that the molar amount of no species can be negative

$$n_i \geq 0 \tag{5}$$

and that the total amounts of all components in the system are conserved

$$\sum_{i=1}^N a_{ij} n_i = b_j \tag{6}$$

where *a_{ij}* is the stoichiometric coefficient of species *i* with respect to element *j* and *b_j* the total amount of element *j* in the system. Because the change in Gibbs energy for every reaction among the species that are present in the system is zero at equilibrium, chemical potentials (molar Gibbs energies) can also be defined for each component in the equilibrium system [5] so that they satisfy the relation

$$\mu_i = \sum_{j=1}^M a_{ij} \pi_j \tag{7}$$

where *π_j* is the chemical potential of component *j* and *μ_i* the chemical potential of any species *i* present in the system.

2.3. Gibbs energy model for Donnan equilibrium

For calculations with Donnan equilibrium, two separate solution phases are defined in the system as separate phases (Table 2). All mobile solutes are present in both phases and normally, as the solvent is the same in both, the thermodynamic data for the solutes in both phases are identical as well. The immobile ions have been defined as species for only one of the phases. Two other modifications to the stoichiometries in the system are needed. To ensure that not only the system as a whole but also both solution volumes separately remain electrically neutral, a new component for the charge in the second solution volume is added. A second new component is introduced to prevent the free movement of the solvent from one side to the other. Without this last added constraint, all the solvent would

typically transfer to the volume containing the immobile ions to make the solution there as dilute as possible (lowering the Gibbs energy of the solvent), a behaviour in real cases generally prevented by a build up of a pressure difference. It could be argued that this last constraint should be for the total volume of the solution in the restricted sub-volume and not just for the molar amount (volume) of the solvent, but the practical problems that the authors have worked with have been with systems that are relatively dilute (especially regarding the bound ions) and where the solution sub-volumes are not very accurately defined. For these purposes, the numerically simple system described in Table 2 is both sufficient and preferable.

With the system definitions described in Table 2, the equilibrium distribution of solutes calculated by minimizing the total Gibbs energy of the system will follow the relation given by Eq. (8)

$$\begin{aligned}\mu_i^2 &= \mu_i^{0,2} + RT \ln a_i^2 = \mu_i^1 + z_i \pi_{\text{charge}_2} \\ &= \mu_i^{0,1} + RT \ln a_i^1 + z_i \pi_{\text{charge}_2}.\end{aligned}\quad (8)$$

The relation between activities in the two solution volumes is therefore

$$\frac{a_i^2}{a_i^1} = \exp\left(\frac{\mu_i^{0,1} - \mu_i^{0,2} + z_i \pi_{\text{charge}_2}}{RT}\right) \quad (9)$$

that can be further simplified when the standard states are equal to

$$\frac{a_i^2}{a_i^1} = \exp\left(\frac{z_i \pi_{\text{charge}_2}}{RT}\right) = \left(\exp\left(\frac{\pi_{\text{charge}_2}}{RT}\right)\right)^{z_i} \quad (10)$$

Comparing Eqs. (3) and (10), we can note the equality

$$F(\psi^1 - \psi^2) = \pi_{\text{charge}_2} \quad (11)$$

which means that the chemical potential of the new component, used for differentiating charges of the species in the two sub-volumes in the system, is directly proportional to the electrical potential difference between those two volumes.

For the solvent, the calculated chemical potentials in the two volumes will differ by the amount of the chemical potential of the new component defined to fix the amount of the solvent in one of the phase volumes.

$$\mu_s^1 = \mu_s^0 + RT \ln a_s^1 \quad (12)$$

$$\mu_s^2 = \mu_s^0 + RT \ln a_s^2 = \mu_s^1 + \pi_{\text{solvent}_2} \quad (13)$$

Naturally, the actual chemical potential of the solvent must be the same in both parts of the equilibrium system. The calculated chemical potentials differ because they do not include the effect of the constraining force required to prevent the flow of the solvent from the first solution phase volume to the second one. If the solvent is considered incompressible, the actual equilibrium condition is

$$\mu_s^2 = \mu_s^0 + RT \ln a_s^2 + V_s^m (p^2 - p^1) = \mu_s^1 \quad (14)$$

Comparing Eqs. (13) and (14), we obtain an equation for the relationship between the calculated chemical potential of the

component restricting the movement of the solvent in the model and the pressure difference actually required to have the solvent in equilibrium when the solute concentrations are unequal

$$p^2 - p^1 = -\frac{\pi_{\text{solvent}_2}}{V_s^m} \quad (15)$$

In the discussion above, it has generally been assumed that the solute standard state values are the same on both sides of the system. This is what one would expect if the partitioning membrane or other structural feature that makes some of the ions non-mobile does not prevent the movement of the solvent molecules. However, the standard state values could also be adjusted to reflect observed partition coefficients as in the Donnan equilibrium based modelling work for ionic drugs in Ref. [3] where hydrophobic interactions between a fixed charged membrane and drug molecules are taken into account by using partition coefficients of this kind. Finally, while the model has been presented for the case of two solution volumes, the extension to an arbitrary number of volumes is straightforward, requiring two additional components for each added sub-volume (phase).

3. Results and discussion

Thermodynamic models as described above have been used by the authors in co-operation with other researchers [1,6] to model ion-exchange phenomena in pulp suspensions in conditions relevant to practical industrial processes. In those models, the two (aqueous) solution volumes are the water contained by the fibres themselves and the surrounding water in the suspension. The immobile ions are organic acidic groups that are chemically bound to the fibre structure. pK_a values determined by titration are used to set suitable thermodynamic values for the dissociation of these acids while standard state values acquired from various published data compilations are used for the other solutes, gaseous species and potential precipitates. Equal standard state values have been used for the

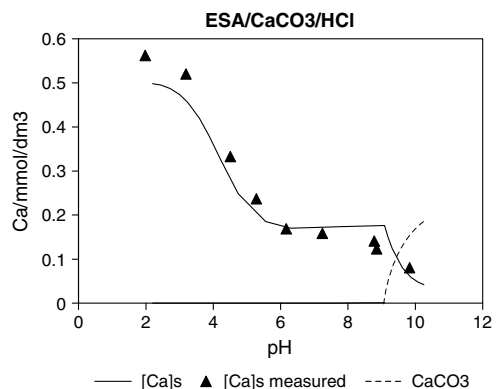


Fig. 1. Modelled and measured Ca concentrations in a CaCO_3 containing pulp suspension as function of pH. Modelled amounts of remaining solid CaCO_3 are also shown.

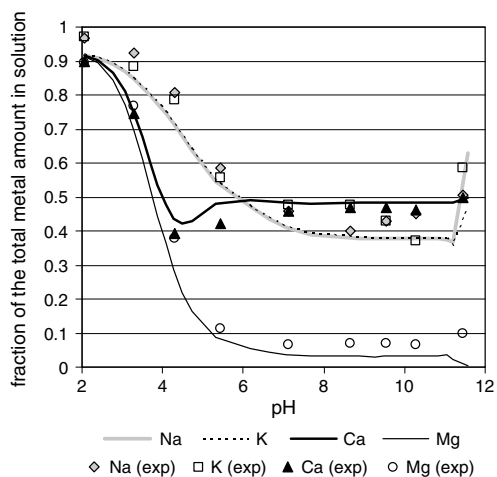


Fig. 2. Calculated and experimental ratio between the metal amounts in solution and the total metal content of the pulp as function of pH in a suspension treated with EDTA. Experimental values and chemical inputs for the model based on Ref. [10].

two aqueous volumes. The activity coefficients for the ions have been modelled using the Pitzer equations [7], which reduce to activity coefficient expressions similar to the Davies equation in dilute solutions or when no ion-specific interaction parameters are available. The equilibrium calculations have been done mostly using ChemSheet [8], which is a part of the widely used Solgasmix/ChemSage/ChemApp program family—in principle, any Gibbs energy minimizer program that allows the user to define stoichiometries and thermodynamic data for the phases and their constituents could be used.

Modelled and experimental Ca concentrations together with the modelled solid CaCO_3 amount in a 1% consistency eucalyptus sulphate pulp suspension containing CaCO_3 are shown in Fig. 1. The CaCO_3 content is 0.05 mol/(kg of dry fibre), while the acidic group content of the fibre is 0.067 mol/(kg of dry fibre). The amount of bound water in the fibre was estimated to be 1 kg/(kg of dry fibre). The experimental results are from Ref. [9]. The Ca content in the solution rises with the pH value, first with the dissolving CaCO_3 and then as the acidic groups become deprotonated releasing the Ca-ions bound by the fibres at higher pH values.

Modelling results for a 4.8% consistency pulp suspension treated with EDTA chelating agent are shown in Fig. 2. At very low pH, the organic acids are not deprotonated and the metal concentrations would be expected to be roughly equal in the fibres and in the surrounding solution. With increasing pH, the negatively charged fibres will attract cations, the effect as described by Eqs. (3) and (10) being stronger for divalent than monovalent ions. Formation of negatively charged complexes with EDTA explains why a larger fraction of Ca than Mg remains in the solution with pH values greater than 4.

In general, the thermodynamic model presented here has been found to be able to give useful results on pH values and

concentrations of inorganic ions in pulp suspensions, though both kinetic effects and complex interactions with various organic components in the system can affect the accuracy of the model predictions [1,11]. The models have been applied to planning and modelling of actual industrial pulp and paper-making processes [12,13].

4. Conclusion

A computational model for solving multi-phase chemical equilibrium problems with Donnan ion-exchange phenomena has been constructed. Using the model, it is possible to consider ion-exchange effects in chemical systems using commercially available Gibbs energy minimizers. In the field of pulp and paper industries, the resulting models have been used to simulate both laboratory experiments and planned and existing industrial processes. The method could be expected to be useful in other areas where Donnan type ion-exchange equilibrium needs to be considered in chemically reactive systems.

Acknowledgements

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IV

Risto Pajarre, Pertti Koukkari, Toshihiro Tanaka (2013)

Surface tension of a liquid metal-oxygen system using a multilayer free energy model

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Constrained and extended free energy minimisation for modelling of processes and materials



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HIGHLIGHTS

- Extended range of free energy minimisation applications explored.
- Applied to constrained reaction rates and additional energy terms.
- Both equilibrium and non-equilibrium systems discussed.

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ABSTRACT

Computational methods in chemical equilibrium thermodynamics have found numerous application areas in diverse fields such as metallurgy, petrochemistry, the pulp and paper industry, the study of advanced inorganic materials, environmental science and biochemistry. As many of the cases of interest are not actually in equilibrium, there is a need for methods that extend the application area of multiphase equilibrium solvers to non-equilibrium systems. Likewise there is a need for efficient handling of thermochemical systems that are described by parameters other than those most commonly associated with Gibbs energy, namely temperature, pressure and fixed elemental (and charge) balances.

In the work computational methods and related theory are presented that can be used with a standard Gibbs energy minimiser to solve advanced thermochemical problems. The actual calculations have been performed using the ChemSheet software, but the presentation has aimed to be generic and applicable to other thermochemical codes that allow the user to define thermodynamic data and the stoichiometries of the constituent species in the system.

The examples discussed include electrochemical Donnan equilibrium (particularly applied to aqueous pulp suspensions), surface and interfacial energies of liquid mixtures, systems affected by external magnetic fields and systems with time-dependent reaction extents and diffusion-constrained para-equilibrium. A number of practical applications have been achieved with the models that combine reaction kinetics with partial thermodynamic equilibrium calculation and ion exchange models based on Donnan equilibrium, that have both been applied with success in real-life industrial design and development work with multicomponent, multiphase systems. The method has been successfully applied to liquid surface energies of systems with multiple components and complex non-equilibrium data.

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1. Introduction

Computational chemical equilibrium thermodynamics has been applied extensively in diverse fields such as metallurgy, petrochemistry, the pulp and paper industry, the study of advanced inorganic materials, environmental science and biochemistry (Jäntschi and Bolboacă, 2014; Gmehling, et al., 2012; Letcher, 2004; Hack, 2008; Alberty, 2003). Efficient and practical models have been developed for complex mixtures for high

temperature slags and melts as well as concentrated aqueous solutions while simultaneously the multicomponent methodology has been successfully applied to various interrelated material properties. Thermodynamic databanks cover fields for many classes of substances ranging from organic and biochemical systems to various inorganic and metallurgical materials. The systematic data storage and management in connection with the increasing numerical capability of modern computers enables treatment of the thermochemistry of complex systems as a whole. Thus, accurate theoretical studies of the phase stability and equilibria of systems with a great number of chemical components can be made. The progress is not surprising considering the general

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applicability of the thermodynamic relations, theoretical and data development over a century and finally the rapid improvements in computational methods during the last few decades. A large number of computer codes and programmes have also been developed for accurate handling of thermochemical systems and effective, robust and practical determination of the equilibrium state based on the minimisation of the Gibbs free energy of the system.

As many of the cases of interest are not in actual equilibrium, there is a need for methods that extend the application area of chemical equilibrium solvers to non-equilibrium systems, including those that are at least in part constrained by slow reactions while the assumption of local chemical equilibrium (LCE) is valid for fast 'unconstrained' reactions. Likewise there is a need for efficient handling of thermochemical systems that are described by parameters other than those most commonly associated with Gibbs energy, namely temperature, pressure and fixed elemental (and charge) balances. These include parameters that connect electromagnetic and mechanic functions to chemical or phase changes, i.e. the conjugate variables that are used to define e.g. electrochemical, electromagnetic or mechanical work.

The purpose of this work has been to explore, develop and collect a systematic set of computational methods that can be used with a standard Gibbs energy minimiser for solving advanced thermochemical problems. In earlier work (Koukkari and Pajarre, 2011) the authors have used the term Constrained Free Energy (CFE) method to describe the approach in which additional constraints were added to standard Gibbs energy minimisation. In the present paper, additional constraints and energy terms are treated in a more systematic fashion, and the application area is also broadened. The actual calculations have been done using the ChemSheet or ChemApp software (Koukkari, et al., 2000; Petersen and Hack, 2007), but the presentation has aimed to be generic and applicable to other thermochemical codes that allow the user to define thermodynamic data and the stoichiometries of the constituent species in the system. The functioning of those codes, such as finding the global free energy minimum reliably and computationally efficiently in systems containing multiple components (dozens, if required), and potentially multiple non-ideal mixture phases has not been considered a part of this work. Such topics are discussed in detail e.g. by Harvey et al. (2013) and references therein.

2. Thermodynamic basis

In this work it is assumed that the system considered is either isotropic, having the same values for temperature, chemical potentials, pressure and other work-coefficients throughout the system, or that it can be divided into a finite number of such parts. If not explicitly stated otherwise, the model equations are written for one isotropic part of the system.

2.1. Gibbs free energy

The change in internal energy of a system can be given (Haase, 1990) by the Eq. (1)

$$dU = TdS + \sum_j L_j \cdot dl_j + \sum_i \mu_i dn_i \quad (1)$$

while the corresponding Euler form for internal energy is

$$U = TS + \sum_j L_j \cdot l_j + \sum_i \mu_i n_i \quad (2)$$

where L_j is the generalized work coefficient with intensive character and l_j is the corresponding generalized work coordinate with extensive character. Example cases have been listed in Table 1.

Table 1
Common examples of thermodynamic work coefficients and coordinates.

work coefficient L_j	work coordinate l_j
$-P$ (pressure)	V (volume)
σ (surface tension)	A (surface area)
ϕ_j (electric potential)	Q_j (charge)
\mathbf{E} (electric field strength)	\mathbf{p} (electric dipole moment)
\mathbf{B} (magnetic flux density)	\mathbf{m} (magnetic moment)

While the expression of the generalized work [Eq. (1)] has been adapted from the comprehensive treatment of Haase (1990), the further nomenclature mostly follows Alberty (2001).

For the internal energy U , the natural variables are S , l_j and n_k , meaning that if U is known as a function of those extensive variables, all the other thermodynamic properties of the system can be derived (Alberty, 2001).

Common definitions (Haase, 1990) for enthalpy (H), Helmholtz (F) and Gibbs (G) free energy are given by (Eqs. (3)–5)

$$H \equiv U - \sum_j L_j \cdot l_j \quad (3)$$

$$F \equiv U - ST \quad (4)$$

$$G \equiv U - ST - \sum_j L_j \cdot l_j \quad (5)$$

In this work the extensive work coordinates l_j are divided to partial molar contributions from each species following Eq. (6)

$$l_{j,i} \equiv \left(\frac{\partial l_j}{\partial n_i} \right)_{T, L_k, n_{k \neq i}} \quad (6)$$

so that

$$l_j = \sum_i l_{j,i} n_i \quad (7)$$

For the practical applicability with a Gibbs energy minimiser, in the present work it has been further assumed that the partial molar properties expressed by Eq. (6) are not functions of phase composition.

Gibbs energy expression on a molar basis is given by Eq. (8)

$$G_i \equiv U - S_i T - \sum_j L_j \cdot l_{j,i} = \mu_i \quad (8)$$

For a closed system with a constant temperature and L_j (including P) the condition for a spontaneous process is $dG \leq 0$, so that G has its minimum value in equilibrium state.

2.2. Systems with constant work coordinates

In cases in which some of the work coordinates (and not the corresponding work coefficients) are constant, a corresponding free energy function can be defined (Alberty, 2001).

$$G' \equiv G + \sum_h L_h \cdot l_h = \sum_i \mu_i n_i + \sum_h L_h \cdot l_h \quad (9)$$

where the summation is over the constant values of l_h . G' obtains its minimum value at the equilibrium corresponding to the new set of constraints. A corresponding molar free energy, $\mu_i^{\prime\alpha}$ in this work¹ that includes a contribution to the work coordinate amount

¹ Here the superscript α is used to denote a specific phase or part of the system in which the work coefficient of interest applies. When superscripts α and β are used, the species that n_i^α and n_i^β or μ_i^α and μ_i^β refer to are the same chemical species in different parts or phases of the system.

specific to the species i can be defined as

$$\mu_i^{\alpha} \equiv \left(\frac{\partial G}{\partial n_i^{\alpha}} \right)_{T, L_j, n_{k \neq i}, n_m^{\beta}} = \mu_i + \left(\frac{\partial G}{\partial h} \right)_{T, L_j, n_k} \left(\frac{\partial h}{\partial n_i^{\alpha}} \right)_{T, L_j, n_{k \neq i}} = \mu_i + L_h n_{h,i}^{\alpha} \quad (10)$$

Eq. (10) applied to a pure phase gives the standard state free energy with the additional work co-ordinate contribution as

$$\mu_i^{\alpha,0} = \mu_i^0 + L_h n_{h,i}^{\alpha} \quad (11)$$

For simplicity, (Eqs. (10) and 11) are written for the case where only one work coordinate h is kept constant. In the constrained equilibrium, i.e. the minimum of G' , the chemical potential is still as a state variable the quantity that is phase independent – i.e. equal throughout the system.

$$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i \quad (12)$$

In terms of activities the chemical potential can be expressed as

$$\mu_i = \mu_i^{\alpha} - L_h n_{h,i}^{\alpha} = \mu_i^{\alpha,0} + RT \ln a_i - L_h n_{h,i}^{\alpha} \quad (13)$$

2.3. Systems with constant chemical potentials

With regard to systems in chemical equilibrium, Eq. (2) can be written in terms of independent variables, so that the species in the system are replaced by components, whose number is less than the number of species assuming chemical reactions or mass transfer between phases are taking place.

$$U = TS + \sum_j L_j \cdot l_j + \sum_k \pi_k b_k \quad (14)$$

The chemical potential of a component k in this work has been denoted by symbol π_k , and its molar amount by b_k to make them easier to distinguish from the chemical potential μ_i and molar amount n_i of a species i .

A suitable free energy function when some component chemical potentials are kept at a constant value by material bath is given by

$$G' \equiv G - \sum_h \pi_h b_h \quad (15)$$

where the summation is over the non-constant values of b_h .

Mathematically Eqs. (9) and (15) represent Legendre transforms of the free energy function to a new one with a new set of independent variables (Alberty, 2001). The transforms allow solving of the equilibrium state and all its thermodynamic functions specified by the natural variables, where the natural variables can be freely chosen from the conjugate pairs of molar amounts and chemical potentials; temperature and entropy as well as work coordinates and work coefficients.

2.4. Systems with other than work coordinate constraints

If other constraints (e.g. due to slow reaction rates) that are not related to an additional work term ($L_j \cdot l_j$) are relevant to the system, the form of the energy functions [(Eqs. (2)–5)] is not altered. The free energy corresponding to any specific composition remains unchanged. However, the possible states of the system are reduced and the equilibrium is generally sifted to some state with higher free energy than without the constraint. When the states of the system are constrained by a relation or relations that can be expressed as linear combinations of amounts of species, the effective number of components in the system is increased, as was first noted by J.W. Gibbs who called these kinds of constraints “passive resistances” (Gibbs, 1876; Koukari, et al., 2008b). Constraints of this kind are discussed in more detail together with

systems constrained by slow kinetics and mass transfer as well as nanoparticles.

3. Use of a free energy minimiser

3.1. Traditional problem statement

The basic problems to be solved with a typical free energy minimiser are of the type: Find the minimum of function \mathbb{G} :

$$\mathbb{G} = \sum_{\alpha} \sum_i \mathbb{G}_i^{\alpha} (x_j^{\alpha}, T, P) n_i^{\alpha} \quad (16)$$

subject to constraints

$$n_i^{\alpha} \geq 0 \quad \forall i \quad (17)$$

and

$$\mathbf{A}\mathbf{n} - \mathbf{b} = 0 \quad (18)$$

where matrix element a_{ji} of matrix \mathbf{A} is the stoichiometric coefficient between component j and species i , vector element n_i the molar amount of species i and vector element b_j the (fixed) molar amount of component j in the system. The \mathbb{G} in Eq. (16) is the free energy of the system, either G (Gibbs energy) or G' as defined by Eq. (5) or Eq. (9), depending on whether additional work co-ordinate constraints have been applied. When \mathbb{G} equals G , the molar quantity \mathbb{G}_i equals the chemical potential μ_i .

In the minimum free energy (\mathbb{G}) state, the derivatives of the Lagrangian function L (Smith and Missen, 1991)

$$L = \mathbb{G} - \lambda^T (\mathbf{A}\mathbf{n} - \mathbf{b}) \quad (19)$$

(where λ is a vector of Lagrange multipliers) with respect to molar amounts and individual Lagrange multipliers must be zero, so that

$$\frac{\partial L}{\partial n_i} = \frac{\partial \mathbb{G}}{\partial n_i} - \sum_j \lambda_j a_{j,i} = \mathbb{G}_i - \sum_j \lambda_j a_{j,i} = 0 \quad (20)$$

The chemical potential or molar Gibbs energy of species in calculations are expressed in the following or equivalent form:

$$\mu_i = \mu_i^0(T, P) + RT \ln a_i \quad (21)$$

The Lagrange multiplier for a component can be equated with its chemical potential as

$$\pi_j \equiv \left(\frac{\partial \mathbb{G}}{\partial b_j} \right)_{T, P, b_{k \neq j}} = \lambda_j \quad (22)$$

both when \mathbb{G} equals G and when it equals G' . Eq. (20) can also be applied to species that are not present in the equilibrium, allowing the calculation of molar free energy for a species that is not present in the equilibrium state and for which Eq. (21) is not directly applicable (Eriksson, 1975).

Equilibrium solvers typically allow the calculation of problems where the equilibrium chemical potentials of certain species are fixed while the corresponding feed amounts are allowed to vary. The problem, after defining the system components so that the species of interest is one of them, is equal to the one described by Eq. (15). Computationally it can be solved (Cheluget and Missen, 1987), (Norval, et al., 1991) by normal numerical routines by noting that (here summation index h goes over the components whose chemical potentials are held constant)

$$\begin{aligned} G' &\equiv \sum_i \mu_i n_i - \sum_h \pi_h b_h = \sum_i \left(\mathbb{G}_i^0 + RT \ln a_i \right) n_i - \sum_i \pi_h a_{h,i} n_i \\ &= \sum_i \left(\left(\mu_i^0 - \sum_h \pi_h a_{h,i} \right) + RT \ln a_i \right) n_i \end{aligned} \quad (23)$$

This means that the correct free energy function is minimised if the standard state values of those species containing

the components with fixed chemicals potential are adjusted according to Eq. (24)

$$\mu_i^{\prime 0} \equiv \mu_i^0 - \sum_h \pi_h a_{h,i} \quad (24)$$

Additionally the mass balance constraints Eq. (18) related to components h need to be relaxed (the components are removed from the matrix \mathbf{A})

3.2. Additional work coefficients

In conventional Gibbs energy minimising software dealing with chemical equilibrium problems, the thermodynamic data is not given as a function of any other work coefficients than pressure, that is, all other work coefficients are assumed to be zero. The Gibbs energy, as defined by Eq. (5) is the minimised free energy function for also non-zero constant values of L_j . Gibbs energy is given by (from (Eqs. (1) and (5))

$$\left(\frac{\partial G}{\partial L_j}\right)_{T, L_k \neq j, n_i} = -l_j \quad (25)$$

$$G(T, P, L_j) = G(T, P, L_j = 0) - \int l_j \cdot dL_j \quad (26)$$

while the change in chemical potential is given by

$$\left(\frac{\partial \mu_i}{\partial L_j}\right)_{T, L_k \neq j, n_k} = -\left(\frac{\partial l_j}{\partial n_i}\right)_{T, L_k \neq j, n_k} = -l_{j,i} \quad (27)$$

and therefore standard state value corresponding to a non-zero L_j is

$$\mu_i^0(T, P, L_j) = \mu_i^0(T, P, L_j = 0) - \int l_{j,i} dL_j \quad (28)$$

In order to avoid handling vector components separately it is assumed for Eq. (28) that $L_h \cdot l_{h,i}$ can be replaced with $L_h l_{h,i}$ (L_h and $l_{h,i}$ are either scalars or they are aligned).

As an example, for a ferromagnetic material as a pure phase when the magnetization is assumed to be constant

$$\mu_i^0(T, P, B) = \mu_i^0(T, P, B = 0) - m_i B \quad (29)$$

and for paramagnetic material, if magnetization is directly proportional to the external field

$$\mu_i^0(T, P, B) = \mu_i^0(T, P, B = 0) - 0.5 \chi_i B^2 \quad (30)$$

The chemical potential for a mixture phase is then given by

$$\mu_i(T, P, L_j) = \mu_i^0(T, P, L_j) + RT \ln \gamma_i x_i \quad (31)$$

The practical applicability of the Eq. (31) is greatest when the dependency of the activity coefficients on L_j can be ignored.

3.3. Addition of new components to computational systems

Addition of a new component/constraint to a computational system adds a new row to matrix \mathbf{A} and new elements to the vectors $\boldsymbol{\lambda}$, \mathbf{n} and \mathbf{b} in Eq. (19). The resulting Lagrangian function L is identical to one defined for a system with the original components, but with an adjusted free energy function G' defined by

$$\begin{aligned} G' &\equiv G - \lambda_r \left(\sum_i a_{r,i} n_i - b_r \right) = \sum_i \mu_i n_i - \lambda_r \left(\sum_i a_{r,i} n_i - b_r \right) \\ &= \sum_i (\mu_i - \lambda_r a_{r,i}) n_i + \lambda_r b_r \end{aligned} \quad (32)$$

so that the adjusted free energy function is one where the molar contributions have been augmented by the factor $-\lambda_r a_{r,i}$

$$\mu'_i = \mu_i - \lambda_r a_{r,i} \equiv \mu_i - \pi_r a_{r,i} \quad (33)$$

while the free energy function includes an additional term

$$\lambda_r b_r = \pi_r b_r \quad (34)$$

The minimum energy condition corresponding to Eq. (20), together with the original mass balance constraints, is now

$$\mu_i^{\prime 0} + RT \ln a_i - \pi_r a_{r,i} = \sum_{j \neq r} \pi_j a_{j,i} \quad (35)$$

The quantity on the left side of Eq. (35), marked with μ'_i in Eq. (33), replaces the original chemical potential expression ($\mu_i^0 + RT \ln a_i$) as the quantity that must be equal in phases and parts of the system that are in equilibrium with each other, that is, it is the chemical potential in the system. The comma in $\mu_i^{\prime 0}$ is used to denote that the standard state value may have been adjusted from the value used in the unconstrained system if new work coordinate has been applied, in concurrence with Eq. (10)

$$\mu_i^{\prime 0} = \mu_i^0 + L_h^i a_{h,i}^\alpha \quad (36)$$

where $L_h^i a_{h,i}^\alpha$ is the work coefficient for pure species i in phase system part α . In the example cases discussed in this work, it is zero except with surface tension-related calculations, where it equals the surface tension of the pure substance.

Comparing Eq. (35) with Eq. (13) we have, for cases where the constraint can be equated with a fixed work co-ordinate, the equality

$$L_h^i a_{h,i}^\alpha = \pi_r a_{r,i}^\alpha \quad (37)$$

For the practical applicability with Gibbs energy minimisers, it is also required here that $a_{r,i}$ is not a function of π_r . Therefore, it is assumed that $l_{h,i}^\alpha$ can be factored to two parts, separating the possible dependency on L_j from the dependency on i .

$$l_{j,i} = l_j^i(L_j) l'_{j,i} \quad (38)$$

(Subscript α omitted from the equation for clarity as a continuously repeating element) Provided that Eq. (38) is valid, the stoichiometric coefficient $a_{r,i}$ can be defined by

$$a_{r,i} = \frac{l'_{j,i}}{l_j^i} \quad (39)$$

and the corresponding work coefficient as

$$L_j = \frac{\pi_r}{l_j^i} \quad (40)$$

In (Eqs. (39) and (40), l_j^i is a normalisation constant with the same units as $l'_{j,i}$ and an arbitrary but fixed numerical value.

Formally then, if a work coordinate related stoichiometric coefficient can be deduced on physical basis, the $\min(G)$ procedure can incorporate such factors in its multiphase calculation. According to Eq. (34) the respective component potentials become solved as additional Lagrange multipliers within the minimisation.

If the applied constraint cannot be equated with a work coordinate, the corresponding term does not enter Eq. (5), so for example for the case of system with a constant temperature, (external) pressure and a non-work constraint the Gibbs energy remains

$$G \equiv U - ST + PV = \sum_i \mu_i n_i \quad (41)$$

In terms of original components the minimised free energy nevertheless has an additional term as expressed by Eq. (32). With a molar free energy defined as

$$G'_i = \left(\frac{\partial G'}{\partial n_i}\right)_{T, P, n_j \neq i, b_r} \quad (42)$$

we have from Eq. (35) an equality that is valid also for rate constrained systems.

$$G_i = \mu_i^0 + RT \ln a_i - \pi_r a_{r,i} = \sum_{j \neq r} \pi_j a_{j,i} \quad (43)$$

3.4. Applying additional components for calculations with additional non-zero constant work coefficients L_h

In principle, the application of Eq. (28) to adjusted standard state values is the only thing that is required for calculations when the value of a new work coefficient instead of the corresponding work coordinate is specified (it is assumed here that the activity coefficients are not explicit functions of L_h). As one often wants to do repeated calculations with many different values of L_h and the databases used and free energy minimiser programmes do not necessarily readily support this, an alternative is to define a new component for the stoichiometry of the relevant species and adjust the chemical potential of that component.

From (Eqs. (23) and 28)

$$\int l_{j,i} dL_j = \pi_{h,i} a_{h,i} \quad (44)$$

As before, it is assumed here that $\int l_{j,i} dL_j$ can be factored into two parts, separating the possible dependency on L_j from the dependency on i as shown by Eq. (38) so that

$$\int l_{j,i} dL_j = l'_{j,i} \int l_j dL_j \quad (45)$$

Applying Eq. (39) for the stoichiometric coefficient with (Eqs. (44) and 45), the value of the corresponding chemical potential is given by

$$\pi_r = \frac{l'_{j,i}}{a_{r,i}} \int l_j dL_j = l_j^0 \int l_j dL_j \quad (46)$$

If $l_{j,i}$ is not a function of L_j , the equations for the stoichiometric coefficient and component chemical potential simplify to

$$a_{r,i} = \frac{l_{j,i}}{l_j^0} \quad (47)$$

$$\pi_r = L_j l_j^0 \quad (48)$$

3.5. Additional components as constrained reaction extents

The constraints-related slow reaction kinetics largely follows the same mathematical rules as those related to added work coefficients and coordinates.

In a system where a single reaction of the form



or

$$\sum_i v_i n_i = 0 \quad (49)$$

where v_i equals w_i for products and $-w_i$ for reactants, the extent of reaction is defined as

$$d\xi = \frac{dn_i}{v_i} \quad (50)$$

In a system with multiple possible reactions, it is in general impossible to define the change in the extent of any individual reaction $d\xi$, based on the change in system composition unless the other linearly independent reactions forming a basis spanning the reaction space are first defined. When they are, the equation for $d\xi$

can be solved

$$d\mathbf{n} = \mathbf{v} d\xi \quad (51)$$

where $d\mathbf{n}$ is the vector of changes of molar amounts of the N constituents in the system, $d\xi$ a vector of changes in extents of the NR specified reactions, and \mathbf{v} a $N \times NR$ matrix of stoichiometric coefficients of the reaction vectors spanning the reaction space.

For an equilibrium system the matrix equation

$$\mathbf{A}\mathbf{v} = 0 \quad (52)$$

where \mathbf{A} is a $M \times N$ matrix of stoichiometric coefficients between the N constituents and M components ($M = \text{rank}(\mathbf{v})$) forms a link between the system stoichiometry and the reactions allowed by it (Smith and Missen, 1991; Alberty, 1989, 1991; Keck and Gillespie, 1971; Keck, 1990; Koukkari and Pajarre, 2006b). Any kinetic restrictions in the possible reactions that cause the system to develop towards some other state than full equilibrium will lead to a new matrix equation

$$\mathbf{A}'\mathbf{v}' = 0 \quad (53)$$

where \mathbf{v}' is a $N \times NR'$ matrix ($NR' < R$) of made of the reduced reaction set and \mathbf{A}' is the corresponding $M' \times N$ matrix ($M' = M + NR - NR' = M + C$) of stoichiometric coefficients for the new augmented matrix of stoichiometric coefficients. Each linearly independent restriction on the set of reactions allowed to freely equilibrate corresponds to an additional stoichiometric constraint, or a row in the \mathbf{A} matrix, that is linearly independent of the existing component balances or previously defined reaction kinetic constraints. A practical way of defining a restricted reaction in a multispecies constrained equilibrium system is by Eq. (54)

$$d\xi_j \equiv \sum_i a_{M+j,i} dn_i = db_{M+j} \quad (54)$$

where $a_{M+j,i}$ is matrix element in the augmented matrix \mathbf{A}' , where the $M+j$ th row defines the constraint related to the reaction and db_{M+j} change in the value of the corresponding element in the augmented component vector. The matrix form corresponding to Eq. (54) is

$$d\xi = \mathbf{A}'' d\mathbf{n} = d\mathbf{b}'' \quad (55)$$

where \mathbf{A}'' is the $C \times N$ submatrix forming the lower part of \mathbf{A}' .

If the number of restricted reactions defined equals R , so that no unrestricted linearly independent reactions remain, \mathbf{A}'' in Eq. (55) can be replaced with \mathbf{A}' , and $d\xi$ with $d\xi'$, where the first $N-R$ components of the $d\xi'$ vector equal zero, and the last NR components are the same as in $d\xi$.

$$d\xi' = \mathbf{A}' d\mathbf{n} \quad (56)$$

As the matrix \mathbf{A}' has linearly independent rows it is invertible. The matrix $(\mathbf{A}')^{-1}$ contains coefficients for reaction like transformations for the set of species, so that in each transformation the amount of one of the components is increased by one, while the amounts of other components are kept constant. In matrix form this can be stated as.

$$(\mathbf{A}')^{-1} \mathbf{A}' = \mathbf{I} \quad (57)$$

Multiplying the Eq. (56) by $(\mathbf{A}')^{-1}$ one obtains

$$(\mathbf{A}')^{-1} d\xi' = d\mathbf{n} \quad (58)$$

The first M transformations are not allowed as they violate the normal component balances, and the corresponding values in the change of advancement vector $d\xi'$ are zero, while the remaining reactions are the constrained ones defined by Eq. (55), so that the lower NR rows of matrix $(\mathbf{A}')^{-1}$ equal matrix \mathbf{v} and the last NR values vector $d\xi$ in Eq. (51), so that the definition in Eq. (55) becomes equivalent with the one in Eq. (51).

As a schematic example, for a system with the following species H_2 , CH_4 , C_2H_4 , C_2H_6 and C_3H_8 $N = 5$ and $M = 2$, so that it is possible to define a maximum of three independent constrained reactions using the formalism of Eq. (54), corresponding to, for example to the following A' matrix where the first two rows are refer to the elements C and H and the last three to the added constraints

$$A' = \begin{matrix} & H_2 & CH_4 & C_2H_4 & C_2H_6 & C_3H_8 \\ \begin{matrix} 0 \\ 2 \\ 0 \\ 1 \\ 0 \end{matrix} & \begin{matrix} 1 \\ 4 \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 2 \\ 4 \\ 0 \\ -1 \\ 0 \end{matrix} & \begin{matrix} 2 \\ 4 \\ 0 \\ 0 \\ 1 \end{matrix} & \begin{matrix} 2 \\ 6 \\ 0 \\ 0 \\ 1 \end{matrix} & \begin{matrix} 3 \\ 8 \\ 1 \\ 0 \\ 0 \end{matrix} \end{matrix} \quad (59)$$

by inspection or by linear algebra one can derive

$$(A')^{-1} = \begin{matrix} H_2 \\ CH_4 \\ C_2H_4 \\ C_2H_6 \\ C_3H_8 \end{matrix} \begin{bmatrix} 2 & -0.5 & -2 & 2 & -1 \\ -3 & 1 & 1 & -2 & 0 \\ 2 & -0.5 & -2 & 1 & -1 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \end{bmatrix} \quad (60)$$

where the last three columns give in the traditional reaction equation format the following three rate constrained reactions compatible with both (Eqs. (51) and 55)



However, the three reaction constraints given by matrix (59) are also unambiguously defined individually, while the reaction equation format Eqs. (2')–(4') is properly defined only for a full set of independent equilibrium or non-equilibrium reactions.

With the reaction equations defined by the added components, many of the mathematical relationships defined in earlier sections can also be applied. The affinity of a restricted reaction j , \mathbb{A}_j , in a constrained equilibrium system is directly related to the chemical potential of the corresponding component.

$$\mathbb{A}_j = - \left(\frac{\partial G}{\partial \xi_j} \right)_{T,P,b_i \xi_k \neq j} = - \left(\frac{\partial G}{\partial b_j} \right)_{T,P,b_i \xi_k \neq j} = -\pi_j + M \quad (61)$$

where b_i is the amount of any of the components $b_1 \dots b_M$ in the system. For any chemical reaction that is not one of those defined by Eq. (54) the affinity is obtained as a linear combination of them and equilibrium reactions

$$\begin{aligned} \mathbb{A}_j &= - \sum_i \nu_{ij} \mu_i = - \sum_i \nu_{ij} \sum_{k=1}^{M+C} a_{ik} \pi_k = - \sum_i \nu_{ij} \sum_{k=M+1}^{M+C} a_{ik} \pi_k \\ &= - \sum_{k=M+1}^{M+C} a_{kj} \pi_k \end{aligned} \quad (62)$$

where ν_{kj} is the stoichiometric coefficient between the reaction j and component k .

It is possible that in a system where the extent of one or more reactions are constrained, the modelled time behaviour of the system approaches a state where the affinity or affinities are zero without the state in question being the actual equilibrium state of the system. Such a state would be a local, but not global free energy minimum of the system in respect to the specified reaction extents. Provided that the applied reaction rates give a sufficiently accurate description of the real reactions taking place in the system, such a local minimum state corresponds to a real long term metastable state. In such cases constrained chemical

Table 2
Systems with a constrained work coordinate.

System	Work coefficient	Work coordinate
Surface	σ (surface energy)	$A = \sum_i A_i n_i$ (area)
Donnan equilibrium	$\Delta \phi^e$ (electrochemical potential difference)	$-q^e = - \sum_i F z_i n_i^e$ (charge)
Constrained volume	ΔP^s (osmotic pressure difference)	$V^s = - \sum_i V_i n_i^s$ (subvolume)

Table 3
Systems with a constrained work coefficient (field).

System	Work coefficient	Work co-ordinate
Magnetized	B (magnetic flux density)	$m = \sum_i m_i n_i$ (magnetic moment)
Electrically polarized	E (electric field)	$p = \sum_i p_i n_i$ (dipole moment)

potential (affinity) could not be reasonably used as an alternative to constrained reaction extent for specifying the state of the system.

Corresponding to Eq. (35) it is possible to form a relationship between chemical potentials in a rate constrained system

$$\mu_i^0 + RT \ln a_i - \sum_r \pi_r a_{r,i} = \mu_i^0 + RT \ln a_i + \sum_r \mathbb{A}_r a_{r,i} \quad (63)$$

Setting the affinity (corresponding component chemical potential π_j) to a fixed value can be used to calculate restricted equilibrium states with a fixed affinity or deviation from equilibrium, or when affinity is set zero, equilibrium (in respect to the specified fixed reaction) without redefining the system stoichiometry. A standard state value for species for a system with given T , P and \mathbb{A}_r could be defined following Eq. (15) by relation Eq. (64)

$$\mu_i^0(T, P, \mathbb{A}_r) = \mu_i^0(T, P, \mathbb{A}_r = 0) + \mathbb{A}_r a_{r,i} \quad (64)$$

but typically applying the fixed chemical potential condition via the added component is more practical.

3.6. Application examples

A collection of various example systems and their related work coefficients and coordinates is presented below. In Table 2 systems with a fixed work coordinate are shown.

The minimised free energy function G' and the molar free energy are given by (Eqs. (9) and 10), the adjusted standard state by Eq. (36), and the equipotential between species of the same stoichiometry in different phases or parts of the system (chemical or electrochemical potential) is given by Eq. (13). The stoichiometric coefficient between the new component and each species is given by Eq. (47) and the relationship of the corresponding chemical potential and work coefficient by Eq. (48).

Example cases with a fixed work coefficient are given in Table 3. The minimised free energy function G is given by

$$G = G = \sum_i \mu_i n_i \quad (65)$$

when the effect of constant work coordinate is applied by modified standard states [following Eq. (28)] and from the equation

$$G' = G = \sum_i \mu_i n_i - \pi_j b_j \quad (66)$$

when the effect of the work co-ordinate (field) is applied via a new component. The molar free energy in both cases is the chemical potential. When new components are used, (Eqs. (39) and 46)

apply for the stoichiometric coefficients and the component chemical potential.

Analogous to the examples in Table 3, non-specific ionic interactions (Debye–Hückel and various variations of the Davies equation) can also be handled via Legendre transform (Alberty, 2003; Blomberg and Koukkari, 2009). From the computational point of view the system behaves as if the semi-empirical interaction energy were a product of an electrostatic work coefficient and coordinate.

$$G_{ex} = -\frac{\alpha RT\sqrt{I}}{1+B\sqrt{I}} z_i^2 n_i \quad (67)$$

The corresponding stoichiometric coefficients for the specified ionic strength and fixed chemical potential are

$$a_{r,i} = z_i^2 \quad (68)$$

$$\pi_r = -\frac{\alpha RT\sqrt{I}}{1+B\sqrt{I}} \quad (69)$$

The related effects caused by constant activities (including pH) of certain species can be applied directly based on Eq. (24).

Example systems where the applied constraint and the corresponding chemical potential do not form a work coefficient and coordinate pair are listed in Table 4.

In these cases when the component amount is constrained, the minimised free energy function is the Gibbs energy of the system as defined by Eq. (41). The energy and entropy terms (and therefore chemical potentials) may still contain added work coefficient-dependent terms (as they do in the nanoparticle case).

4. Results

4.1. Surface and interfacial energy

The model application for surface and interfacial systems has been discussed previously both for a liquid surface in (Pajarre, et al., 2006a, 2006b), where the single surface layer is modelled as a separate phase whose constituents interact only with each other, and for a multilayer model (Pajarre, et al., 2013) including non-ideal interactions between different layers that has been developed for metal-oxide surface, and tested for liquid-liquid metal alloy interfaces.

In a system with a liquid–vapour surface or liquid-liquid interface the derivative of the free energy with respect to interfacial area is the surface or interfacial tension

$$\left(\frac{\partial G}{\partial A}\right)_{T,P,n_i} = \sigma \equiv L_h \quad (70)$$

In the current work the surface or interface has been modelled with a finite number, one or more, individual monomolecular layers. With the simplifying assumption that the molar surface

areas of individual constituents are independent from system composition

$$\frac{\partial A_i}{\partial X_j} = 0 \quad (71)$$

the contribution of an individual interfacial layer k on the surface or interface energy can be included in the free energy equation as

$$\mu_i^k = \sum_{j=1}^M a_{j,i}\pi_j + \sigma^k A_i = \sum_{j=1}^M a_{j,i}\pi_j + a_{ji}\pi_{M+k} \quad (72)$$

with the following relations based on (Eqs. (39) and 40)

$$a_{k+M,i} = \frac{A_i^k}{A_0} \quad (73)$$

$$\sigma^k = \frac{\pi_{M+1}}{A_0} \quad (74)$$

where the normalization constant A_0 has the units of $\text{m}^2\text{mol}^{-1}$. NL in Eq. (72) is the number of interfacial layers. σ^k refers to the interfacial energy contribution of an individual layer, the physical interfacial energy given by

$$\sigma = \sum_{k=1}^{NL} \sigma^k \quad (75)$$

The μ_i^k in Eq. (72) is the molar free energy of constituent i on the layer k , as stated in Eq. (10). In the models described here, it has been assumed that the direct energetic effects related to the surface were restricted to the top most atomic or molecular layer of the surface. With that convention applied, following (Eqs. (13) and (36)), the chemical potential can be expressed on the layer closest to the surface by equation (superscripts s and b denote the surface layer and bulk respectively)

$$\mu_i^s = \mu_i^{s,0} + RT \ln a_i^s - \sigma A_i = \mu_i^{b,0} + \sigma_i A_i + RT \ln a_i^s - \sigma A_i = \mu_i^b = \mu_i \quad (76)$$

and on other interfacial layers by (superscript α denotes the interfacial layer)

$$\mu_i^\alpha = \mu_i^{b,0} + RT \ln a_i^\alpha - \sigma A_i = \mu_i^b = \mu_i \quad (77)$$

The molar free energies for the surface and interfacial species, as defined by Eq. (10), can be calculated for example based on the Redlich–Kister model (Pajarre et al., 2006b, 2013). In Pajarre et al. (2013) the excess energies were evaluated considering both the compositions of the individual layer in question and its nearest neighbours using the equation

$$G^{ex,k} = n^k \sum_i \sum_j \left(\frac{1}{2} (1-m^0) \Omega_{ij}^{k,k} x_i^k x_j^k + \frac{1}{2} m^0 \left(-\frac{1}{2} \Omega_{ij}^{k+1} x_i^{k+1} x_j^{k+1} - \frac{1}{2} \Omega_{ij}^{k-1} x_i^{k-1} x_j^{k-1} + \Omega_{ij}^{k,k+1} x_i^k x_j^{k+1} + \Omega_{ij}^{k,k-1} x_i^k x_j^{k-1} \right) \right) \quad (78)$$

for the excess free energy for an individual layer k , where $\Omega_{ij}^{k,k}$, $\Omega_{ij}^{k,k+1}$ and $\Omega_{ij}^{k,k-1}$ are composition dependent interaction energies within layer k and between it and its nearest neighbours and m^0 a geometric parameter expressing the factor of nearest neighbours of a species that are in one of the adjacent layers in a compositionally uniform system. For the derivation thermodynamically consistent relations it was necessary for the multilayer system to add further constraint(s) that kept the composition of the interfacial layer closest to the bulk equal to that of the bulk, the interfacial energy contribution of the additional constraints approaching zero with an increasing number of layers (Pajarre, et al., 2013). Example results for calculations in metal alloy and metal–oxygen systems are shown in Fig. 1.

Table 4

Example system with additional components that are not directly linked to a work coordinate.

System	Stoichiometric coefficient for the constraint	Component chemical potential
Spherical nanoparticle	$(A_i - \frac{2V_i}{r}) \frac{1}{A_0}$	$\sigma_i A_0$ (surface energy · normalization constant)
Reaction extent or affinity constrained system	$\xi_r = \sum_i a_{r,i} n_i$ (extent of reaction r)	$-\Delta_r$ (affinity of reaction r)

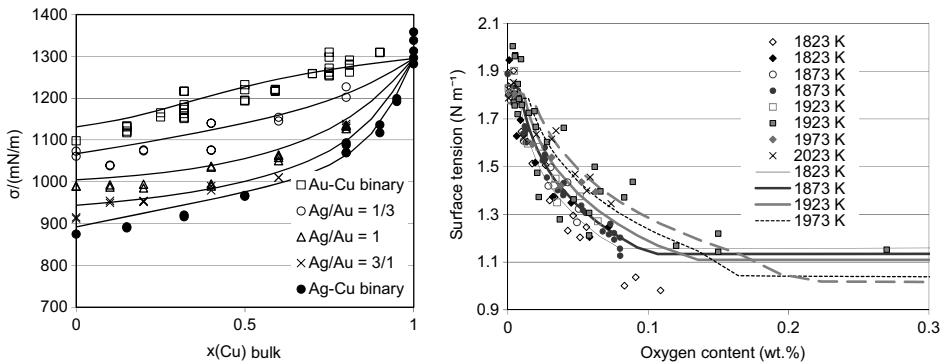


Fig. 1. Surface tension in Ag–Au–Cu metal alloys system (left) and iron–oxygen system (right). The model and experimental data for Ag–Au–Cu alloy as presented from a previous work by the authors (Pajarre et al., 2006b, 2013).

Table 5
Stoichiometry for a nanoparticle model.

Phase	Species	Components	
		Me	Geo
Solid surface	Me ^s	1	$\left(-\frac{2V_{Me}^s}{r} + A_{Me}^s\right) \frac{1}{\lambda_0}$
Liquid surface	Me ^l	1	$\left(-\frac{2V_{Me}^l}{r} + A_{Me}^l\right) \frac{1}{\lambda_0}$
Solid second layer	Me ²	1	$-\frac{2V_{Me}^2}{r} \frac{1}{\lambda_0}$
Solid core	Me ^c	1	$-\frac{2V_{Me}^c}{r} \frac{1}{\lambda_0}$

4.2. Volume-constrained system

In a system in which the volume of part of the system is constrained, an additional pressure component, affecting its chemical potential, applies to that part. For straightforward application of the current method it is necessary that the partial molar volumes are not functions of phase composition, although they could be functions of pressure. In an ion-exchange model, such as the one made for pulp fibres in Koukkari et al. (2002) and Pajarre et al. (2006a), a constraint on the water volume is an essential feature. Only the molar volume of the water itself (assumed to be incompressible) is considered here. The free energy from Eq. (9) can then be stated as

$$G' = \sum_i \mu_i n_i - \Delta P \cdot V_{H_2O} n_{H_2O}^\alpha = G - \Delta P V^\alpha = G^\beta + F^\alpha + V^\alpha p^\beta \quad (79)$$

where the last term is constant. The stoichiometric coefficient related to the constraining component is directly proportional to the molar volume.

$$a_{r,i} = \frac{V_{H_2O}}{V_j^0} \quad (80)$$

The osmotic pressure difference is consequently obtained as

$$\Delta P = -\pi_r V_j^0 \quad (81)$$

In principle it could be expected to be possible to predict the swelling behaviour of the fibres applying the calculated osmotic pressure together with the modelled charge state and a model for the fibre wall elasticity, but even a semi-quantitative model has been found to be elusive.

4.3. Nanoparticles with a combined area and volume constraint

Small-scale systems can have volume and surface that area interlinked. Considering the simplest case of a spherical particle, the changes in volume and area are connected by the equation

$$dA = \frac{2dV}{r} \quad (82)$$

Therefore, the balance equation for surface area related to molar area and volume can be written as

$$\sum_i dn_i \left(A_i - \frac{2V_i}{r} \right) = 0 \quad (83)$$

If the change in total volume (and therefore radius) is relatively small, the value in brackets in Eq. (83) can be taken as a constant similarly to molar volumes and areas in the previous sections. If one considers the system to be made of a surface layer (1) and a core and takes as the limiting phase transition for melting the formation of liquid surface layer on a solid core, one can define a system with stoichiometry according to Table 5, where the core is divided into an inner core (c) and a monolayer (2) closest to the surface layer.

The components of the system are for the elements (in this example only one element), and for the surface area of the particle (Geo). To simplify the computational system the liquid–solid interfacial energy of a partially molten system is considered to be a property of the liquid layer alone. The definition of free energy in the system is somewhat subtle as discussed by Reiss (1965). As a simplification, here it is assumed that a suitable constant average value can be used for the surface energy of the solid. The Euler equation for internal energy of a fully solid or liquid particle is given following Eq. (4)

$$U = TS - P^0 V + \sigma_{Me(\alpha)} A + \mu_{Me(\alpha)}(P^0) n_{Me} \quad (84)$$

where (α) denotes the physical state (solid or liquid) and P⁰ is used to emphasise that the standard state value is the one based on the external pressure of the system. The minimised free energy when there is no external constraint on the surface energy or surface area² is given by

$$G' \equiv U - ST + P^0 V = \mu_{Me}(P^0) n_{Me} + \sigma_{Me(\alpha)} A \quad (85)$$

² The added constraint in the stoichiometry in Table 4 (or Eq. (83)) is really for particle sphericity and the assumption that the number of spherical particles is not changed. While not discussed here, with orientation dependencies ignored, the spherical form is the one corresponding to minimum energy.

Correspondingly, the standard states for the core and the second layer can be given by

$$\mu_{Me(\alpha)}^{i,c,0} = \mu_{Me(\alpha)}^{i,2,0} = \mu_{Me(\alpha)}^0(P^0) \quad (86)$$

and for the solid surface by

$$\mu_{Me(s)}^{i,1,0} = \mu_{Me(s)}^0 + \sigma_{Me}^s A_{Me}^s \quad (87)$$

and for a liquid surface on a solid core:

$$\mu_{Me(l)}^{i,1,0} = \mu_{Me(l)}^0 + \sigma_{Me}^l A_{Me}^l + \sigma_{Me}^{sl} A_{Me}^l \frac{A^2}{A^1} \quad (88)$$

The ratio of the area of the interface between the first and second atomic layers, A^2 , and the surface area, A^1 in Eq. (88) can be estimated by

$$\frac{A_2}{A_1} = \left(1 - \frac{3V_{Me(l)}}{A_{Me(l)}r}\right)^{\frac{2}{3}} \quad (89)$$

The chemical potential of the component Me , π_{Me} is the chemical potential of the macroscopic unconstrained substance Me in the system. With the definitions used, it is given for one chemical component fully solid or liquid system by Eq. (90) (superscript α refers to either solid or liquid state)

$$\pi_{Me} = \mu_{Me}^{0,\alpha} + \frac{2V_{Me}^\alpha}{rA_0} \pi_{AConstrain} = \mu_{Me}^{0,s} + \frac{2V_{Me}^\alpha}{r} \sigma_{Me}^\alpha \quad (90)$$

The differences in chemical potential in the particle and a macroscopic phase in a same state can be related to the differences in vapour pressures. The familiar Kelvin equation directly follows from Eq. (90).

$$\pi_{Me} - \mu_{Me}^{0,\alpha} = RT \ln \frac{P_{Me}}{P_{Me}^{0,\alpha}} = \frac{2V_{Me}}{r} \sigma_{Me}^s \quad (91)$$

where P_i^0 is the partial pressure of substance i in equilibrium with a macroscopic phase in state α . The total free energy for the particle is given by

$$P_{Me}^0 = P^{ref} \exp\left(\left(\mu_i^{0,\alpha} - \mu_i^{0,g}\right)/RT\right) \quad (92)$$

On component basis the free energy of the system is given by

$$\begin{aligned} G' &= b_{Me} \pi_{Me} + b_{Geo} \pi_{Geo} = n_{Me} \left(\left(\mu_{Me}^{0,\alpha} + \frac{2V_{Me}^\alpha}{r} \sigma_{Me}^\alpha \right) + \left(\frac{V_{Me}^\alpha}{r} \sigma_{Me}^\alpha \right) \right) \\ &= n_{Me} \left(\mu_{Me}^{0,\alpha} + \frac{3V_{Me}^\alpha}{r} \sigma_{Me}^\alpha \right) = n_{Me} \mu_{Me}^{0,\alpha} + A \sigma_{Me}^\alpha \end{aligned} \quad (93)$$

in agreement with (Eqs. (85) and 90) integrated over particle size.

The graphs in Fig. 2 for melting of tin and silver nanoparticles have been calculated assuming the interfacial energy between the

solid and liquid follows the perfect wetting condition (Eq. (94)) (Eustathopoulos, 1983).

$$\sigma^{sl} = \sigma^s - \sigma^l \quad (94)$$

The data used in calculations is listed in Table 6.

The model based on stoichiometry in Table 5 and standard states given by (Eqs. (86)–88) compared with experimental data for Sn (left) and Ag (right). Experimental data are from Tang et al. (2012) and Chen et al. (2010) for silver and from Lai (1996) for tin.

While a reasonably good match between the basic model (solid curve) and the experimental data was found with Sn, an agreement with Ag data could be reached only assuming (following (Sim and Lee, 2014)) that the effective solid surface energy (taking into account as adjustable correction factor the effect of surface strain and anisotropic nature particle surface) was higher than the tabulated one.

The dotted curve on the right side of Fig. 2 is calculated assuming a correction factor of 1.17.

$$\sigma_{Ag}^{s(effective)} = 1.17 \sigma_{Ag}^s \quad (95)$$

It can be noted that the model used approximately matches the one were the melting point of the particle is calculated based on equal chemical potential (not free energy) (Lee, et al., 2007; Sopousek, et al., 2014; Sim and Lee, 2014). Assuming the thickness of a monolayer is small compared with the particle radius (and for simplicity that the differences in molar volumes and solids can be ignored), the condition for free energy change being favourable for the formation of a molten surface layer in the model described above is given by

$$\frac{\Delta G_i^{fus}}{V_m} + (\sigma^l - \sigma^s) 4\pi(r)^2 + \sigma^{sl} 4\pi(r - \Delta r)^2 < 0 \quad (96)$$

This can be further simplified assuming $\Delta r \ll r$ and that Eq. (94) is valid in a form that could be derived assuming equal chemical potentials for solid and liquid particles.

$$\Delta G_i^{fus} < \frac{2(\sigma^s - \sigma^l)V_m}{r} \quad (97)$$

4.4. Systems with an external magnetic field

The chemical system for a free energy minimiser can be defined either following Eq. (28) and modifying the standard states for the given field strength (without defining any additional components), or by applying one or more additional components whose chemical potentials are set following Eq. (46) based on the field

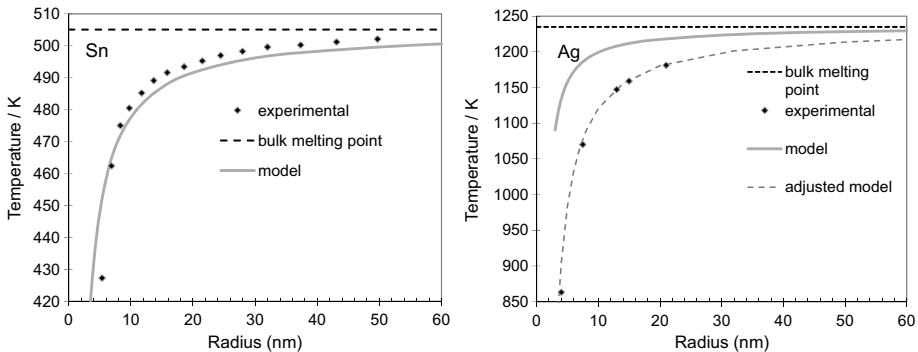


Fig. 2. Melting temperature of metallic nanoparticles.

Table 6
Thermodynamic data for the nanoparticle calculations.

Surface tension	σ_{Ag}^s (N/m) = 0.9256 – 0.000228(T/ K – 1234.93) (Lee, 2004)
	σ_{Ag}^l (N/m) = 1.1 – 0.00047(T/ K – 1234.93) (Murr, 1975)
	σ_{Sn}^s (N/m) = 0.5472 – 0.000065(T/ K – 505.08) (Lee, 2004)
	σ_{Sn}^l (N/m) = 0.671 – 0.00013(T/ K – 505.08) (Alchgirov, et al., 2001)
Molar volume (Iida and Guthrie, 1988)	V_{Ag}^s (m ³ /mol) = 11.6 · 10 ⁻⁶ (1 + 0.000098(T/K – 1234.93))
	V_{Ag}^l (m ³ /mol) = 11.2066 · 10 ⁻⁶ (1 + 0.000098(T/K – 1234.93))
	V_{Sn}^s (m ³ /mol) = 17 · 10 ⁻⁶ (1 + 0.000087(T/K – 505.08))
	V_{Sn}^l (m ³ /mol) = 16.6 · 10 ⁻⁶ (1 + 0.000087(T/K – 505.08))
Free energy of melting (Dinsdale, 1991, 2009)	G_{Ag}^{fus} (J/mol) = 11025.076 – 8.89102(T/K) – 1.033905 · 10 ⁻²⁰ (T/K) ⁷
	G_{Ag}^{as} (J/mol) = 11025.076 – 8.89102(T/K) – 1.033905 · 10 ⁻²⁰ (T/K) ⁷

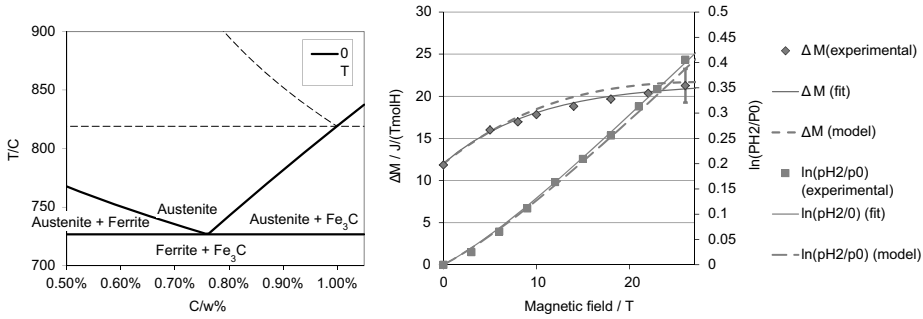


Fig. 3. Left: Effect of magnetic field on the equilibrium phase diagram in the Fe–C system. Right: Equilibrium hydrogen pressure and magnetic moment as a function of magnetic field strength with a LaCo₅-H system. Experimental data points (Yamamoto et al., 1995) shown with a smoothed fit together with a model curve for both equilibrium pressure and magnetization based on measured magnetic moment and pressure values respectively. Error bars for ΔM from the original paper.

strength dependent magnetisation properties of the matter. The second method has been found by the authors to be more readily applicable to calculations that are repeated with multiple field strengths. The applicable equations in this case are

$$a_{r,i} = \frac{m_i^n}{m_i^0} \tag{98}$$

for the stoichiometric coefficient, and

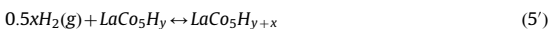
$$\pi_r = m^0 \int m' dB \tag{99}$$

when the molar magnetic moment can be factorized

$$m_i \equiv m'(B)m_i' \tag{100}$$

If the magnetic moment is assumed to have a constant (= saturation) value, the m' in (Eqs. (99) and 100) can be set to unity. For example, the effect of magnetic field on the equilibrium between austenite (γ -Fe, FCC) and ferrite (α -Fe, BCC) as described by Ludtka, et al. (2005) can be calculated by this way as shown in Fig. 3, left, with $a_{r,BCC} = 12.6$ corresponding to $m = 12.6 \text{ J} \cdot \text{mol}^{-1} \text{ T}^{-1}$ (Ludtka, et al., 2005) and $\pi_r = B \cdot (\text{Jmol}^{-1} \text{ T}^{-1})$. The thermodynamic data otherwise is from FactSage 6.3 (Bale, et al., 2002, 2008).

In a paramagnetic system, such as the one studied by Yamamoto et al. (1995) the magnetic moment is a function of the field strength. In that work, the equilibrium between LaCo₅ hydrides and hydrogen gas was explored. ΔM in Fig. 3 is defined as the change in saturation moment per desorbed mol of hydrogen atoms. The adsorption-desorption reaction in the system can be written as



so that the standard chemical potential of LaCo₅H_{4.2+x} can be determined by the equations

$$\mu_{LaCo_5H_{y+x}}^0(B=0) = \mu_{LaCo_5H_y^0} + \frac{x}{2} RT \ln \left(\frac{P_{H_2}(B=0)}{p^0} \right) \tag{101}$$

and

$$\mu_{LaCo_5H_{y+x}}^0 = \mu_{LaCo_5H_{y+x}}^0(B=0) - x \int_0^B \Delta M dB \tag{102}$$

A good correspondence between magnetically induced changes in phase equilibria and independently measured magnetization of phases could be obtained by the current authors by applying (Eqs. (101) and 102) for either calculating the equilibrium hydrogen pressure with an applied additional work term (Section 3.4) corresponding to smoothed experimental magnetization change, or in reverse for calculating the required change in magnetisation caused by desorption to match the experimental hydrogen pressure data (Fig. 3, right).

The discussion here has been restricted to magnetic fields, but the basic formulation of the problem with electric fields would be analogous.

4.5. Donnan equilibrium

For a system in which the electrochemical Donnan equilibrium is present, a new component needs to be defined for the electrical charge for each additional subvolume in the system (Koukkari, et al., 2002; Pajarre et al., 2006a, 2006b). The related new constraint equation is

$$\sum_i n_i^z z_i = 0 \tag{103}$$

The potential difference in a Donnan equilibrium system is caused by electrically charged species that are not freely mobile. The electrical work related to them can be stated (taking into account Eq. (103)) as

$$dW = \sum_i \Delta\phi^\alpha Fz_i dn_{i(\text{immobile})}^\alpha = - \sum_i \Delta\phi^\alpha Fz_i dn_{i(\text{mobile})}^\alpha \quad (104)$$

A Donnan equilibrium free energy problem requires at least two additional components related to the charged species. At least one constraining the immobile species, amount of which in the pulp suspension models is a fixed quantity (bound, carboxylic or sulphonic acid groups), and whose chemical potential is without practical interest, and one for the overall charge balance. Based on Eq. (104), the work term common to all the charged species is

$$L_{j,i} n_i = - \Delta\phi^\alpha Fz_i n_i \quad (105)$$

Setting $a_i \equiv z_i$ the Donnan potential difference is obtained as

$$\Delta\phi^\alpha \equiv (\phi^\alpha - \phi^\beta) = - \frac{\pi_r}{F} \quad (106)$$

The equipotential, commonly called the electrochemical potential, that is the same in both aqueous phases for mobile ions, following Eq. (13), is given by

$$\mu_i = \mu_i^0 + RT \ln a_i + \Delta\phi^\alpha Fz_i = \mu_i^0 + RT \ln a_i + \Delta\phi^\alpha Fz_i \quad (107)$$

The μ_i in Eq. (107) [rather than merely 'chemical' part of it ($\mu_i^0 + RT \ln a_i$)] is the chemical potential of the species i as defined by Eq. (1) and other fundamental relationships in thermodynamics. As pointed out by for example Guggenheim (1967), the 'chemical' and 'electric' parts of it are not experimentally measurable and have questionable meaning as physical entities. For the purposes of computational thermodynamics it is useful to define individual ion activities and activity coefficients that are compatible with well definable and measurable activities and activity coefficients of neutral combinations of them. The models used by the authors have in common that the aqueous solution has been modelled applying the Pitzer non-ideality model (Harvie, et al., 1984) while the multicomponent model has also included solid precipitates, and when applicable, a gas phase exchanging carbon dioxide with the solution. The specifics of the individual ion activity coefficients and the corresponding implicit pH scale have been discussed e.g. by Harvie, et al. (1984).

An example of the Donnan theory applied to a laboratory system is presented in Fig. 4. All the calculation results for each pH are from a single multi-component equilibrium calculation, just as the various metal amounts were determined from a single sample. The

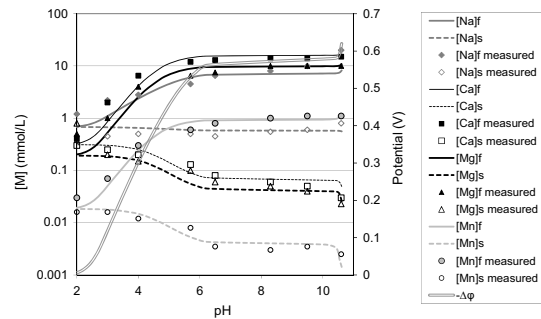


Fig. 4. Experimental and modelled concentrations inside and outside pulp fibres together with the modelled Donnan potential in a (single) aqueous pulp suspension sample. Drawn based on the model and data presented by Koukkari and Pajarre (2006a).

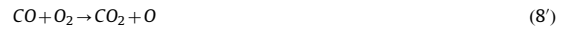
Pitzer model was used to describe the aqueous phase non-ideality. The formation of solid precipitates is predicted close to pH 11.

The process simulation work based on applying ion exchange phenomena in the CFE framework has been done both for relatively simple models with small number of free energy minimisation units and process integrates of paper machines and pulping mills with a few hundred chemistry units (Koukkari, et al., 2007) (Pajarre, et al., 2008) (Kangas, et al., 2012) and (Kalliola, et al., 2012).

4.6. Systems constrained by reaction kinetics

Reaction constrained free energy models have been presented e.g. for industrial production of precipitated calcium carbonate (PCC) (Koukkari, et al., 2011) and high temperature oxidation of TiCl_4 to TiO_2 (Koukkari, et al., 2008a) and studies of biomass gasification. (Kangas, et al., 2014a, 2014b; Kangas, 2015; Yakoboylu, et al., 2015). Here, a short introduction to utilising reaction-constrained free energy models is given with modelling of nitric oxide emissions used as an example.

Thermal NO emissions in high temperature post flame conditions can be described with the Zeldovich mechanism (Zeldovich, 1946), described by Eqs. (5') and (6'). However during the oxidation of hydrocarbons the radical over-shoot increases the NO emissions rapidly, which cannot be modelled with the Zeldovich mechanism alone. Thus this simplified model is extended with a description of carbon monoxide oxidation and oxygen radical build-up (cs (7') and (8'))



When the NO emissions are considered, the reaction (6') is immediately followed by reaction (7'). The rate of formation of NO is given in Eq. (108). The oxidation of CO is described as the sum of reactions (8') and (9') and rate Eq. (109) is applied. As a numerical simplification, when the difference in the rates of reactions (8') and (9') is estimated at less than 10% of the rate of reaction (8'), the O-radical concentration is estimated by the quasi steady-state approximation [Eq. (110)]. Reverse reaction rates are included for all reactions with the method described by Koukkari et al. (2011).

$$r_{\text{NO}} = 2r_1 = 2k_1[\text{N}_2][\text{O}] \quad (108)$$

$$r_{\text{CO}} = -r_2 - r_3 = -k_2[\text{CO}][\text{O}_2] - k_3[\text{CO}][\text{O}][\text{M}] \quad (109)$$

$$[\text{O}] = k_2 k_3^{-1} [\text{O}_2][\text{M}]^{-1} \quad (110)$$

The constraints for the system are set for the O, NO and CO species. Detailed description of kinetic parameters applied here are given in an earlier work (Coda Zabetta and Hupa, 2008), where also large detailed kinetic model (DKM) of the oxidation of carbohydrates and formation of nitric oxides is described. The steady state condition has been set via the affinity (A_{O}) of the oxygen dissociation reaction (10')



The affinity can be expressed by thermodynamic and kinetic parameters and concentrations of other species than oxygen by applying (within vicinity of the steady state)

$$\frac{A_{\text{O}}}{RT} = - \ln \left(\frac{Q_{\text{O}}}{K_{\text{O}}} \right) = - \ln \left(\frac{\sqrt{x(\text{O}_2)} [\text{O}]}{K_{\text{O}} [\text{O}_2]} \right)$$

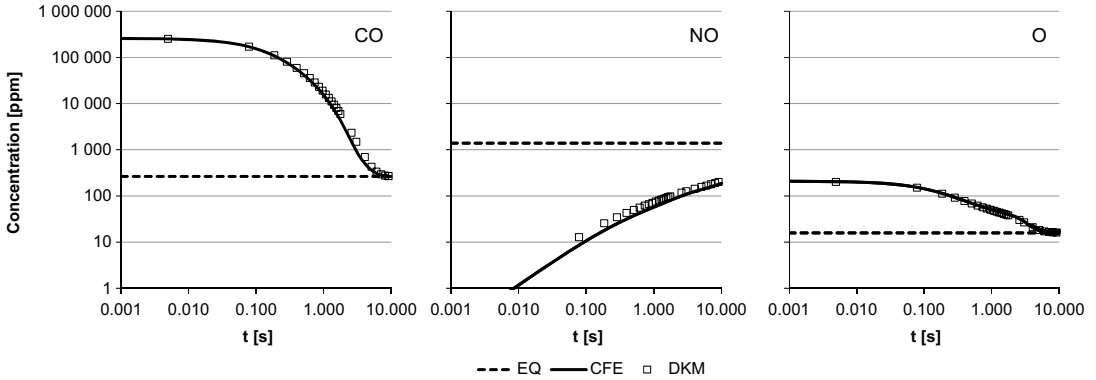


Fig. 5. NO emissions during carbon monoxide oxidation. Results from the CFE model compared to the detailed kinetic model (DKM) (Coda Zabetta and Hupa, 2008) and equilibrium value (EQ). Temperature is 1500 °C, dry air (21 v-% O₂ and 79 v-% N₂) and excess air, λ = 1.2 applied.

$$= -\ln\left(\frac{1}{[M]} \frac{k_2}{k_3} \left(\frac{1 - Q_2}{1 - \frac{Q_2}{K_o}}\right) \sqrt{x(O_2)}\right) \quad (111)$$

The last part of Eq. (111) could be factored to

$$\begin{aligned} \frac{A_0}{RT} &= -\ln\left(\frac{1}{[M]} \frac{k_2}{k_3} \left(\frac{1 - Q_2}{1 - \frac{Q_2}{K_o}}\right) \frac{[O_2] \sqrt{x(O_2)}}{[O] K_o}\right) - \ln\left(\frac{[O] \sqrt{x(O_2)}}{[O_2] K_o}\right) \\ &= -\ln\left(\frac{r_2}{r_3}\right) - \frac{A_{O(\text{steady})}}{RT} \end{aligned} \quad (112)$$

where the second term is the affinity (divided by RT) at the quasi steady-state.

The DKM is used to calculating the validation data for this example. Fig. 5 illustrates a case where carbon monoxide is combusted in dry air (79 v-% of nitrogen and 21 v-% of oxygen; lambda 1.2). A laminar plug-flow reactor model is applied with a residence time of 10 s. The temperature is 1500 °C.

Nitric oxide formation and oxidation of carbon monoxide are similar when the results from the CFE and DKM models are compared. The radical over-shoot at the beginning of combustion can be predicted correctly with the CFE method. More details for applying CFE method when modelling the nitric oxide emission is given by authors in Kangas et al. (2015).

4.7. Mass transfer between phases and paraequilibrium

From the computational point of view, a mass transfer process between two phases is a reaction in which the species *i* in phase *α* is transformed into the same species (or a species of equal stoichiometry) in another phase. Therefore, the reaction rate and affinity equations derived earlier also apply equally to such mass transfer processes. As a specific example, the metallurgical paraequilibrium can be considered where new phases are formed so that they have the same alloy composition as the parent phase but substitutional elements like carbon can equilibrate between them. The constraints in a free energy model are of the form Pelton et al. (2014).

$$\sum_i (Y_{Me} a_{Me,i}^\alpha - a_{Fe,i}^\alpha) n_i^\alpha = 0 \quad (113)$$

where *Y_{Me}* is the mole ratio of iron (or other reference metal chosen for the system) and metal *Me* in the parent phase. The superscript *α* refers to the new formed phase under study. In general, a description for a system with *M* metallic components (including the reference metal, typically iron) and *P* phases

(including the original parent phase) will contain (*M*−1)(*P*−1) constraints.

As a simple example in the paraequilibrium between FCC and BCC iron in *Fe* : *Cr* : *Ni* : *C* system with the relative molar amounts of 6:2:3, the matrix coefficients corresponding to Eq. (113) result

$$A' = \begin{array}{c|cccc|cccc} & \text{FCC} & & & & \text{BCC} & & & & \\ \hline \text{Fe} & \text{Fe:C} & \text{Cr} & \text{Cr:C} & \text{Ni} & \text{Ni:C} & \text{Fe} & \text{Fe:C} & \text{Cr} & \text{Cr:C} & \text{Ni} & \text{Ni:C} \\ \hline & 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 \\ & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 1 \\ & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 3 & 3 & 0 & 0 \\ & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & 0 & 2 & 2 \end{array} \quad (114)$$

The three first rows correspond to the elements *Fe*, *Cr*, *Ni* and *C*, the two last ones to constraint equations of Eq. (113) relative to *Cr* and *Ni*. Paraequilibrium systems and the corresponding phase diagrams are discussed in more detail in Pelton et al (2014).

5. Discussion

The thermodynamic framework has been applied to many kinds of systems. The basic thermodynamic relationships are universally valid. The extensive range of application of the constrained Gibbs energy minimisation descends from this generic base. For the best practical applicability of the models, some additional assumptions that are only possibly or approximately valid typically need to be made. For example, in the surface monolayer model the assumption of no interactions between the surface layer and the bulk make the model elegantly simple as a mathematical construction. It is also obvious that is not physically reasonable to assume it to be strictly accurate. However, as a practical tool it has found wide use (Egry, et al., 2010; Tanaka, et al., 1996) and has shown to work reasonably accurately for many, even if not all, kinds of systems. Additional assumptions, which are validated only insofar as the resulting model gives reasonable predictions compared with experimental data, are needed for the mono- or multilayer excess energies.

To operate with constant stoichiometric coefficients (that are not functions of composition) in a Gibbs energy minimiser, it has been assumed in all models that the molar work coordinate contributions (such as molar areas and volumes) are not functions of composition. While not actually studied, it is the opinion of the

authors that in a typical inorganic interfacial systems the inaccuracy related to this is not significant compared with both inaccuracies related to experimental data and assumptions made regarding the form of the thermodynamic excess energy functions when the bulk data are adapted to a surface or an interfacial layer.

The fundamental guiding principle of work related to systems with reaction constraints has been to strive towards a model containing only the necessary amount of kinetic complexity while applying the constrained equilibrium thermodynamics as much as possible. Highly complex reaction kinetic models have been criticized in the area of gas phase chemistry on the basis that because of uncertainties related to modelling parameters, the increased complexity is unlikely to bring additional value to the results (Keck, 2008). With multiphase processes and kinetics the uncertainties will probably tend to be even greater. Therefore, it has been considered valid in the work regarding reaction-constrained systems to aim at system descriptions that capture the most essential parts of the rate-dependent processes with only a few constrained reactions. Such descriptions are of course only an approximation of the physical system; shortcomings of the approach are probably more likely to become apparent when behaviour of complex systems is studied over moderate temperatures and short time intervals (Kangas, 2015).

The Donnan equilibrium model application for pulp suspensions has been found to be valuable to predict the chemical phenomena and process behaviour in pulping, bleaching and paper machines (Kalliola, et al., 2012; Kuitunen, 2014), while the assumed non-specific nature of ion-exchange interactions is known to face limitations with di- and multivalent ions, especially in systems with high ionic strengths (Kangas, et al., 2012; Sundman, et al., 2010; Sundman, 2008).

6. Conclusions

The topic of this work has been to extend the application area of traditional Gibbs energy minimisers with systems of theoretical and practical interest. The aim has been to develop methods that are as generic as possible, within the possibilities offered by the minimisers, for both greater understanding the thermodynamic relationships in the systems and for easier future application of the method to systems that are not handled in present work.

The application area of standard Gibbs energy minimisers has been extended, for the most part using existing published phase models with new data and stoichiometry definitions.

The chemical problems that have been worked on have included reaction rate constrained systems, surface and interfacial tension in molten systems, Donnan equilibrium as part of a multiphase model, and systems with external magnetic fields.

The greatest practical success has been achieved with the models that combine reaction kinetics with partial thermodynamic equilibrium calculation and ion exchange models based on Donnan equilibrium which have both been applied with success in real-life industrial design and development work with multicomponent, multiphase systems. Elementary kinetic models and steady-state assumptions can be incorporated as part of the reaction-constrained free energy models, providing an alternative for large detailed kinetic models in some practical problems, while the combination of fairly simple kinetics and multiphase calculations has been found to be valuable in many practical problems. Applied to liquid surface energies the method has been successful in handling systems with multiple components and complex non-equilibrium data.

List of symbols

A	$(M \times N)$ matrix of stoichiometric coefficients
A	surface or interfacial area (m^2)
\mathbb{A}_i	affinity of reaction i ($\text{J} \cdot \text{mol}^{-1}$)
a_i	activity of species i
$a_{j,i}$	stoichiometric coefficient between component j and species i , matrix element of A
B	magnetic flux density ($T = V \cdot s \cdot \text{m}^{-2}$)
b	$(M \times 1)$ column vector of molar amounts of components (mol)
b_k	molar amount of component k (mol)
Q_j	reaction quotient of reaction j
E	electric field ($\text{N} \cdot \text{C}^{-1}$)
F	Helmholtz free energy (J)
F	Faraday constant ($\approx 96485 \text{ J} \cdot \text{mol}^{-1} \cdot \text{V}^{-1}$)
G	Gibbs free energy (J)
G'	free energy function (other than G) matching system specific constraints (J)
\mathbb{G}	free energy function as calculated by a free energy minimiser (J)
\mathbb{G}'	modified minimised free energy function in a free energy minimiser (J)
H	enthalpy (J)
k_i	reaction rate constant of reaction i
K_j	equilibrium constant of reaction j
L	Lagrangian function
L_j	thermodynamic work coefficient j
L_j^i	thermodynamic work coefficient j for a species i as pure phase (such as surface tension σ_i)
l_j	thermodynamic work coordinate j
$l_{j,i}$	molar contribution to the thermodynamic work coordinate j by species i
M	number of components in the system
m	magnetic moment ($\text{J} \cdot \text{T}^{-1}$)
N	number of species in the system
NR	number of reactions
n	$(N \times 1)$ column vector of molar amount of species (mol)
n_i	molar amount of species i (mol)
P	pressure ($\text{Pa} = \text{N} \cdot \text{m}^{-2}$)
P_i	partial pressure of species i (Pa)
p^{ref}	reference pressure ($10^5 \text{ Pa} = 1 \text{ bar}$)
p	electric dipole moment ($\text{C} \cdot \text{m}$)
Q	heat (J)
q	charge (C)
R	gas constant
r_X	rate of formation of species x ($\text{mol} \cdot \text{s}^{-1} \cdot \text{cm}^{-3}$)
r	radius of a particle
S	entropy ($\text{J} \cdot \text{K}^{-1}$)
T	temperature (K)
U	internal energy (J)
V	volume (m^3)
v_i, w_i	stoichiometric coefficient of species i in a reaction
V	volume (m^3)
ΔG^{fus}	Gibbs free energy of fusion (J)
ϕ	electric potential (V)
λ_j	Lagrange multiplier related to component j ($\text{J} \cdot \text{mol}^{-1}$)
λ	column vector of Lagrange multipliers related to component j ($\text{J} \cdot \text{mol}^{-1}$)
μ_i	chemical potential of species i ($\text{J} \cdot \text{mol}^{-1}$)
μ_i^0	standard state chemical potential of species i ($\text{J} \cdot \text{mol}^{-1}$)
μ_i^f	molar free energy of species i ($\text{J} \cdot \text{mol}^{-1}$)
$\mu_i^{f,0}$	standard state molar free energy of species i ($\text{J} \cdot \text{mol}^{-1}$)
ξ	$(R \times 1)$ column vector of extents of R reactions

ξ_r	extent of reaction r
μ_k	chemical potential of component k (J mol^{-1})
σ	surface energy (J m^{-2})
σ_i	surface energy of pure substance i (J m^{-2})
χ_i	molar magnetic susceptibility of i ($\text{J T}^{-2} \text{mol}^{-1}$)

Subscript and superscript related terminology (X is a generic Roman or Greek character)

X_i	where i can be also be j , k or l , partial molar quantity corresponding to the integral quantity X of the whole system (unless X_i is explicitly given in the preceding list)
X^α, X^β	part or value of the quantity X related to the part α or β only
\mathbf{X}^T	transpose of matrix \mathbf{X}

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Chemical thermodynamics offers a universally applicable and rigorous method to describe the possible processes and final states in any chemically reactive system. Numerical programmes that minimise Gibbs energy have been used for decades to calculate equilibrium compositions and phase diagrams. Such software has been especially focussed on materials and metallurgical chemistry, combustion and aqueous solutions. A considerable amount of work has been spent to make the programs robust and efficient.

In this work, the use of Gibbs energy-minimising programmes is extended to novel systems by using additional constraints and by adjusting the data input to include the effects of various kinds of thermodynamic work. The same principle applies to non-equilibrium processes constrained by slow reaction kinetics as well as for systems restricted by system geometry. The method is shown to be applicable to reactive chemical systems, aqueous pulp suspensions, liquid surface properties and nanoparticle phase transformations.



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