

Calculating Thermochemical Equilibrium for Multiphysics Simulations of Nuclear Materials

Development of Yellowjacket Gibbs Energy Minimiser

by

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An oral defense of this thesis took place on 15-November-2022 in front of the following examination committee:

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The above committee determined that the thesis is acceptable in form and content and that a satisfactory knowledge of the field covered by the thesis was demonstrated by the candidate during and oral examination. A signed copy of the Certificate of Approval is available from the School of Graduate and Postdoctoral Studies.

Abstract

Nuclear fuels and structural materials are highly complex systems that are remarkably challenging to understand and model. Material behaviours are influenced by many different phenomena such as mechanics (e.g., dislocations, cracking, etc.), chemistry (e.g., oxidation, reactive transport, corrosion, etc.), heat and mass transport, amongst others. Moreover, lower scale phenomena inform and drive the phenomena at larger scales. The strong interactions between multiple physics at different length and time scales creates a need for multi-scale, multi-physics modelling tools. In nuclear fuels and structural materials, the problem gets compounded by the fact that, in addition to an extreme environment, the composition of the system changes with time. For such complex systems, computational thermodynamics plays a valuable role in predicting many phenomena and is, at minimum, necessary for understanding and informing others. For this reason, there has been an increasing interest in incorporating equilibrium thermodynamics calculation in multi-physics frameworks such as Multiphysics Object Oriented Simulation Environment (MOOSE).

A phenomena of great interest in advanced reactors that employ high-temperature fluids, such as molten salts, is that of corrosion of fluid-facing structural materials. A new MOOSE-based tool named Yellowjacket has been developed to simulate such corrosion and the primary objective of this work is to develop a new equilibrium thermodynamic solver to provide thermodynamic material properties and boundary conditions for Yellowjacket and other MOOSE-based simulation codes. While several thermodynamics codes already exist, the new software, called Yellowjacket–GEM, aims to bring native equilibrium thermodynamic capability to the MOOSE framework and aims to address several concerns such as computational performance, limitations on system size and models, and software quality assurance.

Yellowjacket–GEM exploits the fundamental laws of thermodynamics and uses state-of-the-art numerical solvers and global optimisation algorithms to accurately and efficiently model and predict phase evolution in nuclear materials. By using the advanced solver capabilities of Portable, Extensible Toolkit for Scientific Computation (PETSc) and coupling them with comprehensive global optimisation algorithms, the rate of convergence and robustness of the equilibrium calculations has been enhanced. The equilibrium thermodynamics solver has also been coupled with the MOOSE Phase Field module to improve the fidelity of molten-salt corrosion models.

Keywords: Computational Thermodynamics; Gibbs Energy Minimisation; Global Optimisation; Yellowjacket Gibbs Energy Minimiser; Mutiphysics Object Oriented Simulation Environment (MOOSE)

Author's Declaration

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Statement of Contributions

As of May 2018, all theses and dissertations are required to have a Statement of Contributions, which appears immediately before the Table of Contents. The Statement of Contributions must indicate the unique contributions of the author in the context of collaborative research that may have involved others who worked on various parts of the research described in the thesis. Types or contributions can include identification and design of the research project, performance of various parts of the research, and data analysis. In addition, if any parts of the thesis research have been published as an article, or is under consideration for publication, then the publication information must also be included here.

Example 1

The work described in Chapter 4 was performed at the Futuristic Automotive Research Centre of Excellence (FARCE) in Hill Valley, California, using the Flux Capacitor testing laboratory operated by Dr. Emmett Brown. I was responsible for installing and testing flux capacitors in my automotive prototype vehicles.

Example 2

Part of the work described in Chapter 5 has been published as:

J.T.S. Allan, L.E. Prest, E.B. Easton, "The sulfonation of polyvinyl chloride: Synthesis and characterization for proton conducting membrane applications", Journal of Membrane Science, 489 (2015) 175-182. doi: 10.1016/j.memsci.2015.03.093.

I performed the majority of the synthesis, testing of membrane materials, and writing of the manuscript.

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*This perpetual motion machine she made today is a joke, it just keeps going faster and
faster...*

Lisa ... In this house, we OBEY the laws of thermodynamics!

Homer Simpson

1

Introduction

Over the years, nuclear science and technology has made many positive contributions towards improving the quality-of-life of millions of people. Nuclear provides the world's second-largest source of low-carbon energy but it also helps control the spread of diseases, assists in diagnosis and treatment of cancer, powers space exploration missions, and drives the advancement of industry, agriculture and technology. Nuclear energy is not only at the core of world's sustainable development efforts but is also poised to take on an even bigger role as the world collectively moves to decarbonise many hard-to-abate sectors of the economy.

As of 2022, around 440 nuclear plants around the world supplied 2653 TW h of electricity, around 10% of the world's total electricity [7]. Despite the strong support for, and growth in, intermittent renewable electricity sources in recent years, the fossil fuel contribution to power generation has remained virtually unchanged over the last decade and a half [7]. In its World Energy Outlook 2021, the Organisation for Economic Co-operation and Development (OECD) International Energy Agency (IEA) has proposed an ambitious *Sustainable Development Scenario* consistent with the goals clean and reliable energy and a reduction of air pollution, among other aims. In the scenario, by year 2050, nuclear based electricity generation should increase by 75% to 4714 TW h, a capacity growth to 669 GW_e [8]. Key to a sustained growth of nuclear power is demonstrating their safety, reliability and economy.

Though many nations across the globe, both industrialised and developing, are confident of the potential of nuclear energy, several challenges related to sustainability, reliability, economic competitiveness, safety, risk of proliferation, anticipated future needs beyonds electricity, and need for government support remain [9]. To meet these challenges and develop future nuclear energy systems, the Generation IV International Forum (GIF) is undertaking necessary research

and development to develop the next generation of innovative nuclear energy systems that can supplement today's nuclear plants and transition nuclear energy into the long term [10]. While promising in terms of sustainability, economics, safety and reliability, and proliferation resistance and physical protection, the Generation IV nuclear reactors pose unique challenges in terms of engineering design, modelling and construction of these reactors. The design issues are themselves quite complicated and span a wide array of knowledge domains such reactor physics, chemistry, materials science, fluid flow and heat transfer, etc. Safe and economical operation of any nuclear system relies heavily on the success of nuclear fuels and structural materials which must operate under extreme environments. Compared to current generation of reactors, advanced reactors will operate at higher temperatures, under higher irradiation, at higher pressures, and in some cases, like Molten Salt Reactors (MSRs), with fluids that present more challenging corrosion problems [11].

1.1. Material Challenges in Nuclear Systems

Design and discovery of materials most suited for a specific application is an intrinsic part of development of new technology as many engineering designs can only be as good as the materials available during design and innovation. In conventional materials, the mechanical, thermophysical and chemical properties are often of main interest but nuclear materials must overcome significant challenges to provide the desired levels of reliability and safety commensurate to strict quality assurance requirements. Nuclear reactors present extreme environments for components irrespective of the reactor technology and not only do materials need to meet the physical and chemical performance requirements, but must also demonstrate desirable nuclear physics characteristics. The core in particular presents an exceptionally harsh environment of high temperature, high pressure, high stresses, intense radiation and a chemically aggressive environment and the properties desirable from a nuclear perspective, such as high power density, exert high operational burdens on fuels and structural materials [12]. As advanced reactor designs gain increasing traction, the material-challenges are only going to get worse. Advanced reactors, such as Molten Salt Reactors, operate not only at higher temperature, pressure and irradiation flux but also with coolants that present more challenging corrosion problems than the current lot of Light Water Reactors (LWRs) and Heavy Water Reactors [11]. Moreover, Generation IV reactors are expected to have a longer operating time of at least sixty years. Some of the materials challenges are as follows:

- Nuclear materials must satisfy the standard design requirements like tensile properties, thermal creep, cyclic fatigue and creep fatigue but such properties are significantly affected

by degradation mechanisms resulting from radiation damage. Bulk radiation leads to low temperature radiation hardening and embrittlement, solute segregation and phase stability, irradiation creep, void swelling and high temperature helium embrittlement [13, 14].

- The LWR cores must behave well under mechanical stress, irradiation and corrosion due to hot water and steam. pH control and scavenging of radiolysis products has significant impact on corrosion, stress-corrosion cracking and CRUD formation.
- Extended operation and new operating regimes pose a new challenge as new degradation mechanisms due to corrosion or ageing may be revealed. This adds an extra layer of uncertainty to the material design and discovery process.
- Behaviour of oxide fuels interacting with Zr alloys under irradiation conditions is still an area of open research. Hydrogen/deuterium uptake and radiation induced hardening can compromise the cladding's resistance to pellet-cladding interaction under reaction-induced accident scenarios. In loss of coolant accident type scenarios, Zr oxidation can rapidly degrade cladding material properties.
- In advanced LWRs such as small modular reactors (SMRs), advanced manufacturing techniques, such as additive manufacturing, may be deployed but it would be important to compare the impact of microstructural difference on bulk material properties.
- In advanced reactors such as MSR, sodium-cooled fast reactor (SFR), and lead-cooled fast reactor (LFR), there will be an increased emphasis on strength, creep and creep-fatigue behaviour due to very high radiation damage driven by void swelling and phase stability.
- In high-temperature, high-dose advanced reactors, chemical interaction between coolant and structural materials will result in additional degradation mechanisms. In particular, corrosion of molten salt-facing structural materials in MSRs is expected to cause significant leaching and deposition.

1.2. Thermochemistry in Nuclear Systems

Thermochemistry and principles of computational thermodynamics play a key role in nuclear material modelling. Since, nuclear materials are continuously evolving due to transmutations and fission product generation, so do their material properties. The laws of thermodynamics

govern many phenomena in nuclear materials and are important for applications such as understanding the phase stability which affects nucleation and dissolution of phases, oxidation potential of cladding, thermochemical properties of fuels and many others. As such, thermodynamic principles are sufficient for predicting many phenomena and are, at a minimum, imperative to understanding more complex and dynamic physics. Some of the key applications of thermodynamics which make it an indispensable part of material design and discovery process include but are not limited to:

1. Understanding the fuel and cladding composition and microstructure, manufacturing and design of fuel and cladding materials, and prediction of thermal stability of fuel and cladding materials.
2. Understanding fission product chemistry and their effect on material properties.
3. Predicting chemical interactions between fuel and cladding materials and coolant.
4. Source term analyses and predicting phases that form between reactor materials under severe accident scenarios.
5. Optimising fuel salt composition and predicting impact of impurities on molten salt corrosion in MSRs

While the concepts of thermodynamics can be embodied in both non-equilibrium and equilibrium descriptions, it often thermodynamic equilibrium which is leveraged in applications. Even when the materials are, in many cases, in non-equilibrium conditions, an understanding of the phases that shall form under equilibrium conditions provides valuable knowledge as it gives the direction of evolution of the system. In fact, in nuclear materials, the high temperature conditions lead to a rapid approach to equilibrium and under suitable conditions, make equilibrium thermodynamics a suitable approximation.

1.3. Modelling and Simulation

Modern materials, including nuclear materials are developed using a combination of discovery, which involves evaluating existing materials to identify candidates with desirable properties, and design, which aims at creating new materials with predefined qualities [15]. While the traditional approach to discovery and design of materials was almost entirely experimental, recent developments in modelling and high performance computing have resulted in a much stronger collaboration and integration among theory, experiments and computational science. Multiscale, multiphysics models and simulations enable investigations over a wide range of

length and time scales which would otherwise be unfeasible using only experiments. Thus, computational models help augment and guide experimental campaigns and support economical discovery and design of materials within reasonable lead times.

Nuclear materials are subjected to extreme radiation environments that continuously complicate the physics and chemistry, and alter the thermo-mechanical properties of the material [15]. Complex interactions between the different physical phenomena occurring in the materials are often very tightly coupled and many important aspects are inherently multidimensional as well [16]. As an example, one can consider MSRs where, as shown in figure 1.1, multiple physics are required for understanding the behaviour and for predicting phenomena such as mass accountancy. Another aspect to consider is that of the different time and length-scales involved with length-scales ranging from inter-atomic spacing to meters, and time-scales ranging from microseconds to years. For example, radiation defects start within picoseconds at the atomistic scales and propagate to larger length-scales over time-scales which are several magnitudes longer.

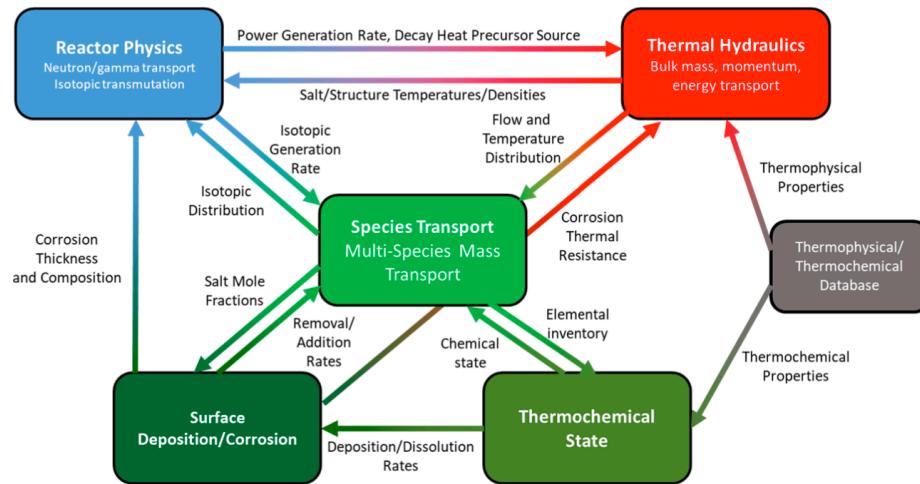


Figure 1.1: Multiphysics phenomena in molten salt reactors (MSRs) [17].

Evidently, modelling and simulation of nuclear materials requires a multiscale, multiphysics approach. However, such simulations have been decently challenging until recently and with significant limitations on the amount of computational resources available even a couple of decades ago, a majority of modelling and simulation efforts adopted an operator-splitting approach based on Picard iterations. Such simulations usually focussed on only the engineering scale behaviour and usually relied on continuum or bulk description of the phenomena. In doing so, experimental observations and operational experience were relied on for the validity of results and often very conservative safety margins were added to design parameters. As an example, nuclear fuel behaviour has been modelled as a solid mechanics problem coupled with conductive

heat transfer and fission gas release wherein the material properties are often either assumed to be constant or described using simplified models based on empirical correlations. Though these methods were suitable for previous and current generation of nuclear reactors, addressing the materials challenges for advanced reactors is usually beyond their capability. In fact, there has been an increasing impetus on leveraging lower scale information to inform models on larger scales and solving the governing equations as a system rather than as individual problems. Since such an approach is rooted in fundamental principles, the transfer of information between scales, through characteristic parameters such as density, energy, temperature, etc., results in a much more accurate description of material behaviour [15]. The numerous modelling and simulation tools available at different length and time scales are shown in figure 1.2.

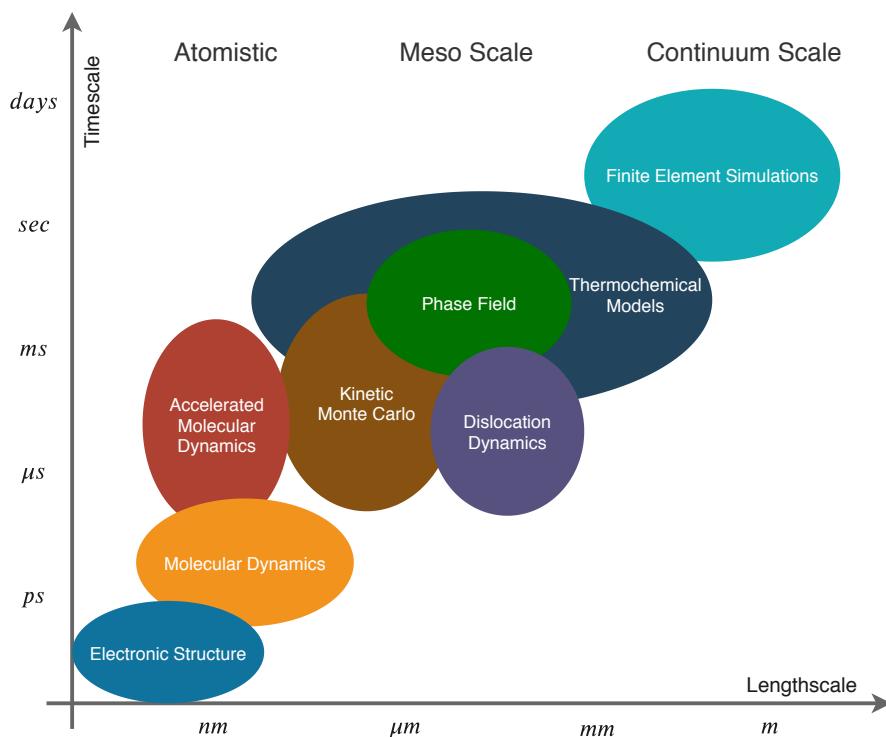


Figure 1.2: Multiscale theoretical and computational methods used for materials model development and computer simulation [15].

1.3.1. Computational Thermodynamics

The modelling and simulation tool that is of particular relevance to this work is computational thermodynamics. Phase and chemical behaviour of nuclear materials is governed by the thermochemical equilibrium state and, though in many systems, equilibrium may not be achieved, a thorough understanding of both transport and chemical evolution, and subsequently material

properties, is based on an accurate representation of thermochemical equilibria [18]. As an example, the oxygen chemical potential acts as the driving force for transport of oxygen in oxide fuels but a determination of these chemical potentials is impossible without determining the stable phases which depends on the oxygen-to-metal ratio which in turn is a function of burnup. For such complex systems, computational thermodynamics is an essential tool for calculating both phase equilibria and thermodynamic properties of the system. Computational thermodynamics is rooted in the *CALculation of PHAse Diagram* (CALPHAD) approach shown in figure 1.3. CALPHAD combines experimental and theoretical information and tunes parametric models to describe thermodynamic properties of materials like Gibbs energy, enthalpy, heat capacity, etc. [19].

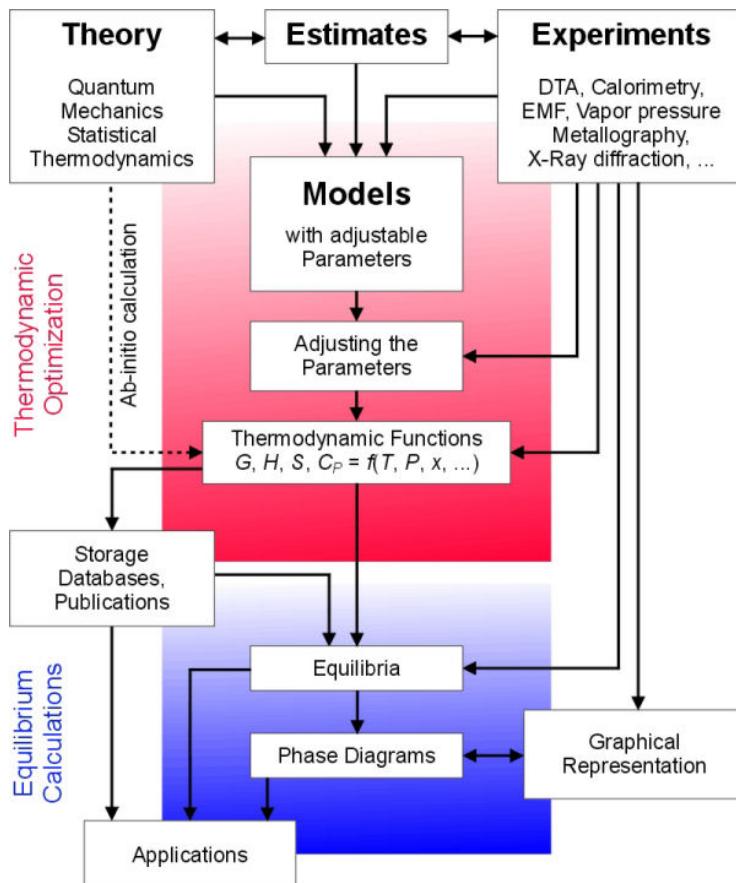


Figure 1.3: Principle of CALPHAD method by Zinkevich [20].

Capturing thermodynamic equilibria in multiphysics codes has traditionally relied on empirical correlations and the interest in direct coupling of thermodynamic equilibrium codes with multiphysics model is only a recent trend. While the empirical correlations do not convey the high fidelity of original thermodynamic analysis, performing thermodynamic equilibrium analy-

sis within multiphysics codes is normally a very complex process and can significantly impede the computational performance of such codes. However, the recent developments in high performance computing have facilitated the use of equilibrium thermodynamics in multiphysics simulations. Computational thermodynamics is of ever more importance in the discovery and design of materials for advanced reactors and is allowing phenomena hitherto not very well-understood even in current generation of reactors despite the years of experience.

The inputs and outputs of thermodynamic equilibrium calculations are shown in figure 1.4. Since thermodynamic equilibriums are isothermal and isobaric in nature, temperature and pressure are required as inputs along with the elemental composition of the material. While the equilibrium calculations are mathematically rigorous they do require thermodynamic models of materials to describe some parameters. This makes computational thermodynamics partly-empirical in that the thermodynamic models are often created from experimental data but efforts to use atomistic calculations to inform and improvise the thermodynamic models are gaining traction. The results from equilibrium calculations include the stable phases, speciation of the stable phases, and several thermodynamic properties like Gibbs energy, chemical potentials, heat capacities, etc.

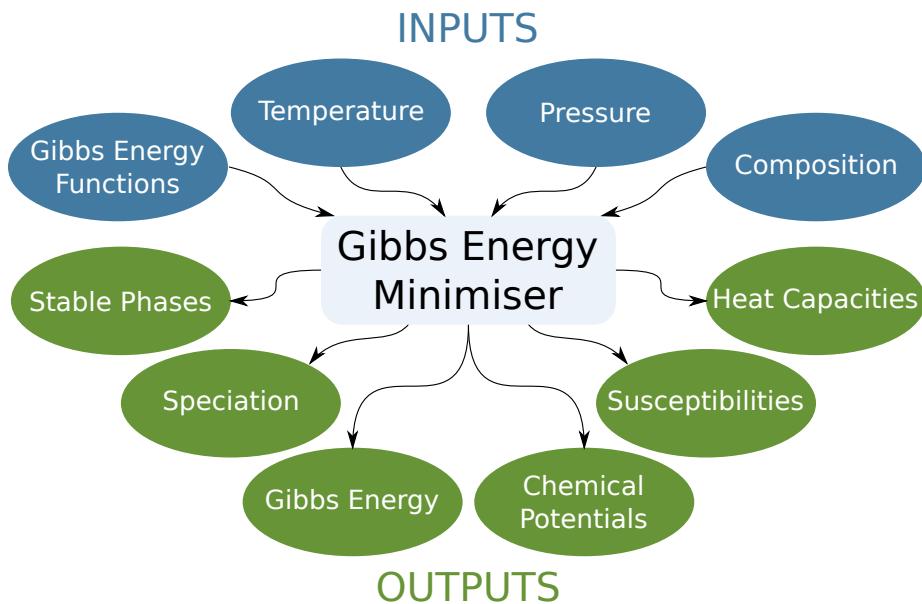


Figure 1.4: Input and output parameters of thermodynamic equilibrium calculations.

1.3.2. Multiphysics Object Oriented Simulation Environment

The Multiphysics Object Oriented Simulation Environment (MOOSE) is a simulation framework that has been developed with the aim of harnessing modern massively parallel computing

resources to perform complex multiphysics simulations. Exploiting the modern computational power is in itself a daunting task but the task of achieving complex simulations becomes ever more daunting for users when considerations such as numerical solve, discretisation of partial differential equations, etc. are added. The goal of MOOSE is to provide simplified interfaces for user facing tasks such as specification of partial differential equations, boundary conditions, material properties and all aspects of a simulation while handling complex background tasks such as parallel, adaptive, nonlinear, finite element solve internally [21]. Through the use of interfaces and inheritance, each portion of a simulation becomes reusable and an ecosystem for multiphysics simulations is formed allowing people from different groups and backgrounds to share code with growing capability. Originally created at the Idaho National Laboratory in the United States, MOOSE is open-source framework which leverages state-of-the-art libMesh code [22] for finite elements and the Portable Extensible Toolkit for Scientific Computation (PETSc) [23, 24] for leading-edge numerical methods/solvers. MOOSE has been used to build multiple community-developed physics "modules" [25–29] and several application libraries which are used by governments, industry and academia with applications ranging from nuclear fuel modelling to porous flow in 3D fractured porous media. MOOSE's capability is in contrast to what is often seen in commercial packages, where custom material models can limit the parallel scalability, forcing serial runs in the most severe cases [30].

For nuclear reactor modelling, apart from the MOOSE modules, several export-controlled applications have been developed. These include RELAP-7 [31] for system level thermal hydraulics, Rattlesnake [32] for neutronics, etc. For nuclear material simulations, the MOOSE framework consists of two main applications the macroscale fuel performance code Bison [16] and the mesoscale phase field code Marmot [33].

Simulation of nuclear reactor fuel performance involves complex thermomechanical processes between fuel pellets, made of fissile material, and the protective cladding barrier that surrounds the pellets. Bison is an engineering scale code developed to predict the nuclear fuel performance under normal, off-normal, and accident conditions. By using highly efficient computational methods, it enables three dimensional, fully coupled multiphysics simulations on high fidelity geometric representations of fuel pins/pellets. Bison has been designed to be highly scalable and does not require the use of operator splitting, staggered or predictor-corrector approaches [16].

Due to its simple concept and large range of applicability, the phase field approach is a popular and powerful tool to model microstructure and has been applied in problems such as grain boundary migrations, martensitic transformation, two-phase flow, etc. The phase field approach treats all material interfaces as diffuse by representing structural features with contin-

uous variables which smoothly transition from one value to another. Thus, phase field method not only eliminates the need to explicitly discretise boundaries and interfaces, it also enables describing microstructure through a system of partial differential equations. The Marmot phase field application has been developed to enable simulations of the microstructure evolution of nuclear fuels and materials under irradiation. By exploiting the object-oriented architecture of MOOSE, Marmot allows easy coupling of phase field with additional physics such as solid mechanics or heat conduction, to effectively predict the microstructural evolution at mesoscale. This allows prediction of evolution of material properties of nuclear materials under irradiation and can be used to inform engineering scale simulations and reduce the dependence of such simulations on empirical correlations. As a result, the multiscale framework can achieve true predictability even in compositional and operational regimes where little or no experimental data exists.

The software developed as part of this work adds native equilibrium thermodynamic capability to MOOSE and its applications.

1.3.3. Yellowjacket

Many emerging nuclear technologies, such as MSRs, use high temperature fluids like molten fluoride/chloride salts, which can lead to the corrosion of salt-facing structural materials. Not only does corrosion impact the performance of structural materials with the possibility of compromising their integrity but it can also lead to other problems just as blocking of salt flow loops due to leaching from hot sections of the loop and deposition in the colder sections. Molten salt corrosion is fundamentally different from corrosion in LWRs, where oxidation leads to formation of a passive oxide layer creating a self-healing mechanism, and most of the methods to control corrosion developed over previous centuries are of limited value [34]. In fluoride salts, the protective oxide layer on alloys typically relied upon for high-temperature corrosion resistance dissolves, thereby exposing the fresh alloy surface to the molten salt. In molten chloride salts, passivity has been observed; however, the oxide layer is prone to attack and may not provide the necessary corrosion protection [35]. The corrosion process is accelerated by the impurities present in the salt and enhanced further by the presence of dissimilar metals due to activity-driven corrosion. It has been observed the corrosion in molten salt is a microstructural phenomena with preferential leaching at grain boundaries as compared to bulk of the grain but there are significant gaps in the scientific understanding of the governing mechanisms such as the impact of impurities and irradiation [36–41].

Corrosion is an electrochemical process composed of oxidation and reduction reactions, which are defined by the thermodynamics and kinetics of the system. While thermodynamics

controls whether or not a material may corrode, kinetics influences how quickly the material will corrode. This corrosion behaviour is also significantly affected by the material microstructure and predicting corrosion therefore requires a multiphysics approach that can couple quantitative electrochemistry models of corrosion and chemical reactions with thermochemical equilibrium computations. Effectively, predicting corrosion and related phenomena like leaching and deposition requires a multiscale, multiphysics approach [42]. However, there has been a lack of dedicated tools for modelling molten salt corrosion and to bridge this gap, a suite of tools have been developed under the Nuclear Energy Advanced Modelling and Simulation (NEAMS) program of United States Department of Energy (US-DOE). The goal of this suite, shown in figure 1.5, is to couple atomistic and mesoscale modelling to thermochemical equilibrium calculations to create a unique corrosion modelling capability on the microstructural scale and use it to inform engineering scale codes aimed at solving species transport problem. At the core of the corrosion suite is the MOOSE-based application Yellowjacket that couples quantitative models of corrosion with thermodynamic equilibrium and chemical kinetics models to predict the rate of material loss, corrosion product production and precipitate production in advanced nuclear reactors. Yellowjacket relies on the phase field method for structural evolution and couples it with electrochemical descriptions, fracture models and thermochemical equilibrium solver to create a holistic environment for corrosion modelling and simulation [43].

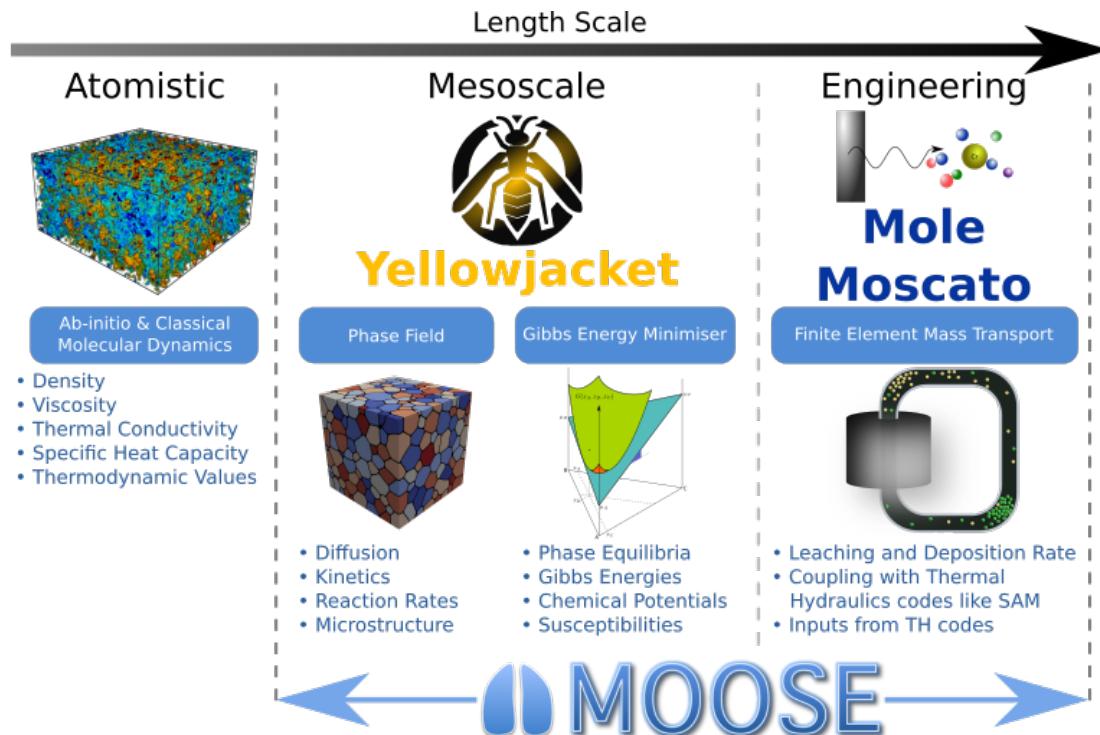


Figure 1.5: Yellowjacket corrosion suite.

In the case of Yellowjacket, as shown in figure 1.6, the phase field model requires several thermodynamic properties like Gibbs energies, chemical potentials and driving forces for the various phases which can be present in the system. This requires knowing the molar amounts of the different phases which would be present under given temperature, pressure and composition. However, at the interfaces, more than one phase can co-exist and the phase field models face a challenge in estimating the assemblage and thermodynamic properties. In such cases, a thermodynamic equilibrium solver can provide the required information to the phase field module. This is the prime driving force behind the development of Yellowjacket–GEM. One may argue that the system will not be at equilibrium and that kinetics of the system will drive the corrosion behaviour and therefore might question the appropriateness of thermochemical equilibrium calculations. While the system is not really at equilibrium, it can be safely assumed that in the limiting case the system will be at equilibrium at any point in space and time.

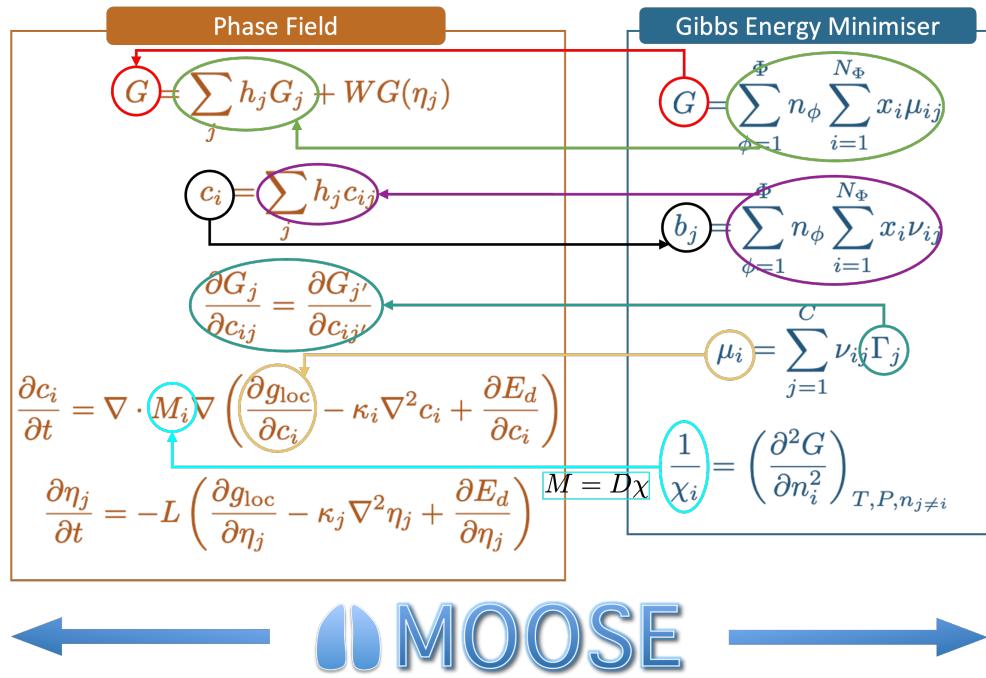


Figure 1.6: Information exchange between the phase field and equilibrium thermodynamics modules of Yellowjacket.

Yellowjacket is a multi-institutional collaborative effort between the Idaho National Laboratory, University of Florida, and Ontario Tech University. In Yellowjacket, the phase field module was implemented at University of Florida, computational thermodynamics development was performed as part of this PhD thesis at Ontario Tech University and MOOSE-integration was primarily done at Idaho National Laboratory. The main motivation behind this work was to enable direct coupling of thermodynamic equilibrium calculations in MOOSE-based multiphysics

simulation and a new Gibbs energy minimiser called Yellowjacket–GEM and the objectives, tasks and main outcomes are described in the next chapter.

The rest of this thesis is organised as follows: the motivation, objectives and deliverables are shown in [Statement of Work](#). A comprehensive literature review of the current computational thermodynamics methods and codes and global optimisation tools for phase equilibria is performed in [Literature Review](#) followed by a description, in [Thermodynamic Basis](#), of the basic thermodynamics principles that form the basis of this work. Conditions of phase equilibrium and the methods for computing them are described in ?? and their implementation in Yellowjacket–GEM is discussed in namerefchap:implementation. To highlight the capability and potential impact of the developed tool, several application of Yellowjacket–GEM are shown in [Results and Discussions](#) and is followed by the [Conclusions](#) and [Recommendations](#).

2

Statement of Work

2.1. Problem Statement

Facilitating the discovery and design of nuclear materials for innovative nuclear materials requires multiscale, multiphysics models and simulations and equilibrium thermodynamics forms an integral part of such simulations by calculating phase stability and other thermodynamic quantities required for many physical phenomena. The main motivation behind this research is to create native computational thermodynamics capability for the multiphysics framework MOOSE. The computational thermodynamics solver allows replacing empirical models of material properties with calculations rooted in laws of thermodynamics and allows one to capture the effect of system evolution on material properties and, by incorporating equilibrium thermodynamics in multiphysics simulations, an unprecedented level of sophistication can be achieved.

Achieving this objective, however, comes with several challenges. Equilibrium thermodynamic calculations are intrinsically very expensive and adding such calculations to any multiphysics simulation can massively increase the amount of time and resources required to solve the multiphysics problem. Not only is the cost of equilibrium calculations among the highest in the different physics involved in nuclear material simulations but it also scales very rapidly with the size of the system. In fact, the computational cost scales cubically ($O(C^3)$) as the number of components C in the system is increased and has the potential of making large simulations practically infeasible. This means that any thermodynamics code included in multiphysics simulations must be carefully designed to reduce the overheads and minimise the computational cost when possible. However, in doing so the reliability of such calculations can not be comprised since this can have obvious safety implications. Another challenge that is encountered in com-

putational thermodynamics is the dependence on thermodynamic databases wherein a poorly performed thermodynamic treatment can lead to spurious results that can be far from reality. While this is a challenge that cannot be addressed within a computational thermodynamics solver, having the capability of incorporating data from multiple sources and building flexibility in the code to adapt to changes in thermodynamic modelling can help mitigate some of these problems. Lastly, integration into multiphysics simulation is itself challenging because different simulation can have different requirements and the interface between thermodynamics and other physical models must be accommodating to the varying requirements. As an example, the thermodynamic quantities needed in a phase field simulation is often significantly different from those in source term analyses and the same interface to equilibrium calculation should be pluggable into both types of simulations without the need of significant redevelopment.

While several codes with the capabilities developed as part of Yellowjacket–GEM already exist, the rationale behind developing a new equilibrium thermodynamics code lies in the numerous limitations of these pre-existing tools. As all but a handful of these codes are standalone codes aimed at single calculations, phase diagram generation and database optimisation, the computational time is not of high importance and there has been an insignificant interest in improving their computational performance. Moreover, in order to maintain numerical stability, most of the current codes restrict the number of system components but the intended applications mean that systems with a very large number of components must also be handled. Among the codes that do exist with the capability of handling large systems and are aimed at multiphysics simulations, there are still several drawbacks. Thermochimica, for example, is well suited for incorporating in multiphysics codes but it doesn't meet the MOOSE software quality assurance (SQA) requirements and often the interface must be redeveloped based on specific applications. The procedural approach adopted in the development also makes reusing the existing code to adapt to new models harder and adding new capabilities can require significant developmental effort. A couple of other examples of codes falling into this category are OpenCalphad and PyCalphad and have similar considerations as Thermochimica.

2.2. Objectives

The overarching objective of this work is to incorporate native computational thermodynamics capabilities in multiphysics framework MOOSE through the development of a new state-of-the-art Gibbs energy minimiser called Yellowjacket–GEM. The software consolidates and integrates years of advancements and research in computational thermodynamics and leverages state-of-the-art nonlinear equation solvers and optimisation algorithms to enable real-time thermodynamic property calculation in multiphysics simulations.

Though the most substantial contribution of this work is the creation of the software from grounds up, it is not merely an exercise in software development. First, though several algorithms from literature are used, their implementation has a significant impact on the computational performance and the implementation had to be cognisant of this fact and the implementations in the literature were modified to reflect the evolution in computing architectures. Seconds, despite years of research into model and database development, it was realised that knowledge gaps exist in the understanding of many models such as the modified quasichemical model (MQM) and this work helped in improving the understanding of such models. Third, there is often a lack of understanding about the algorithms, their capabilities and limitations, and the interpretation of the results from equilibrium thermodynamics softwares and, through this work, an effort was made to clarify some of these choices. Lastly, despite years of research into global optimisation algorithms, a majority of current equilibrium codes use a rather simplistic sampling approach in identifying phases with negative driving force which often leads to failure in converge or inaccurate results. This work uses an experimental approach to quantitatively compare some promising global optimisation approaches in terms of their applicability to the phase equilibria problem.

Thus, while the creation of Yellowjacket–GEM in itself counts as an advancement in the field of computational thermodynamics, several contributions extending beyond the software tools have also been made. The major contributions of the work can be summarised as follows:

1. Development of a new MOOSE-based Gibbs energy minimiser written in C++ with support for several thermodynamic models used in nuclear material modelling. Since the code is currently export controlled, it has not been included here but the algorithms used have been shown through flowcharts in [Computational Implementation](#).
2. Development of interfaces for full integration of Yellowjacket–GEM in multiphysics simulations.
3. Improved understanding of the modified quasichemical model (MQM) which is the most widely used thermodynamic model for treating short-range ordering such as in molten salts. See [Thermodynamic Basis](#).
4. Quantitative comparison of global optimisation algorithms for application in phase equilibria calculations and incorporation of these algorithms in Yellowjacket–GEM. See [Computational Implementation](#).
5. Software quality assurance with rigorous source code control, continuous integration (CI)

and verification to comply with NQA-I standard of MOOSE and MOOSE-based applications.

2.3. Deliverables

The outcomes of this research were communicated in several ways including publications in peer reviewed journals, conference presentations and annual progress reports submitted to Idaho National Laboratory. The main deliverables of this work were as follows:

1. Code base for Yellowjacket–GEM delivered to Idaho National Laboratory's via export controlled repository on Nuclear Science User Facility (NSUF) High Performance Computing (HPC)'s GitLab instance.
2. Annual progress reports submitted to Idaho National Laboratory in September 2019, September 2020, August 2021 and September 2022.
3. Four publications in peer-reviewed journals and one on global optimisation for phase equilibria which is currently in preparation. See [List of Publications](#).
4. Conference talks and posters presented at several conferences including NuFuel, Candu Fuels Conference and TMS Annual Meeting & Exhibition. See [List of Publications](#).
5. An internship at Idaho National Laboratory from June 2021 to September 2022, working on MOOSE integration of Yellowjacket–GEM.

3

Literature Review

Robust and fast methods for computing chemical equilibrium in complex systems are widely used in materials and chemical industries. While industrial applications essentially require calculation tools capable of discriminating between stable and unstable phases and converging to nontrivial solutions, numerical equilibrium calculations have historically focussed on representing dominant chemical reactions using the Law of Mass Action. It was only during and after World War II that numerical approaches amenable to computer programming were developed. Since then, there has been significant growth in the number of methods and softwares for solving the equilibrium thermodynamics problem.

3.1. Numerical Methods for Thermodynamic Equilibrium

Up until the 1940s, chemical equilibria computations were based on two different methods. The first relied heavily on the assumption that only a few molecular species would be present in the final equilibrium and the law of mass action could be applied to these systems and the resulting system of non-linear equations was solvable using the relatively unsophisticated techniques of the time. The second method relied on a tedious trial-and-error approach with the user's intuition playing a significant role [44]. It was only during the Second World War that, fuelled by the development of rockets, research towards developing computational methods for chemical equilibrium gained momentum. This research was mainly driven by the fact that an accurate knowledge of chemical equilibrium of the propellants was a requirement for the design of rockets. However, all the methods developed at the time were based on the law of mass action and the procedure was not scalable to very large systems where it would be difficult to

account for all the possible reactions.

The first major breakthrough in computerising chemical equilibrium calculations was made after the Second World war. In 1946, Brinkley came up with a generalised scheme to approach equilibrium computation by giving an analytical criterion for the number of independent components in a multi-component system [44]. However, the most significant breakthrough in the calculation of thermodynamic equilibria was made at the RAND Corporation by White, Johnson and Dantzig [45]. Since then a few other methods have been proposed but none has found as much success as the method proposed by White *et al.* In fact, even the method proposed by White *et al.* has only undergone a few minor changes and more recent algorithm developments have focussed on other complimentary routines, such as initialisation, describes later. This section reviews the major methods that have been proposed to compute thermodynamic equilibria.

3.1.1. Equilibrium constants

The earliest computational method for finding thermodynamic equilibrium relied on the equilibrium constants of individual reactions and were primarily applied to gas phase equilibria. The equilibrium constant, K , is defined as follows:

$$K = \frac{\prod^{N_p} x_{i,p}^{\nu_i}}{\prod^{N_r} x_{i,r}^{\nu_i}} \quad (3.1)$$

where, $x_{i,p}$ and $x_{i,r}$ denote the mole fractions of species i in product and reactants respectively, ν_i denotes the stoichiometric coefficient of i , and, N_p and N_r denote the number of product and reactants, respectively.

While equation (3.1) is easily applicable to single reactions, calculating the concentration of species in multiple simultaneous reactions each with a unique equilibrium constant is quite laborious. The first computational procedure for the calculation of the composition at chemical equilibrium of systems of many constituents was proposed by Brinkley [46] and is known as *Brinkley's method*. Subsequently, a number of modifications were made to this method resulting in a number of other variant methods, such as the *Brinkley-Krieger-White method* [47], the *NASA method* [48], etc. The Brinkley-Krieger-White method, also known as the *Brinkley-Newton-Raphson* method, is perhaps the most popular and, as is evident from the name, used the Newton-Raphson method to solve the system of non-linear equations [44]. The NASA method [48] shares the same fundamentals as the Brinkley's method.

Although Brinkley's method serves well for small systems suitable for hand calculations, it

relies heavily on user intuition and prior knowledge of the reactions taking place. Furthermore, it neglects the effects of non-ideality and its derivatives due to mathematical difficulties [48]. Eventually, owing to generalities and numerical superiorities of the Gibbs Energy Minimisation (GEM) method, the Brinkley method fell out of favour among the scientific community.

3.1.2. Gibbs energy minimisation (GEM)

The numerical technique of minimising the Gibbs energy of the system was originally proposed by White, Johnson and Dantzig [45] and is based on the method of steepest descent of second order and was therefore referred to as the *Second Order Steepest Descent Method*. This methodology, now commonly described as *Gibbs energy minimisation*, has also been called as the *RAND method* owing to the employer of the developers of the method.

Gibbs energy minimisation is based on identifying a unique combination of species and phases that yield a minimum in the integral Gibbs of a closed isothermal isobaric system from amongst the many possible candidates. The selection of candidates is based on the first and second laws of thermodynamic and is subject to the conditions of thermochemical equilibrium - satisfaction of the Gibbs phase rule, conservation of mass. Numerically, this amounts to systematically adjusting the Lagrangian multipliers - some which represent the chemical potential of the system components - to change the estimated amount of each species, making the Gibbs energy of the system progressively more negative.

While the initial popularity of the GEM method was fuelled by its generality, reduced dependence on user intuition and convenience of programmability [48], several other advantages have become more apparent as time has progressed. Boynton advanced the method to include stoichiometric phases coexisting with solution phases [49] and Eriksson [50] demonstrated the use of the method for non-ideal solutions and showed that when dealing with multiple solution phases, the numerics does not get significantly complicated. In fact, the number of simultaneous linear equations to be solved is equal to the number of system components and the number of phases estimated to be stable at equilibrium [44, 49–51].

Over a period of time, a number of other techniques have been proposed for the thermochemical equilibrium problem. Most of them, however, have relied on the original GEM method [45] as the fundamental approach with minor modifications to adapt to the nature of specific problem at hand. These modifications include accounting for charged species [52], accounting for non-traditional effects such as surface tension [53], magnetic ordering [54] and Donnan effect [55]. Some of the more significant variations, such as the *First Order Steepest Descent Method* proposed by Storey and van Zeggeren [56], demonstrated poorer performance and lacked the ability to distinguish between local minima and maxima [44, 56]. Another varia-

tion relies on removing the mass balance constraint resulting in an unconstrained optimisation problem. This method, proposed by Lantagne *et al.* and based on a penalty function using the Broyden-Fletcher-Goldfarb-Shanno (BFGS), technique simultaneously minimises two objective functions - Gibbs energy of the system and the residual of the mass constraint vector [57, 58]. The method must also satisfy the linear inequality constraints related to mole numbers being non-negative. While the approach offers the advantage of solving fewer linear equations, the dual optimisation method is less numerically stable compared to single optimisation methods [58].

An impediment in numerically solving thermodynamic equilibria is the requirement of an initial estimate for the optimisation. Eriksson and Thompson [59] proposed a method called *levelling*, which is capable of closely estimating the dominant species and their quantities in the phase assemblage. The process requires a relatively small number of iterations and the number of iterations to reach convergence does not rapidly increase with the number of species in the system. These characteristics of levelling are well suited to large systems, such as nuclear materials. Another problem that arises when using GEM method is the negative mole fraction arising due to the evaluation of logarithmic term while computing the chemical potentials. White *et al.* proposed using a numerical dampening technique to avoid erroneous results. Finally, ensuring that the Gibbs energy of the system is at global minimum and not at one of the many local equilibria is a significant challenge that must be handled properly to ensure correct results. Despite the challenges, GEM has been shown to be the best available method for computing thermodynamic equilibrium and is the de-facto default solver in almost all the thermodynamic equilibrium codes.

3.1.3. Partitioning of Gibbs energy (PGE)

The developer of Gibbs energy minimisation, W.B. White, proposed another numerical technique named *Partitioning of Free Energy* [60], which is substantially different from the GEM method. In this method, the mass equations are differentiated with respect to Lagrange multipliers and though a number of numerical advantages were shown, the method was only applicable to homogeneous systems comprised of ideal gas and could not be used for heterogeneous systems involving pure stoichiometric phases and/or multiple solution phases [44, 60]. The significant disadvantages of this method compared to GEM led to it being mostly dismissed by the thermodynamic community until Piro [5] reconsidered a modified form of the method by incorporating principles of the levelling method and employed it in the development of thermochemistry library Thermochimica [61].

Piro's approach [61] constraints the Gibbs' phase rule and the Gibbs energy of the system

while iterating to satisfy the mass balance constraint. The method constrains the chemical potential of the species and phases in terms of the chemical potentials of the system components, thus formally relating the mass balance to chemical potential of system components. The objective of the method is to partition the Gibbs energy of the system among the elements to minimise the residuals of the mass balances. Thus, in this method, the solver attempts to find the roots of the mass balance residual vector while the Gibbs criteria is inherently verified and need not be verified at every iteration thus simplifying the numerical approach. This approach can then be used for heterogeneous systems, which may include stoichiometric phases, ideal solution phases and even non-ideal solution phases.

Numerically, GEM is an optimisation procedure while PGE solves for the roots of a simultaneous system of linear equation [44]. As a result, the chemical potential terms for the solution phase are included in the GEM method but absent from the functional vectors in PGE. Additionally, the approaches differ in the computation of a new set of mole numbers, which must be positive. Computation of non-negative logarithmic terms can result in non-real numbers in GEM causing numerical difficulties and necessitating the use of numerical dampening which in turn reduces the rate of convergence. However, in PGE, additional dampening is not required since the mole fractions, being defined as exponentials of real numbers, will always be positive.

A disadvantage of the PGE method is that it requires moles fractions to be explicitly expressed as functions of chemical potentials of the species. As shown before, chemical potentials of the species can be uniquely expressed as a functions of mole fraction but not the other way around. Thus for non-ideal species, the PGE method fails in the absence of explicit functions of mole fractions in terms of chemical potentials. Despite all its numerical advantages, the PGE method proved to be less robust than the GEM approach and was eventually replaced by GEM in Thermochimica. Though promising, the method has only been used in a limited number of other applications, a couple of them being by Riel *et al.* [62] and by Kruskopf [63].

3.1.4. Other Methods

Several other numerical methods have been proposed for computing thermodynamic equilibria but none has received success like GEM. The most notable of these is the approach by Srinivas and Rangaiah which uses the Random Tunnelling Algorithm (RTA) based on the concept of Terminal Repeller and Unconstrained Subenergy Tunnelling (TRUST) algorithm [64]. The TRUST algorithm is akin to the steepest descent method but differs in that the minimisation is performed in two stages - a local minimisation followed by global minimisation through tunnelling [58]. However, the method is limited by the system size and shows satisfactory performance for relatively small systems of up to 10 variable [58].

Another method that was proposed by the developers of the GEM method is based on linear programming. George B. Dantzig applied the Simplex method to thermodynamic equilibrium problem at constant temperature and pressure [65, 66]. In the simplex method, a linear approximation of Gibbs energy of the system is minimised instead of the non-linear system. The linearised model is obtained by representing the logarithmic function in the chemical potential term by the following:

$$\beta_i = \alpha_i \ln \alpha_i \quad (3.2)$$

which is represented as a piecewise linear approximation as shown in fig. 3.1. Though the

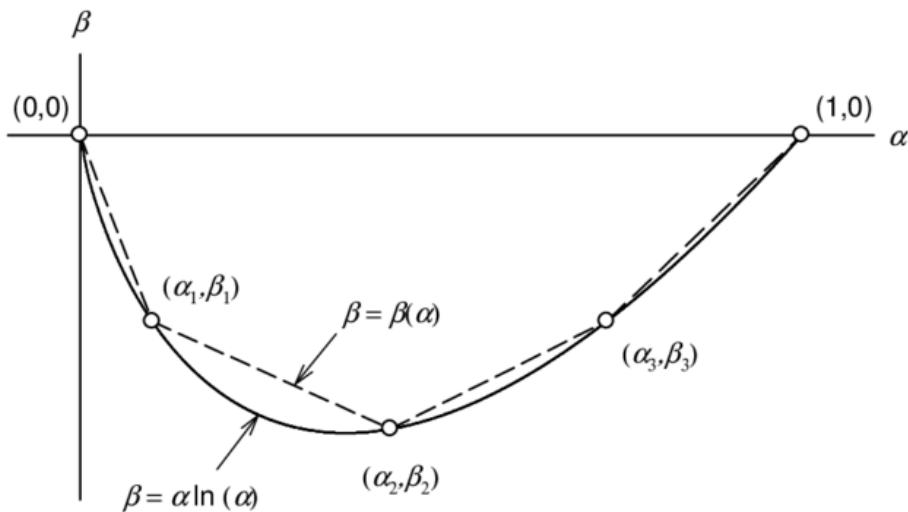


Figure 3.1: Approximation of the function β in Simplex method. Reproduced by Piro [5] from Dantzig *et al.* [65]

Simplex method has been successful in many optimisation problems [67], the linearisation of β generates a relatively large number of additional unknowns and the computational expense becomes quite large. Furthermore, the method is unable to determine the composition of dilute species [44]. As a result, the simplex method has not received widespread usage in thermodynamic equilibrium calculations.

3.2. Gibbs Energy Minimisers

Over the years, a number of codes have been developed to compute thermodynamic equilibria in complex systems and many of these codes are summarised in table 3.1. The most noticeable of these codes include SOLGAS [68] and its successor SOLGASMIX [50], which are well known for their versatility, computational efficiency and the widespread availability of source code. In fact, SOLGAS has been used as the solver in codes like HSC [69], ChemSage [54] and FACT

[70]. FACT combined the thermodynamic equilibrium solver with a comprehensive thermodynamic database and, by implementing the levelling method, eliminated the need for the user to manually input initial estimates. This made FACT a popular choice in the thermodynamics community. FACT merged with ChemSage to create a new standalone software called FactSage [71], which is the current version of the SOLGAS family. Another app in the family, called ChemApp [72, 73], is a software library that can be called from external codes and has similar capabilities as FactSage.

Another family of popular thermodynamic equilibria tools is ThermoCalc [74] and is widely used in thermodynamic model development, thermodynamic equilibrium calculations, and phase diagram construction. It has been developed for complex heterogeneous interaction systems with strongly non-ideal solution phases and can be applied to any thermodynamic system in the fields of chemistry, metallurgy, material science, alloy development, geochemistry, semiconductors etc. depending on the kind of database it is connected to. A unique advantage of ThermoCalc compared to other thermodynamic codes is that it allows explicit conditions on individual phase compositions or configuration whereas most software can handle conditions on the overall composition only. For example, activities and chemical potentials of the components, volumes, enthalpies, entropies etc can also be set as conditions. OpenCalphad [75] is an open-source code led by Bo Sundmann, one of the original developers of ThermoCalc, and it aims to provide facilities for multicomponent equilibrium calculations using the Compound Energy Formalism (CEF) and other models both for interactive calculations and in application software. It has been designed to allow interested scientists to develop thermodynamic models and assess model parameters for thermodynamic databases to describe experimental data as well as theoretical results from DFT calculations to calculate phase equilibria and phase diagrams. Another notable code developed with the goal of enabling uncertainty quantification is PyCalphad developed by Otis *et al.* [76].

Amongst the many thermodynamic equilibrium codes available in the open literature, one of the common limitations pertains to the relatively small number of standalone calculations that these codes are designed to perform. While suitable for problem specific calculations, where a few failures in convergence would have no significant bearing on the performance, these codes cannot be integrated into multiphysics softwares. In addition, since the mathematical difficulty in achieving convergence increases with the number of phases that can coexist in the system, most of these softwares limit the maximum number of phases and system components that can be simultaneously considered. While this has no bearing on applications such as combustion, the limited number of phases that can be solved creates a severe impediment for nuclear applications.

In the nuclear materials community, three code families have garnered particular attention - GEMINI [77], ThermoCalc [74] and FactSage [71]. Due to their established reputation in the nuclear community, these codes have traditionally been applied in development of several thermodynamic treatments for nuclear fuels and materials. In fact these three codes offer a number of advantages over the other codes reviewed here, including the capability of handling a very large number of system components, phases and species, and the ability to use a wide range of sophisticated thermodynamic models.

Table 3.1: A review of the major thermodynamic equilibrium codes.

Code / Author	Method	Models			
		Stoich.	Ideal	Non-ideal	Ionic
ANGE (SAGE) [78]	GEM	Yes	Yes	Yes	Yes
CALMIX [79]	GEM	Yes	Yes	Yes	No
Cantera [80]	GEM	No	Yes	Yes	No
Castier <i>et al.</i> [81]	GEM	No	Yes	No	No
CatCalc [82]	GEM	Yes	Yes	Yes	No
CEA [83]	GEM	Yes	Yes	No	No
ChemApp [72]	GEM	Yes	Yes	Yes	Yes
ChemSage [54]	GEM	Yes	Yes	Yes	Yes
ChemSheet [84]	GEM	Yes	Yes	Yes	Yes
COEXIST [85]	Levelling	Yes	No	No	No
Dantzig <i>et al.</i> [66]	Simplex	No	Yes	No	No
Ebel <i>et al.</i> [86]	BNR	Yes	Yes	No	No
ESP [87]	LMA	No	Yes	No	No
FACT [70]	GEM	Yes	Yes	Yes	Yes
FactSage [88]	GEM	Yes	Yes	Yes	Yes
GEMINI 1 [77]	GEM	Yes	Yes	No	No
GEMINI 2 [77]	GEM	Yes	Yes	Yes	Yes
GEM-Selektor [89]	GEM	Yes	Yes	No	Yes
GEMIPM2K [89]	GEM	Yes	Yes	No	Yes
Gibbs [90]	C-Hull		Yes	Yes	
GLOPEQ [91]	GEM*	No	Yes	No	No
HALTA [92]	LMA	No	Yes	No	No
HALTAFALL [93]	LMA	Yes	Yes	No	No
Han <i>et al.</i> [94]	LMA*	No	Yes	No	No
HSC [69]	GEM	Yes	Yes	Yes	Yes
Koukkari <i>et al.</i> [53]	Const. GEM	Yes	Yes	Yes	Yes
Kruskopf [63]	PGE	Yes	Yes	Yes	Yes
Lantagne <i>et al.</i> [57]	GEM	No	Yes	Yes	No
Lee <i>et al.</i> [95]	GEM	No	Yes	Yes	No
Lukas <i>et al.</i> [96]	GEM	Yes	Yes	Yes	No
MAGEMin [62]	PGE		Yes	Yes	
MatCalc [97]	GEM		Yes	Yes	
MTDATA [98]	GEM	No	Yes	Yes	No
NUTS [99]	GEM	Yes	Yes	Yes	Yes
OpenCalphad [75]	GEM	Yes	Yes	Yes	Yes

Table 3.1: A review of the major thermodynamic equilibrium codes (contd.).

Code / Author	Method	Models			
		Stoich.	Ideal	Non-ideal	Ionic
PANDAT [100]	GEM	Yes	Yes	Yes	Yes
Pereira <i>et al.</i> [101]	HEM	No	Yes	No	No
PyCalphad [76]	Lower C-Hull	Yes	Yes	Yes	No
Rossi <i>et al.</i> [102]	GEM	Yes	Yes	No	No
Schnedler [103]	GEM	Yes	Yes	No	No
Smith and Missen [104]	GEM	No	Yes	No	No
SOLGAS [68]	GEM	No	Yes	No	No
SOLGASMIX [50]	GEM	Yes	Yes	Yes	No
SOLGASMIX-PV [105]	GEM	Yes	Yes	Yes	No
SOLGASWATER [52]	GEM	Yes	Yes	Yes	Yes
Song <i>et al.</i> [106]	GEM*	Yes	Yes	No	No
Srinivas <i>et al.</i> [64]	GEM-RTA	No	Yes	No	No
STANJAN / EQUIL [107]	PGE	No	Yes	No	No
Storey <i>et al.</i> [56]	GEM	Yes	Yes	No	No
THERIAK [108]	GEM	No	Yes	Yes	No
ThermoCalc [74]	GEM	Yes	Yes	Yes	Yes
Thermochimica [61]	GEM	Yes	Yes	Yes	Yes
ThermoSolver [5]	PGE	Yes	Yes	Yes	Yes
VICTORIA [109]	LMA	Yes	Yes	No	No
White <i>et al.</i> [110]	GEM	No	Yes	No	No
NASA [48]	NASA	No	Yes	No	No

3.3. Global Optimisation

Calculation of thermodynamic equilibrium is a challenging problem since the objective functions are multivariable and can often be non-convex and highly non-linear. Furthermore, additional complexities arise near the phase boundaries, in the vicinity of critical points, etc. [111, 112]. Over the years, a number of different methods have been proposed to find the global minimum for non-convex problems in the applied mathematics community. These methods can be classified into stochastic and deterministic methods. However, even with a large number of different methods available in the literature, finding a method that can be applied to all types of problems has proven impractical. The success of every method is problem-specific and most of the methods reported in the literature have focussed on either relatively small systems, such as liquid-vapour equilibria, or perform relatively small number of calculations.

3.3.1. Deterministic Methods

Deterministic optimisation methods exploit the analytical properties of the problem to generate a deterministic sequence of points converging to a global optimum [113]. While these methods can provide a guaranteed global optimum, they require certain properties of objective function and constraints such as continuity and convexity. These methods include the *Branch and Bound algorithm*, *Homotopy Continuation Methods* and *Interval Analysis* [114].

The branch and bound algorithm is a class of adaptive partitioning strategies that iteratively apply partitioning, sampling and subsequent upper and lower bounding procedures to solve global optimisation problems [114]. These methods typically rely on some *a priori* knowledge of the form of the objective function to develop convex terms of the optimisation problem. However, they are often computationally expensive and slow [111, 115] because the method recursively splits the search space into smaller subspaces and performs function evaluations within each subspace. The homotopy continuation method provides a smooth transition between an approximate solution (often linear) and the true solutions of a non-linear system of equations by gradually introducing the non-linearities through a scalar homotopy parameter [116, 117]. As a result, the method is capable of finding all roots of a set of non-linear equations. While the method guarantees global convergence to a single solution, it does not guarantee global convergence to multiple solutions. Moreover, the method has been successfully demonstrated only for simple polynomials [118]. For the case of thermodynamic equilibrium calculations, Piro and Simunovic [4] have shown that the branch and bound algorithm has proven to be the most promising of all deterministic methods

3.3.2. Stochastic Methods

By employing probabilistic elements and using random sequences in the search for the global optimum, stochastic methods provide a high probabilistic convergence to global minimum with little or no assumption on the characteristics of the optimisation problem [119]. These methods employ heuristics for exploring (diversification) and exploiting (intensification) the search space, and learning strategies are used to find near-optimal solutions at a rapid speed [120]. This class of optimisation methods include *Random Search*, *Tabu Search*, *Random Tunnelling Algorithm*, *Particle Swarm Optimisation*, *TRUST*, etc.

The pure random search algorithm by Brooks [121] is based on generating a sequence of uniformly distributed points in the search space, while keeping a track of the best point that was already found. The method offers a probabilistic asymptotic guarantee that a global minimum will be found with probability equal to one when the sample size grows to infinity. Luus and Jaakola have proposed an *Adaptive Random Search* algorithm which uses random points and

systematic region reduction for locating the global optimum [122].

The Tabu search algorithm proposed by Glover and Laguna [123] is aimed at enhancing the searching capability of the solution space economically and effectively by discarding the points in the solution space, which have been previously evaluated and found to be not feasible. The method has been successfully applied to a wide range of optimisation problems but applications to thermodynamic equilibrium computations have been limited [124, 125]. One of the other notable algorithms is the random tunnelling algorithm which is a derivative of the TRUST algorithm. The TRUST algorithm [126] combines the novel concepts of subenergy tunneling, and non-Lipschitzian terminal repellers. In subenergy tunnelling, non-linear transformation is applied to the objective function resulting in the values of the function that are greater than the value at the current local minimum to be set equal to the current minimum. This flattens the search space and the process gets trapped at the current position because the successive gradients remain within the stopping criterion. At this point, the terminal repeller gets activated to allow an escape from the current solution to a point where the function begins another descent. The random tunnelling algorithm, on the other hand, consists of a combination of a local and global phase. In the global phase, the system is randomly perturbed from the last local minimum and a system of differential equations is solved from the perturbed point to explore new regions of attraction. The local phase employs a fast convergent Quasi-Newton minimisation technique to find an improved point in the new region. Amongst the stochastic global optimisation algorithms, Piro and Simunovic [4] have shown that the particle swarm algorithm has proven to be the most promising of all stochastic methods and will be discussed in more detail in chapter ??.

The diversification and intensification plays a key role in ensuring a compromise between reliability and computational efficiency of stochastic algorithms and while the stochastic algorithms can often locate the global minimum in modest computational times compared to deterministic methods, they do not guarantee global optimality [118, 120].

3.3.3. Global Optimisation Review

A few of the studies on global optimisation in thermodynamic equilibrium calculation have been summarised in table 3.2. While most of the global optimisation methods applied to phase equilibrium have been studied with reference to liquid-liquid or vapour-liquid equilibrium, a few of the remarkable ones can be applied to more general phase equilibrium problems. Chaikunchuensakun *et al.* [127] applied a hybrid algorithm based on non-linear parametric optimisation routines which solves the Kuhn-Tucker conditions by minimising a quadratic subproblem with linearised equality and inequality constraints. While the method can equilibrium

solutions, a global solution cannot be guaranteed [118]. Another notable study is by Nichita *et al.* [115] who tested the tunnelling method for multi-phase equilibrium calculation by direct minimisation of Gibbs energy of the components. Rossi *et al.* [102] applied a convex analysis method to chemical and phase equilibrium of closed multi-component reactive system. Though the method is highly efficient and reliable, it is only applicable to convex functions. A duality based approach proposed by Pereira *et al.* [101] can guarantee the global optimum but requires a differentiable objective function [118].

Amongst the stochastic methods, the most notable works are from Teh and Rangaiah [125] who show that the tabu search is more efficient than the genetic algorithm but requires further improvement for 100% reliability. However, the system size considered by them is relatively small. Srinivas and Rangaiah [64] used the random tunnelling algorithm which can evaluate the global minimum for most of the examples tested but suffers from low reliability and is feasible only for small systems.

In conclusion, the available literature suggests that both deterministic and stochastic methods face difficulties for highly non-ideal mixtures and are prone to convergence problems. Moreover, many of the studies assume the number of phases that would be stable to be known *a priori* which is not true and limits capability. As a result, several calculations must be performed using different combination of phases to arrive at the true global minimum. The global optimisation problem applied to computational thermodynamics warrants a more effective and rigorous study of both deterministic and stochastic methods applied to a variety of case studies with varying levels of complexity. An effort in this direction was made by Piro and Simunovic [4] and they found the PSO and the Branch and Bound algorithms to be the most promising stochastic and deterministic methods respectively.

3.4. Multiphysics Integration of Computational Thermodynamics

The interest in including thermodynamic equilibrium calculations in multiphysics simulations has been relatively recent. Even though the importance of thermodynamic variables in various physical simulations has been long recognised, the limitations on computational resources along with the high cost of equilibrium calculations made thermodynamically informed coupled simulations infeasible for most simulations beyond those aimed at purely demonstrating capability. However, over the last few years, the efforts towards coupling thermochemistry have been ever-increasing. Some of such coupling efforts, primarily the ones focussed on nuclear applications are reviewed here.

Most of the applications of coupling computational thermochemistry have been in nuclear fuel codes with some applications in microstructural evolution using phase field method and

Table 3.2: A review of the global optimisation methods applied to thermodynamic equilibrium calculations.

Method	Class	Problem Formulation
Sampling [128, 129]	Deterministic	Gibbs energy
Branch and Bound [130]	Deterministic	Potential energy
Branch and Bound [4]	Deterministic	Gibbs energy
Convex optimisation [102]	Deterministic	Gibbs energy
Differential evolution and tabu search [124]	Stochastic	Gibbs energy
Differential evolution with tabu list [131]	Stochastic	Gibbs energy
Duality based optimisation [101]	Deterministic	Helmholtz energy
Enhanced simulated annealing [132]	Stochastic	Gibbs energy
Enhanced tabu search [125]	Stochastic	Gibbs energy
Genetic algorithm and simulated annealing [133]	Stochastic	Gibbs energy
Genetic algorithm and differential evolution with tabu list [134]	Stochastic	Gibbs energy with reaction
Hybrid artificial immune system [135]	Stochastic	Gibbs energy with reaction
Hybrid genetic algorithm with interior point method [136]	Stochastic	Gibbs energy
Interval analysis [137]	Deterministic	Gibbs energy surface
Nonlinear parametric optimisation [127]	Deterministic	Gibbs energy
Particle swarm optimisation [4, 138, 139]	Stochastic	Gibbs energy
Random tunnelling algorithm [64]	Stochastic	Gibbs energy
Simulated annealing [140]	Stochastic	Gibbs energy
Successive quadratic programming [141]	Deterministic	Gibbs energy
Tunnelling method [115, 142]	Deterministic	Gibbs energy

even lesser applications in safety analyses. Some of the works that have coupled computational thermodynamics with the commercial software package COMSOL include those of Higgs *et al.*

Piro integrated the thermochemistry solver ThermoChimica into the Advance Multi-Physics AMP code developed by Oak Ridge National Laboratory [5]. This allowed the investigation of an irradiated fuel pellet by using isotopic evolution of irradiated nuclear fuel which was calculated through the software package ORIGEN. The integration of ThermoChimica in AMP is shown in figure 3.2 and the capabilities of this simulation framework were demonstrated through a scenario that simulates the behaviour of highly irradiated UO₂ fuel, results of which are shown in figure 3.3.

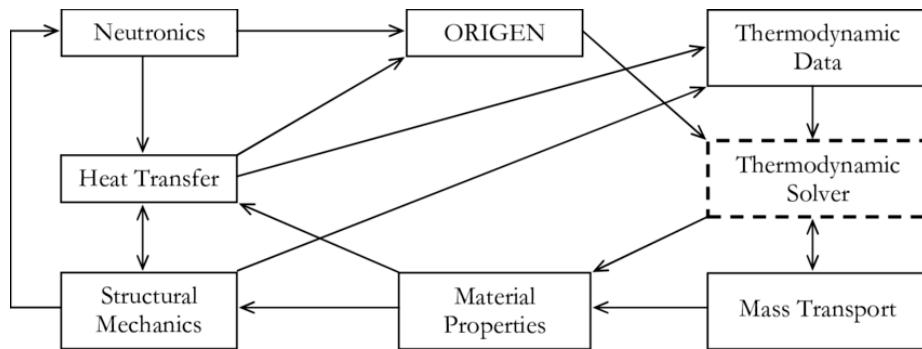


Figure 3.2: A flowchart of the Advanced Multi-Physics (AMP) code illustrating the interaction between the various modules is shown [5].

The software integration of ThermoChimica with Bison was performed by Simunovic and Besmann [143]. The ThermoChimica implementation was demonstrated on modelling oxygen related phenomena in irradiated fuel, such as calculation of oxygen to metal ratio in the fluorite phase, oxygen partial pressure, oxygen chemical potential and oxygen transport. Experimental measurements from the open literature were used to validate the implemented models and illustrate functionality of the developed thermodynamics module. The calculations are based on chemical element inventory provided by neutronics, isotopic depletion, transmutation and decay calculations in the [144] system.

In France, 3D coupled multiphysics simulations of power ramps in Pressurised Water Reactors (PWR) were performed by Konarski *et al.* [145]. The fuel performance code ALCYONE, which is part of the computing environment PLEIADES, was coupled with the thermodynamics code ANGE to provide a description of irradiated fuel thermochemistry with oxygen transport taking into account thermodiffusion. Konarski *et al.* also performed Pellet Cladding interaction (PCI) failure analyses, by coupling thermochemistry and thermo-mechanics to investigate both chemical and mechanical factors simultaneously. 3D thermochemical-mechanical simulations

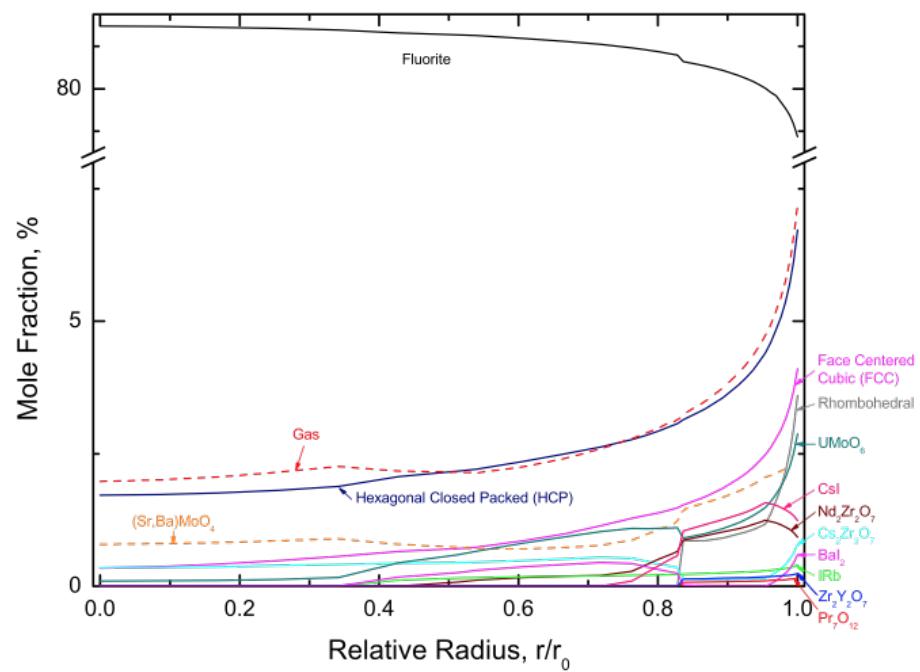


Figure 3.3: The predicted distribution of phases across the pellet is shown for an average pellet burnup of 102 GW d t(U)⁻¹ [1].

of PWR power ramps on Cr-doped UO_2 with the fuel performance code ALCYONE including oxygen transport were performed to study the impact of oxygen redistribution on irradiated fuel thermochemistry and on chemically reactive fission gas release.

Recently, Poschmann *et al.* [2] have demonstrated the acceleration of Thermochimica and coupled it with Bison to simulate oxygen diffusion in irradiated fuel rods. Figure 3.4 shows the oxygen vacancy concentration obtained through coupled Thermochimica- Bison simulations. The figure represents the kind of multiphysics simulations that can be performed when thermodynamic equilibrium calculations are coupled with fuel performance codes

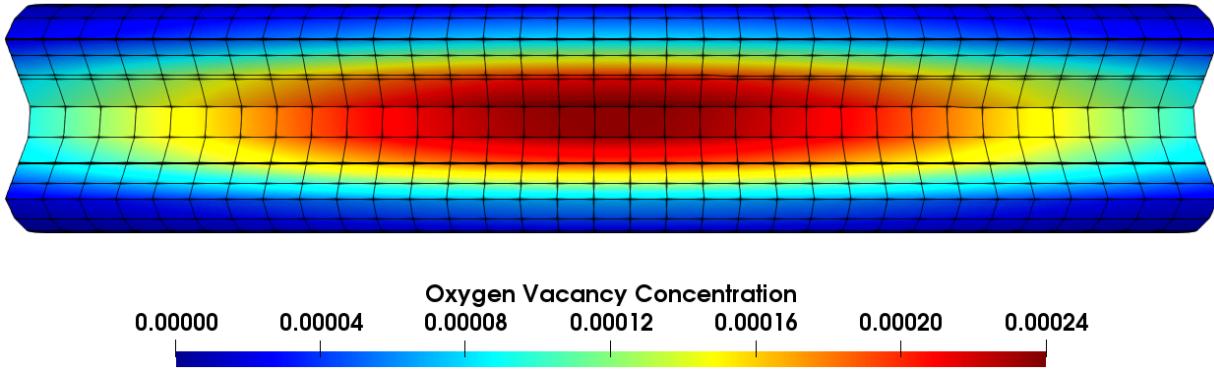


Figure 3.4: Oxygen vacancy concentration in UO_2 fuel obtained by coupling Thermochimica with Bison [2].

Fitzpatrick *et al.* [146] coupled Thermochimica with thermal-hydraulics code COBRA-TF and isotopic evolution code ORIGEN to demonstrate fission product transportation by coolant flow in molten salt reactors.

The presented works demonstrate the variety of problems which can benefit by coupling thermodynamic equilibrium calculations with other physical phenomena. Full integration of a thermodynamic equilibrium code in MOOSE would make such coupled calculations easy and allow high fidelity multiphysics simulations allowing much more realistic simulations of various problems.

4

Thermodynamic Basis

The laws that govern all material systems can be expressed in two seemingly simple statements of Rudolf Clausius - “*Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu.*” and yet thermodynamics has drawn the attention of many great scientists including Maxwell, Boltzmann, Planck and Mach. Physicist Arnold Sommerfeld accounted his experience of thermodynamics as “*Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more*”. A number of definitions and laws of thermodynamics form the basis of equilibrium thermodynamics and the Gibbs energy models and equations play a key role in the structure of the equilibrium solver.

4.1. Fundamental Laws of Thermodynamics

The statements of Rudolf Clausius are now known as the *First and Second Laws of Thermodynamics*. Before looking at these laws, the basic definitions used in subsequent sections are reviewed for clarity. A *thermodynamic system* is a portion of the universe with a perimeter defined by real or imaginary boundaries and usually consists of many chemical components whose thermodynamic behaviour can be analysed. For example, the volume element shown in figure 4.1 can be treated as a thermodynamic system. A system which may exchange matter with its system boundary is called *open* while a system which can only exchange energy and no matter is called *closed*. The term *isolated* is used for a system which is cut off from the

surroundings and can neither exchange matter nor energy. In material thermodynamics, the system is often treated as closed, notable exceptions being chemical reactors where reactants and products continuously flow in and out of the system.

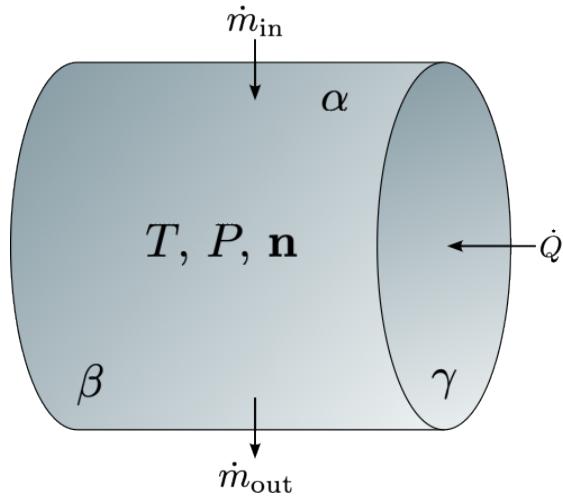


Figure 4.1: Volume element of a general thermodynamic system with mass flow of chemical components \dot{m} and heat flux \dot{Q} . The Greek letters indicate presence of separate phases.

A thermodynamic system can be described macroscopically using *state variables*, which are represented by measurable macroscopic quantities such as temperature, pressure, volume, amounts of different substances, etc. *Intensive variables*, e.g. temperature and pressure, are independent of the amount of matter in the system while *extensive variables*, e.g. volume and total internal energy, are dependent on the mass of the system. With a change in the internal variables, the system undergoes a change in state. If the state of the system can be restored to the original without any change in the state of the surroundings, the process through which the state of the system was changes is described as *reversible process*. However, all real processes are *irreversible processes*, that is, the system cannot be recycled.

Thermodynamics concerns the state of a system as it interacts with its surroundings and is based on two laws of nature, the first and second laws of thermodynamics. The first law of thermodynamics describes those interactions , which can involve exchanges of any combinations of heat, work, and mass, while the second law of thermodynamics governs the evolution of state inside the system. Together, the two laws integrate the external and internal parts of the system.

4.1.1. First law of thermodynamics

The first statement of Clausius and what is now known as the first law of thermodynamics expresses the conservation of energy¹ and is formulated as follows:

Energy cannot be created or destroyed, and the energy increase of a system (dU) equals the sum of the heat absorbed from the surroundings (dQ) and the work (dW) done by the surroundings on the system.

Mathematically, for an open system, the first law can be expressed as:

$$dU = dQ + dW + \sum H_i dN_i, \quad (4.1)$$

where dN_i denotes the amount of component i exchanged with the surroundings and H_i is the unit energy of component i in the surroundings, and the summation is for all the independent components in the system. Since the systems of interest in thermodynamics of materials are closed, there is no exchange of matter between the system and the surroundings and the first law of thermodynamics takes the following form:

$$dU = dQ + dW, \quad (4.2)$$

where both dQ and dW depend on the thermodynamic process and hence do not qualify as state functions.

4.1.2. Second law of thermodynamics

In 1850, Clausius formulated a criterion for the direction of spontaneous processes and called it *entropy*. His second statement translates to entropy of the universe tends to maximum and is now known as the second law of thermodynamics. Formally, the second law states that:

For an internal process to take place spontaneously, or irreversibly, the change in entropy of the system (dS) must be positive.

In mathematical form, the second law can be formulated as:

$$dS = dS_{\text{sys}} + dS_{\text{surr}} \geq 0, \quad (4.3)$$

where the S_{sys} and S_{surr} represents the entropy of the system and surroundings respectively. In the course of a reversible, isothermal process, the entropy change of the system dS_{sys} can be

¹Considering Einstein's mass-energy equivalency, the classical first law can be modified to state that mass and energy together are constant. However, since we are considering chemical equilibrium and not dealing with nuclear reactions, the classical form of first law applies.

defined as the heat exchange divided by temperature:

$$dS_{\text{sys}} = \frac{dQ}{T}. \quad (4.4)$$

4.1.3. Third law of thermodynamics

The third law of thermodynamics allows expressing the absolute value of the entropy in contrast to the internal energy by assigning an entropy equal to zero at 0 K for any pure compound in stable and perfectly crystalline state.

4.2. Enthalpy, and Helmholtz and Gibbs Energies

Three important state functions of great practical importance in thermodynamics are the *enthalpy* H , *Helmholtz energy* F , and *Gibbs energy* G . Enthalpy changes are of importance in calorimetry experiments as they can be directly measured while Helmholtz and Gibbs energies are used in defining chemical equilibrium conditions.

The enthalpy of a thermodynamic system is an extensive property defined as:

$$H = U + PV, \quad (4.5)$$

where U denotes the internal energy, P denotes the pressure the system is at and V represents the volume of the system.

The Helmholtz energy of a thermodynamic system is defined as:

$$F = U - TS, \quad (4.6)$$

where, T denotes the temperature of the system and S represents the entropy of the system.

The Gibbs energy of a thermodynamic system is defined as:

$$G = H - TS. \quad (4.7)$$

The equilibrium criterion can be derived in terms of Helmholtz and Gibbs energies. According to the second law of thermodynamics, a spontaneous irreversible process must be accompanied by an overall positive change of entropy, i.e.:

$$dS_{\text{sys}} + dS_{\text{surr}} > 0. \quad (4.8)$$

For a closed system in thermal and mechanical equilibrium but not in chemical equilibrium

which acquires an infinitesimal quantity of heat from the surroundings:

$$dS_{\text{surr}} = -\frac{dQ_{\text{sys}}}{T}, \quad (4.9)$$

where it is assumed that the mass of the surroundings is large enough so that addition/removal of the heat does not cause a perceptible change in temperature. Thus,

$$dQ_{\text{sys}} - TdS_{\text{sys}} < 0. \quad (4.10)$$

Assuming that the heat exchange causes an infinitesimal change in the internal energy of the system by an amount dU_{sys} , according to the first law of thermodynamics,

$$dU_{\text{sys}} = dQ_{\text{sys}} + dW_{\text{sys}}. \quad (4.11)$$

For a closed, isobaric system the work is purely due to the change in the volume of the system and the following relationship is obtained:

$$dU_{\text{sys}} + PdV_{\text{sys}} - TdS_{\text{sys}} < 0. \quad (4.12)$$

If both the temperature and volume were held constant, the above inequality becomes:

$$dU_{\text{sys}} - TS_{\text{sys}} < 0. \quad (4.13)$$

Since the terms within the parentheses denote the Helmholtz energy, we obtain the criterion for spontaneous change of isothermal, isochoric system, which is expressed as:

$$dF_{\text{sys}} < 0 \quad (4.14)$$

Similarly, if the temperature and pressure were held constant, the inequality becomes:

$$dU_{\text{sys}} + PV_{\text{sys}} - TS_{\text{sys}} < 0. \quad (4.15)$$

The terms inside the parentheses denote the Gibbs energy and subsequently yield the criterion for spontaneous change of an isothermal, isobaric system:

$$dG_{\text{sys}} < 0. \quad (4.16)$$

Thus, for the equilibrium of a closed system at constant temperature and volume, it is

necessary and sufficient that the Helmholtz energy of the system is at minimum and equivalently, the Gibbs energy of the system must be at minimum for equilibrium in systems at constant temperature and pressure. In equilibrium thermodynamics, Gibbs energy is often preferred over Helmholtz energy since controlling pressure is easier than controlling volume during experiments. It must be emphasised that thermodynamic properties are fundamentally concerned with relative changes, a property that is often exploited in computations.

4.3. Gibbs Energy and Chemical Potential

Of particular interest in description of thermodynamic equilibrium are the quantities named *potentials*. A system is in thermodynamic equilibrium when it is simultaneously in thermal, mechanical, electrical and chemical equilibrium. This also refers to the state where there are no unbalanced potentials within the system. J.W. Gibbs used the term *thermodynamic potential* to represent all the relevant system potentials to characterise the conditions of thermodynamic equilibrium [147]. Thermodynamic equilibrium calculations are based on the principle that the potential for each component must be uniform throughout the system at thermodynamic equilibrium. This section and the following describe the relation between Gibbs energy and chemical potentials and their use in computing thermodynamic equilibrium.

The Gibbs energy, G_i [J mol^{-1}], of a pure species i is defined as [148]:

$$G_i = \Delta H_i - TS_i, \quad (4.17)$$

where T [K] is the absolute temperature, ΔH_i [J mol^{-1}] and S_i [$\text{J mol}^{-1} \text{K}^{-1}$] represent the enthalpy and absolute entropy of species i in phase ϕ respectively. Since thermodynamic quantities are relative in nature, equation (4.17) can be expanded as:

$$G_i = \left(\Delta H_i^\circ + \int_{T_0}^T C_{p,i} dT \right) - T \left(S_i^\circ + \int_{T_0}^T \frac{C_{p,i}}{T} dT \right) + \int_{P_0}^P V_i dP, \quad (4.18)$$

where ΔH_i° [J mol^{-1}] and S_i° [$\text{J mol}^{-1} \text{K}^{-1}$] are the standard enthalpy of formation and entropy respectively at standard temperature ($T_0 = 298.15$ [K]) and pressure ($P_0 = 1$ [atm]). The superscript / subscript \circ represents a quantity at standard temperature and pressure, a notation that is used hereafter. $C_{p,i}$ [$\text{J mol}^{-1} \text{K}^{-1}$] denotes the molar heat capacity at constant pressure, P [atm] is the absolute pressure and V_i [$\text{m}^3 \text{mol}^{-1}$] denotes the molar volume. For an ideal gas, from the gas law, the last term in equation (4.18) can be written as $RT \ln(P/P_0)$, where $R = 8.314462$ [$\text{J mol}^{-1} \text{K}^{-1}$] is the ideal gas constant. For a pure ideal gas species i , the

standard Gibbs energy is:

$$G_i = \left(\Delta H_i^\circ + \int_{T_0}^T C_{p,i} dT \right) - T \left(S_i^\circ + \int_{T_0}^T \frac{C_{p,i}}{T} dT - R \ln \left(\frac{P}{P_0} \right) \right). \quad (4.19)$$

The fact that Gibbs energies are relative quantities and can be numerically adjusted as long as the elemental differences are preserved is of practical importance and is often used in thermodynamic equilibrium calculation. Chemical potential of species i in phase λ , $\mu_{i(\lambda)}$ [J mol^{-1}], is a measure of the change of the Gibbs energy of the system by the introduction of species i and incorporates the reference Gibbs energy of pure species, g_i° , and the entropic contribution due to mixing as a function of its mole fraction. Mathematically, the chemical potential of a species i is defined as [148]:

$$\mu_i = \left(\frac{\partial G_{\text{sys}}}{\partial n_i} \right)_{T,P,n_{j \neq i}}. \quad (4.20)$$

For the species of a phase with only ideal mixing, the chemical potential is generally given as:

$$\mu_i = g_i^\circ + \ln x_i. \quad (4.21)$$

For non-ideal solution phases, the chemical potential also includes the partial molar excess Gibbs energy of mixing, g_i^{ex} [J mol^{-1}], to account for non-ideal mixing as follows:

$$\mu_i = \mu_i^\circ + \ln x_i + \mu_i^{ex}. \quad (4.22)$$

While the chemical potential of stoichiometric phases does not include a composition dependent term, the partial molar excess Gibbs energies of mixing for non-ideal solution models depend on the mixing model employed. Some of these models include the Modified Quasichemical Model [149–153], the Compound Energy Formalism [154], etc.

The integral Gibbs energy of a multicomponent, multiphase system is represented as:

$$G_{\text{sys}} = RT \left(\sum_{\phi=1}^{\Phi} n_\phi \sum_{i=1}^{N_\phi} x_i \tilde{\mu}_i \right), \quad (4.23)$$

where R [$\text{J mol}^{-1} \text{K}^{-1}$] is the ideal gas constant, T [K] is the absolute temperature, N_ϕ denotes the number of species in phase ϕ of which there can be a maximum of Φ and x_i represents the mole fraction of species i . For convenience, the Gibbs energy is often split into separates

contributions from solution and stoichiometric phases as follows:

$$G_{\text{sys}} = RT \left(\sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_i \tilde{\mu}_i + \sum_{\omega=1}^{\Omega} n_{\omega} \tilde{\mu}_{\omega} \right), \quad (4.24)$$

N_{λ} denotes the number of species in the solution phase λ and x_i represents the mole fraction of species i in solution phase λ . Λ and Ω represent the number of stable solution phases and stoichiometric phases respectively and the number of moles of the solution phase λ and stoichiometric phase ω are denoted by n_{λ} and n_{ω} [mol] respectively. $\tilde{\mu}_i$ represents the dimensionless form of the chemical potential of species i and is given as $\tilde{\mu}_i = \mu_i / RT^2$. Finally, $\tilde{\mu}_i$ and $\tilde{\mu}_{\omega}$ represent the dimensionless chemical potential of species i in solution phase λ and stoichiometric phase ω respectively.

The Gibbs energy of the system can also be expressed in terms of the element potentials, Γ_j [J mol^{-1}], and the number of moles, b_j [J], of the system components. Mathematically, this can be expressed as:

$$G_{\text{sys}} = \sum_{j=1}^C \Gamma_j b_j, \quad (4.25)$$

where C denotes the number of system components which is normally the number of elements in the system. The mixing models used in materials modelling are briefly described in the following section.

4.3.1. Excess mixing models for Gibbs energy

A number of different models for excess mixing component of Gibbs energy have been proposed in literature. The different models are suitable for different materials, for example the Compound Energy Formalism (CEF) is often used for UO_2 fuels while the Modified Quasichemical Model (MQM) is the state of the art model used to describe molten salts which are of prime interest in the development of MSRs. However, only the relevant equations for some of the most commonly used models are shown here.

1. Substitutional solution models

The regular solution model is a quantitative explanation of non-ideal behaviour. The model assumes that the entropy of mixing is the same as ideal mixing but that the enthalpy of mixing is not zero. A number of different regular solution models have been proposed, the most commonly used ones being based on Kohler-Toop and Redlich-Kister-Muggiano interpolation schemes [19].

²The dimensionless form $\tilde{\mu}_i$ has been used here as it is the preferred form in computational implementations.

- **Kohler-Toop Interpolation**

$$g_{\lambda}^{\text{ex}} = \sum_{z=1}^Z \phi_z(x_1^{d_1} x_2^{d_2} x_3^{d_3}). \quad (4.26)$$

- **Redlich-Kister-Muggiano Interpolation**

$$g_{\lambda}^{\text{ex}} = \sum_{z=1}^Z x_j x_k \sum_{\nu=0}^{\nu} {}^{\nu} L_j. \quad (4.27)$$

2. Compound Energy Formalism (CEF)

Compound Energy Formalism is a multi-sublattice model proposed by Hillert [154] for an adequate description of the properties of solution phases with sublattices. The molar Gibbs energy, g_{λ} , of solution phase λ based on the CEF model is generally given as:

$$g_{\lambda} = \sum_{i=1}^{N_{\lambda}} g_i^{\circ} \prod_{s=1}^{N_s} y_{i(s)} + RT \left(\sum_{s=1}^{N_s} a_s \sum_{c=1}^{N_c} y_{c(s)} \ln(y_{c(s)}) \right) + g_{\lambda}^{\text{ex}}, \quad (4.28)$$

where g_i° is the standard molar Gibbs energy of the pure component i , $y_{i(s)}$ represents the site fraction on sublattice s corresponding to component i , N_{λ} and N_s denote the number of components and number of sublattices in solution phase λ , respectively. The ideal gas constant is represented by R , the absolute temperature by T , the stoichiometry coefficient for sublattice s is represented by a_s , the number of constituents on sublattice s is N_c and the site fraction of constituent c on sublattice s is $y_{c(s)}$. It is to be understood that $y_{i(s)}$ refers to the site fraction of constituent c associated with component i on sublattice s and is thus related to $y_{c(s)}$. Finally, the molar excess Gibbs energy of mixing of solution phase λ is g_{λ}^{ex} and is given as:

$$g_{\lambda}^{\text{ex}} = \sum_{p=1}^{N_p} \left(\prod_{m=1}^{N_s} y_{m(s)} \right) \sum_{z=0}^{N_z} {}^z L_{j,k} (y_j - y_k)^z, \quad (4.29)$$

where N_p denotes the number of excess mixing parameters (note: $N_p \geq N_s$), y_m is the site fraction of constituent m corresponding to mixing parameter p , N_z is the number of terms corresponding to parameter p , and ${}^z L_{j,k}$ is the z th order mixing parameter. A detailed description of CEF can be found in the paper by Hillert [154].

3. Modified Quasichemical Model (MQM)

The Modified Quasichemical Model (MQM) in the quadruplet approximation is the most

generalised thermodynamic model for treating Short Range Ordering (SRO). MQM is fundamentally different than other thermodynamic models in that the focus is not on the mixing of chemical species or constituents on a lattice, but rather the mixing of species as quadruplets to capture SRO of both First Nearest Neighbour (FNN) and Second Nearest Neighbour (SNN) in liquid or solid solutions. The details of evolution of MQM from pair approximation for species mixing on only one sublattice to the current quadruplet approximation are provided by Pelton *et al.* [149–152].

For a solution with two sublattices, which is occupied only by a single species on the second sublattice, the SNN pair exchange can be written as:

$$(A - [X] - A) + (B - [X] - B) = 2(A - [X] - B); \Delta g_{AB/X}, \quad (4.30)$$

where $\Delta g_{AB/X}$ is the non-configurational Gibbs energy for the formation of 2 mol of $(A - [X] - B)$ pairs. Similarly, when there is a single species on the first sublattice, the formation of SNN pairs is captured via:

$$(X - [A] - X) + (Y - [A] - Y) = 2(X - [A] - Y); \Delta g_{A/XY} \quad (4.31)$$

where $\Delta g_{A/XY}$ is the non-configurational Gibbs energy for the formation of 2 mol of $(X - [A] - Y)$ pairs. Among the FNN pairs, the following exchange reaction is considered:

$$(A - X) + (B - Y) = (A - Y) + (B - X); \Delta g_{A/XY}^{\text{exchange}} \quad (4.32)$$

where $\Delta g_{A/XY}^{\text{exchange}}$ is the non-configurational Gibbs energy. Let n_i ($i = A, B, \dots, X, Y \dots$) represent the number of moles of species i , $n_{i/j}$ be the number of moles of FNN ($(i-j)$) pairs, and $n_{ij/kl}$ be the number of moles of the quadruplets. The relationship between the foregoing terms is [152]

$$Z_A n_A = 2n_{A_2/X_2} + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/Y_2} + n_{AB/XY} + \dots, \quad (4.33)$$

$$Z_X n_X = 2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{B_2/XY} + n_{AB/XY} + \dots, \quad (4.34)$$

where Z_A and Z_B are the coordination numbers for A and B, respectively. A generic

statement for a multi-component system is:

$$Z_i n_i = 2n_{ii} + \sum_{j \neq i} n_{ij}. \quad (4.35)$$

The mole fractions then follow:

$$x_i = \frac{n_i}{\sum n_j}, \quad (4.36)$$

$$x_k = \frac{n_k}{\sum n_l}, \quad (4.37)$$

where the indices i and j refer to the species on first sublattice while the indices k and l refer to the species on second sublattice. The FNN pair fractions and quadruplet fractions are defined as:

$$x_{i/k} = \frac{n_{i/k}}{\sum_j \sum_l n_{j/l}}, \quad (4.38)$$

$$x_{ij/kl} = \frac{n_{ij/kl}}{\sum n_{ij/kl}}. \quad (4.39)$$

Another useful term is the coordination equivalent fraction, which is

$$y_i = \frac{Z_i n_i}{\sum Z_j n_j}, \quad (4.40)$$

$$y_k = \frac{Z_k n_k}{\sum Z_l n_l}. \quad (4.41)$$

Omitting detailed description of the derivation of the model, the simplest form of MQM for binary solutions can be written as:

$$G_\lambda = (n_A g_A^\circ + n_B g_B^\circ) - T \Delta S^{\text{config}} + \frac{n_{AB} \Delta g_{AB}}{2} \quad (4.42)$$

where g_i° is the reference molar Gibbs energy of pure i (computed from a database), T is the absolute temperature, and ΔS^{config} is the configurational entropy, given by:

$$\begin{aligned} \Delta S^{\text{config}} = & -R (n_A \ln(x_A) + n_B \ln(x_B) \\ & + n_{AA} \ln(x_{AA}/y_A^2) + n_{BB} \ln(x_{BB}/y_B^2) + n_{AB} \ln(x_{AB}/(2y_A y_B))) \end{aligned} \quad (4.43)$$

MQM is of particular interest in this work because it is the preferred model for thermody-

namic modelling of molten salts. However, from the computational perspective, many a times, the MQM phases pose a unique challenge in that the Hessian matrix resulting from the GEM process can be rank-deficient. Therefore, any attempt to solve the corresponding system of linear equations will fail. Note that in practice it is possible that the system of equations can be solved with a sufficient numerical error associated with machine precision, which will yield some mathematically meaningless results. In this case, one must rely heavily on the quality and robustness of the linear equation solver employed [155].

4.3.2. Chemical potential expressions for excess mixing models

Pertinent to the development of a Gibbs energy minimiser are the chemical potential expressions for the different species in phases represented by each of the excess mixing models. These expressions have been published by Bajpai *et al.* [156] and Poschmann *et al.* [157]. The following pages show the chemical potential expressions for the substitutional solution models and the CEF in the paper titled *Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models* and the expressions for the MQM in section 2 of the paper titled *Recent developments for molten salt systems in Thermochimica*.



Derivations of Partial Molar Excess Gibbs Energy of Mixing Expressions for Common Thermodynamic Models

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Abstract Modern computational thermodynamics methods rely on the use of numerical models that represent chemical systems. Typically, these models are formulated in terms of the Gibbs energy, which must be minimised to find the conditions of thermodynamic equilibrium. Numerous thermodynamic models have been developed to capture the behaviour of regular solid and liquid solutions, ionic ceramics, multi-sublattice metallic alloys, short and long range ordering, and much more. Some classes of commonly used thermodynamic models include substitutional solutions and compound energy formalism. The mathematical formulation of the Gibbs energy of a solution phase represented by any of the aforementioned models takes on a unique form, which requires special consideration for obtaining the partial derivatives in the Hessian matrix of a Gibbs energy minimiser. This paper provides derivations of the partial molar excess Gibbs energy of mixing of some common classes of thermodynamic models for use in a Gibbs energy minimiser.

Keywords CALPHAD · compound energy formalism · Gibbs energy minimisation · regular solution model

1 Introduction

Thermodynamic calculations play a fundamental role in solving a variety of complicated technical problems. In particular, the CALPHAD method^[1] enables the computer calculation of phase diagrams and for calculating the properties of multicomponent, multiphase systems. Thermodynamic quantities such as Gibbs energies, heat capacities, enthalpies, chemical potentials and driving forces can be calculated using CALPHAD techniques.

Computations of thermodynamic equilibrium often exploit the Gibbs Energy Minimisation (GEM) method, which predicts a unique combination of phases and species that yield a minimum in the integral Gibbs energy of a closed isothermal, isobaric system. The objective is often achieved using the method of Lagrange multipliers that simultaneously minimises the integral Gibbs energy and the residuals of mass balance equations. In matrix form, this results in a system of linearised equations as shown by White et al.^[2] For finding the undetermined Lagrange multipliers, the expressions for the Gibbs energy of different phases and the chemical potentials of the species in those phases are required to establish the constraint vector associated with the system of equations and also for computing the molar quantities of these species when using an iterative solver. The requirement for explicit expressions of the non-ideal contribution to chemical potential, i.e. partial molar excess Gibbs energy of mixing, in GEM software is the motivation behind this paper. While the derivations of these equations and the fundamental method

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adopted were initially motivated by the development of Thermochimica,^[3] the equations can be implemented in other software that are based on the GEM methodology,^[2] including the development of thermochemistry solver for the mesoscale corrosion modelling code Yellowjacket.^[4]

In the context of this paper, a *system* is defined as a closed isothermal-isobaric volume with a fixed composition. The system composition is represented by the *system components*, which may be equivalent to the chemical elements, a combination thereof, or an electron corresponding to ionic charge. A *species* is defined as any atom, molecule, ion or vacancy and a *constituent* refers to a certain species on a certain sublattice. In the context of a multi-sublattice phase, a fixed combination of constituents is referred to as a *compound end member*. The selection of the independent variable, for which reference Gibbs energies are defined and solved in the Hessian matrix, varies depending on the type of solution model. For example, a ‘species’ is used in an ideal gas or substitutional solution while a ‘compound end member’ is used in the Compound Energy Formalism (CEF). The derivation of chemical potentials will therefore be made with respect to the foregoing independent variables.

In a multicomponent, multiphase system, the integral Gibbs energy is given by the following expression:

$$G = \sum_{\lambda=1}^{\Lambda} n_{\lambda} g_{\lambda} + \sum_{\omega=1}^{\Omega} n_{\omega} g_{\omega}, \quad (\text{Eq 1})$$

where g_{λ} and g_{ω} represent the molar Gibbs energies (i.e., the Gibbs energy per mole of the phase) of solution phase λ and stoichiometric phase ω , respectively. Quantities n_{λ} and n_{ω} represent the mole number of solution phase λ and stoichiometric phase ω . Λ and Ω denote the number of stable solution and stoichiometric phases, respectively.

Calculation of thermodynamic equilibrium requires a multicomponent database, which provides a consistent description of the thermodynamic functions for all the possible phases in the system. These databases are derived from experimental measurements, sometimes combined with first-principles calculations, to include Gibbs energy expressions as functions of temperature, pressure, and composition. It must be mentioned that since the composition of stoichiometric phases is invariant, their thermodynamic parameters are by definition independent of composition. The solution phase functions, however, do depend on the composition, and a number of models and parameters have been proposed to model different phases. These models include ideal solution models, models for a single sublattice and models for multiple sublattices. Despite the large number of models available to represent the Gibbs energy of a particular phase, the general representative expression is as follows:

$$G_{\lambda} = G_{\lambda}^{\circ} + G_{\lambda}^{\text{id}} + G_{\lambda}^{\text{ex}} + G_{\lambda}^{\text{phys}}, \quad (\text{Eq 2})$$

where the Gibbs energy of phase λ , G_{λ} , is a sum of the reference Gibbs energy, G_{λ}° , the ideal mixing term of Gibbs energy, $G_{\lambda}^{\text{id}} = -TS_{\lambda}^{\text{id}}$, which assumes random mixing of constituents with S_{λ}^{id} denoting the entropy of mixing, and a term to account for excess mixing energy, G_{λ}^{ex} . The term $G_{\lambda}^{\text{phys}}$ captures the various physical phenomena that contribute to the Gibbs energy of the phase. The most important amongst these is the magnetic contribution to the Gibbs energy that results from the unpaired electron spins in atoms of magnetic substances. This paper focuses on the excess Gibbs energy of mixing and its contribution to the chemical potentials of the species in the system. Magnetic and other physical contributions to excess mixing energies will not be discussed here.

The chemical potential of species i of phase λ is the partial derivative of the integral Gibbs energy of the system with respect to the number of moles of that species at constant temperature, T , and pressure, P . Mathematically, this is represented as:

$$\mu_{i(\lambda)} = \left(\frac{\partial G_{\lambda}}{\partial n_{i(\lambda)}} \right)_{T,P,n_j \neq i}, \quad (\text{Eq 3})$$

where n_i represents the number of moles of species i . One can obtain an expanded expression for chemical potential by substituting Eq 1 and 2 into Eq 3 above, which gives the following:

$$\mu_{i(\lambda)} = \underbrace{\left(\frac{\partial G_{\lambda}^{\circ}}{\partial n_i} \right)_{T,P,n_j \neq i}}_{\mu_{i(\lambda)}^{\circ}} + \underbrace{\left(\frac{\partial G_{\lambda}^{\text{id}}}{\partial n_i} \right)_{T,P,n_j \neq i}}_{\mu_{i(\lambda)}^{\text{id}}} + \underbrace{\left(\frac{\partial G_{\lambda}^{\text{ex}}}{\partial n_i} \right)_{T,P,n_j \neq i}}_{\mu_{i(\lambda)}^{\text{ex}}}, \quad (\text{Eq 4})$$

where the contributions to the integral Gibbs energy are obtained as the product of number of moles of a phase and the respective molar Gibbs energy contribution (i.e., $G_{\lambda}^{\circ} = n_{\lambda} g_{\lambda}^{\circ}$, $G_{\lambda}^{\text{id}} = n_{\lambda} g_{\lambda}^{\text{id}}$ and $G_{\lambda}^{\text{ex}} = n_{\lambda} g_{\lambda}^{\text{ex}}$), with g_{λ}° , g_{λ}^{id} and g_{λ}^{ex} denoting the molar reference Gibbs energy, the molar ideal Gibbs energy of mixing and the molar excess Gibbs energy of mixing, respectively. The partial derivative terms are referred to as the partial reference molar Gibbs energy, partial molar ideal Gibbs energy of mixing and partial molar excess Gibbs energy of mixing and are denoted by $\mu_{i(\lambda)}^{\circ}$, $\mu_{i(\lambda)}^{\text{id}}$, and $\mu_{i(\lambda)}^{\text{ex}}$ respectively.

The expressions for molar Gibbs energy terms depend on the solution model used to describe the phase. This paper presents the derivation of the partial excess molar Gibbs energy terms for some commonly employed solution models and the partial molar reference Gibbs energy and partial molar ideal Gibbs energy terms are briefly presented

for completeness. While there are multiple papers in the open literature that describe these models, none give a full derivation of the partial molar excess Gibbs energy of mixing. Section 2 provides background to substitutional solution theory and presents the various parameters used in those models. Sections 3 and 4 provide the derivation of the partial molar excess excess Gibbs energy of mixing terms for the two most common substitutional models, i.e. the simple polynomial model with Kohler–Toop interpolation and the Redlich–Kister polynomial model with Muggiano interpolation. Section 5 describes the multi-sublattice CEF and the derivation of chemical potential for the compound end members of the model is presented. Furthermore, the methodology adopted for deriving the expressions is applicable to other thermodynamic models as well. The remainder of the paper will focus on calculations within a single solution phase, and therefore going forward the phase identifier λ will be omitted to simplify the notation.

2 Substitutional Solution Theory

Several solids and liquids conform to substitutional solution behaviour, which is based on the assumption that the constituents mix randomly on a single lattice.^[5] The reference Gibbs energy of solution phase λ represents the Gibbs energy of an unreacted mixture of the different species and is given as follows:

$$G_{\lambda}^{\circ} = n_{\lambda} \sum_i x_{i(\lambda)} g_{i(\lambda)}^{\circ} \quad (\text{Eq } 5)$$

where $x_{i(\lambda)}$ denotes the mole fraction of species i of phase λ and is related to the molar amount of species i , $n_{i(\lambda)}$ per mole of phase λ , n_{λ} (i.e., $x_{i(\lambda)} = n_{i(\lambda)} / n_{\lambda}$). Since the reference molar Gibbs energy of the independent species, denoted by $g_{i(\lambda)}^{\circ}$, depends only on the temperature and pressure of the system, the molar reference Gibbs energy of the phase is given as:

$$\mu_{i(\lambda)}^{\circ} = g_{i(\lambda)}^{\circ}. \quad (\text{Eq } 6)$$

The term $g_{i(\lambda)}^{\circ}$ is obtained from a thermodynamic database.

The second term of Eq 4 relates to the ideal Gibbs energy of mixing, which is written as:

$$G_{\lambda}^{\text{id}} = n_{\lambda} RT \sum_i x_{i(\lambda)} \ln x_{i(\lambda)} \quad (\text{Eq } 7)$$

where R is the ideal gas constant. This results in the following expressions for the partial molar ideal Gibbs energy of mixing:

$$\mu_{i(\lambda)}^{\text{id}} = RT \ln x_{i(\lambda)}. \quad (\text{Eq } 8)$$

Substitutional solution models represent the excess Gibbs energy of mixing through a polynomial function, which helps in extrapolating the properties of higher order systems from lower order systems. In general, for a multi-component system, the excess molar Gibbs energy of mixing results from binary, ternary and quaternary interactions, which can be described separately as follows:

$$g^{\text{ex}} = g_{\text{bin}}^{\text{ex}} + g_{\text{ter}}^{\text{ex}} + g_{\text{qua}}^{\text{ex}}, \quad (\text{Eq } 9)$$

where the right subscripts bin, ter and qua denote the species interacting in the binary, ternary and quaternary subsystems, respectively.

For a multi-species substitutional solution phase, the binary interactions result in the following contribution to excess molar Gibbs energy of mixing:

$$g_{\text{bin}}^{\text{ex}} = \sum_i \sum_{j > i} x_i x_j L_{ij}. \quad (\text{Eq } 10)$$

The solution parameter L_{ij} represents the interaction between the two species and is, in general, a function of both temperature and composition.

Redlich and Kister^[6] proposed a symmetrical form of the interaction parameter, which is now widely used because of the ease of extrapolating it to ternary and higher-order systems. This is commonly referred to as the Redlich–Kister polynomial and is represented as follows:

$$L_{ij} = \sum_{v \geq 0} {}^v L_{ij} (x_i - x_j)^v, \quad (\text{Eq } 11)$$

where the parameters ${}^v L_{ij}$ are independent of composition but can be temperature dependent, and the number of terms used can be chosen to make an appropriate fit to the available experimental data. The superscript v denotes the order of the interaction parameter terms.

While the Redlich–Kister polynomials are most commonly used to represent a solution parameter, a number of other forms have been proposed, such as simple polynomial form, Lagrange series, etc. Among these, the simple polynomial form is the most commonly used and results in the following:

$$L_{ij} = \sum_{u,v \geq 0} {}^{uv} Q_{ij} x_i^u x_j^v, \quad (\text{Eq } 12)$$

where parameters ${}^{uv} Q_{ij}$ are independent of composition but can be temperature dependent. The two formulations are identical in the case of binary systems and the interaction parameters can be easily converted from one form to another. However, in the case of higher order systems, the interpolations would depend on the series used and the interpolation method.

Considering ternary mixing, interaction requires an additional summation resulting in the following:

$$g_{\text{ter}}^{\text{ex}} = \sum_i \sum_{j > i} \sum_{k > j} x_i x_j x_k L_{ijk}. \quad (\text{Eq } 13)$$

Like the binary subsystems, the interaction parameters for the ternary subsystems can be determined experimentally or based on a number of analytical methods. According to Hillert,^[7] in case of composition dependence, there is no unique way of predicting the binary contribution to ternary and higher order systems and as a result a number of different expressions have been proposed with preference given to the expression suggested by Redlich and Kister.^[6] To interpolate ternaries from their binaries, a number of interpolation schemes have been proposed by Kohler,^[8] Toop,^[9] Colinet,^[10] and Muggiano.^[11] A combination of these models, most commonly Kohler–Toop and Muggiano–Toop, can be used to estimate the energies of higher order systems from their binary subsystems. Among the four interpolation methods, Kohler, Colinet and Muggiano methods are symmetric and treat all the binary subsystems in the same way, but the ternary excess terms are related to the binary excess terms through the composition paths depicted in Fig. 1. It must be emphasised that the components in the illustrated figures refer to the species and not the system components. For example, in Fig. 1(a), the phase has three species i , j and k , which are denoted at the vertices of the triangle.

The composition of the ternary phase is denoted by point p and the points a , b and c represent the binary compositions obtained using the interpolation model in question. In the following discussion, the functional form $g_{ij}(\alpha; \beta)$ will be used to refer to the molar Gibbs energy contribution from a binary system, with α and β representing the projected concentrations of the two species of the binary subsystem. For example, the excess Gibbs energy of mixing in the $i - j$ binary subsystem should be calculated at point a and is given as $g_{ij}^{\text{ex}}(\alpha; \beta)$, where α and β are the equivalent concentrations of species i and j in the binary subsystem, respectively, and $\alpha + \beta = 1$.

- **Kohler:** The Kohler interpolation scheme shown in Fig. 1(a) is symmetric. On the line ap , the ratio $x_j/(x_i + x_j)$ remains constant and the binary contribution of the $i - j$ subsystem to the ternary can be computed by evaluating the binary excess Gibbs energy of mixing of the $i - j$ subsystem at point a .^[13] For a multi-species phase, the ternary excess Gibbs energy is then given as the following:

$$g^{\text{ex}} = \sum_i \sum_{j > i} (x_i + x_j)^2 \cdot g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right), \quad (\text{Eq } 14)$$

where the expression $g_{ij}^{\text{ex}}(\alpha; \beta)$ denotes that excess Gibbs energy of mixing of binary subsystem $i - j$ evaluated at molar equivalent composition α and β and the factor $(x_i + x_j)^2$ is a result of using the interpolation formula instead of the composition of the system.

- **Muggiano:** The Muggiano interpolation scheme is based on the fact that along the line ap shown in Fig. 1(b), the ratios $(1 + x_i - x_j)/2$ and $(1 - x_i + x_j)/2$ both remain constant.^[13] The excess Gibbs energy of mixing takes the following form:

$$g^{\text{ex}} = \sum_i \sum_{j > i} \frac{4x_i x_j}{(1 + x_i - x_j)(1 + x_j - x_i)} \cdot g_{ij}^{\text{ex}} \left(\frac{1 + x_i - x_j}{2}; \frac{1 + x_j - x_i}{2} \right). \quad (\text{Eq } 15)$$

- **Kohler–Toop:** The Kohler–Toop interpolation scheme shown in Fig. 1(c) is an asymmetrical model, which is often used when one species of the subsystem belongs to a group different from the others.^[13] Since the mole fraction x_i is constant along the line ac , and the line bp follows from Kohler interpolation, the excess molar Gibbs energy can be written as follows^[14]

$$g^{\text{ex}} = \frac{x_j}{1 - x_i} \cdot g_{ij}^{\text{ex}}(x_i; 1 - x_i) + \frac{x_k}{1 - x_i} \cdot g_{ik}^{\text{ex}}(x_i; 1 - x_i) + (1 - x_i)^2 \cdot g_{jk}^{\text{ex}} \left(\frac{x_j}{x_j + x_k}; \frac{x_k}{x_j + x_k} \right). \quad (\text{Eq } 16)$$

The Kohler–Toop model depends on the choice of symmetric and asymmetric species and in the Eq 16, species i of Fig. 1(c) has been selected as the Kohler component.

An advantage of using Redlich–Kister polynomials is the fact that when using the Muggiano interpolation method, the binary terms can be used directly in the ternary extrapolations. This is an outcome of the fact that along the line ap shown in Fig. 1(b), the quantity $x_i - x_j$ remains constant.^[13, 15] This results in what is commonly referred to as the Redlich–Kister–Muggiano polynomial model. Also, it must be mentioned that the composition independent parameter ${}^0L_{ij}$ scales the same way irrespective of the model used.

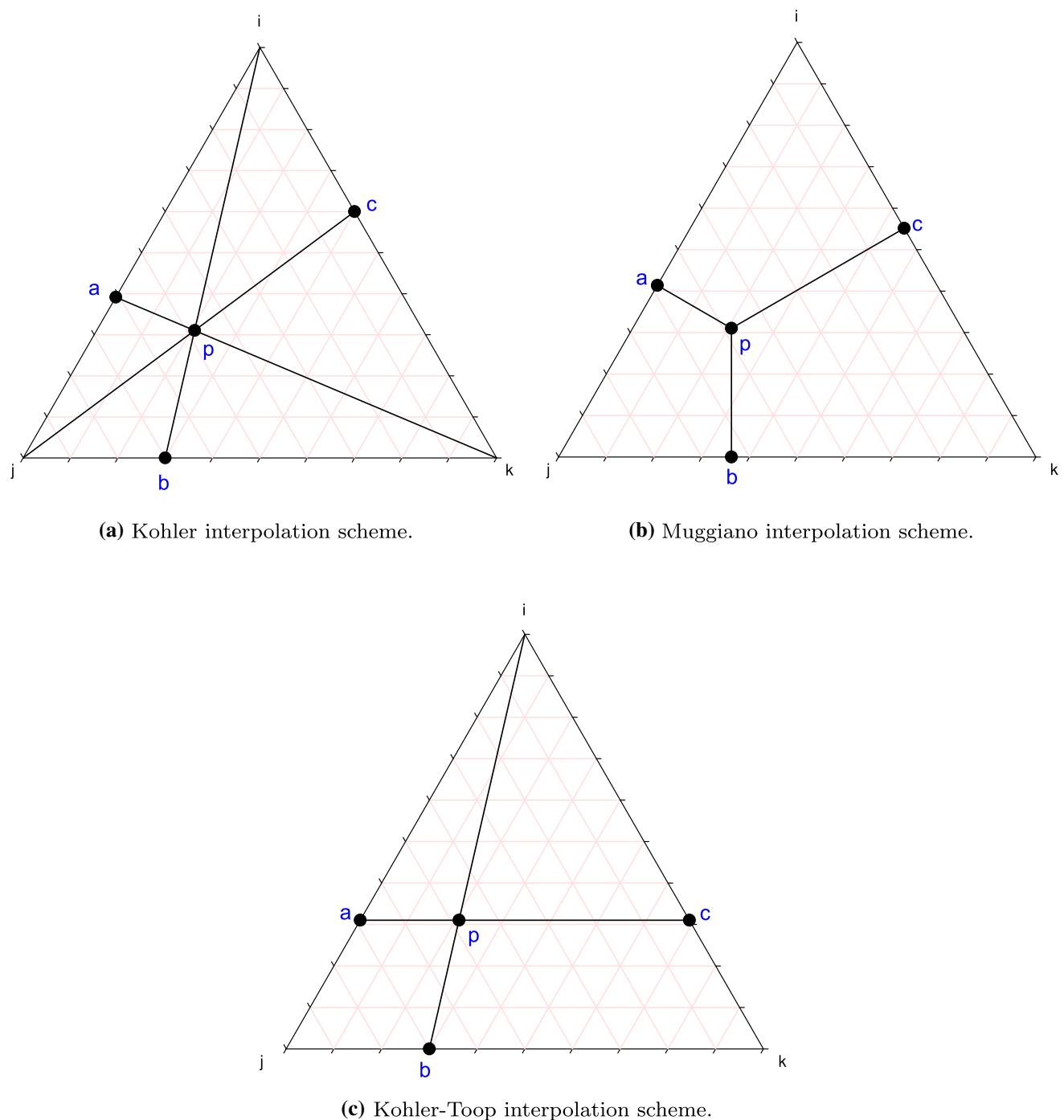


Fig. 1 Commonly used interpolation models^[12]

3 Simple Polynomial Solution Model with Kohler-Toop Interpolation

Substitutional solution models using the simple polynomial form of the interaction parameters often utilise the Kohler-Toop interpolation scheme. The choice of the interpolation scheme for a system of interest is based on the judgement of the model developer, with physical and thermodynamic

factors such as the similarity of species playing key roles in the choice between the symmetric Muggiano or the asymmetric Kohler-Toop models. Chartrand and Pelton have provided a detailed description of the reasoning behind the preferability of the Kohler-Toop model in a number of cases.^[13] While Redlich-Kister polynomials can also be used in place of simple polynomials, the latter has been the standard notation adopted when using the Kohler-

Toop interpolation model. A derivation for the partial molar excess Gibbs energy for this case follows.

3.1 Derivation of Partial Excess Gibbs Energy of Mixing for a Solution Model with Kohler-Toop Interpolation

3.1.1 Derivation of Terms for a Subsystem Modelled by a Simple Polynomial Formulation

In the substitutional solution model using simple polynomials, the molar excess Gibbs energy of mixing is generally given in terms of binary and ternary mixing parameters:

$$\begin{aligned} {}^{\text{SP}}g_{ijk}^{\text{ex}}(x_i; x_j; x_k) \\ = \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk}x_i^u x_j^v x_k^w, \end{aligned} \quad (\text{Eq } 17)$$

where the left-superscript SP indicates the Simple Polynomial formulation and the exponents u , v and w are integers.

Denoting the number of moles of the phase by n , where n is equal to the sum of the number of moles of each species of the solution phase (i.e. $n = \sum_i n_i$) the integral excess Gibbs energy of mixing is:

$$\begin{aligned} {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_{\text{interp}}) \\ = n_{\text{interp}} \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}}\left(\frac{n_i}{n_{\text{interp}}}; \frac{n_j}{n_{\text{interp}}}; \frac{n_k}{n_{\text{interp}}}\right). \end{aligned} \quad (\text{Eq } 18)$$

Equation 18 makes explicit how one may interpolate into subsystems, which will become very useful in the following subsections. The first argument ($\{n_i; n_j; n_k\}$) is the list of molar quantities of species used in the excess mixing term, while the second argument (n_{interp}) is the total number of moles to consider when interpolating into the desired subsystem. For the moment, one may consider the entire system by setting $n_{\text{interp}} = n$ as the second argument.

$$\begin{aligned} {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n) \\ = n \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}}\left(\frac{n_i}{n}; \frac{n_j}{n}; \frac{n_k}{n}\right) \\ = n \cdot \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk}x_i^u x_j^v x_k^w \\ = n \cdot \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \frac{n_i^u n_j^v n_k^w}{n^{u+v+w}} \\ = \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk}(n_i^u n_j^v n_k^w)(n^{1-u-v-w}). \end{aligned} \quad (\text{Eq } 19)$$

The partial molar excess Gibbs energy of mixing of species i resulting from parameters involving species i, j , and k , $\mu_{i(jk)}^{\text{ex}}$, is obtained by taking the partial derivative of Eq 19

with respect to the number of moles of the species, n_i , as per Eq 3:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(jk)}^{\text{ex}} \\ = \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \left[\frac{un_i^{u-1} n_j^v n_k^w}{n^{u+v+w-1}} \right. \\ \left. - (u+v+w-1) \frac{n_i^u n_j^v n_k^w}{n^{u+v+w}} \right]. \end{aligned} \quad (\text{Eq } 20)$$

Substituting molar quantities, i.e. $x_i = \frac{n_i}{n}$, into Eq 20 gives:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(jk)}^{\text{ex}} \\ = \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \left[\frac{u(nx_i)^{u-1} (nx_j)^v (nx_k)^w}{n^{u+v+w-1}} \right. \\ \left. - (u+v+w-1) \frac{(nx_i)^u (nx_j)^v (nx_k)^w}{n^{u+v+w}} \right] \\ = \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} \left[\frac{ux_i^{u-1} x_j^v x_k^w n^{u+v+w-1}}{n^{u+v+w-1}} \right. \\ \left. - (u+v+w-1) \frac{x_i^u x_j^v x_k^w n^{u+v+w}}{n^{u+v+w}} \right]. \end{aligned} \quad (\text{Eq } 21)$$

Simplifying, the following partial molar excess Gibbs energy of mixing of species i in the subsystem is obtained:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(jk)}^{\text{ex}}(x_i; x_j; x_k) \\ = \sum_{u,v,w \geq 0} {}^{uvw}Q_{ijk} [ux_i^{u-1} + (1-u-v-w)x_i^u] x_j^v x_k^w. \end{aligned} \quad (\text{Eq } 22)$$

It is worth mentioning that the expressions for a three species phase can be directly used for a binary phase by setting the exponent w equal to zero. Thus, for a binary phase, the following expression for the integral excess Gibbs energy of mixing is obtained:

$$\begin{aligned} {}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n_j\}, n_{\text{interp}}) \\ = n_{\text{interp}} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}\left(\frac{n_i}{n_{\text{interp}}}; \frac{n_j}{n_{\text{interp}}}\right). \end{aligned} \quad (\text{Eq } 23)$$

The molar excess Gibbs energy of mixing is:

$${}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; x_j) = \sum_{u,v > 0} {}^{uv}Q_{ij}x_i^u x_j^v, \quad (\text{Eq } 24)$$

and the partial molar excess Gibbs energy is:

$$\begin{aligned} {}^{\text{SP}}\mu_{i(j)}^{\text{ex}}(x_i; x_j) \\ = \sum_{u,v > 0} {}^{uv}Q_{ij} [ux_i^{u-1} + (1-u-v)x_i^u] x_j^v. \end{aligned} \quad (\text{Eq } 25)$$

3.1.2 Derivation of Ternary Phase from Binary Subsystems of a Substitutional Solution Model Using Kohler Interpolation

When modelling the ternary phase by geometrically interpolating binary subsystems using Kohler interpolation (indicated in the following with left-superscript KO), the following expression is obtained by substituting Eq 24 into Eq 14 (and including ternary mixing terms as well):

$$\begin{aligned} & \text{KO } g_{ijk}^{\text{ex}} \\ &= (x_i + x_j)^2 \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right) \\ &+ (x_i + x_k)^2 \cdot \text{SP } g_{ik}^{\text{ex}} \left(\frac{x_i}{x_i + x_k}; \frac{x_k}{x_i + x_k} \right) \quad (\text{Eq 26}) \\ &+ (x_j + x_k)^2 \cdot \text{SP } g_{jk}^{\text{ex}} \left(\frac{x_j}{x_j + x_k}; \frac{x_k}{x_j + x_k} \right) \\ &+ \sum_{u,v,w>0} u v w Q_{ijk} x_i^u x_j^v x_k^w, \end{aligned}$$

where the binary subsystems are evaluated as described in section 2, and the summation in the last term is only over ternary parameters. In a ternary subsystem, this summation can be evaluated straightforwardly, and in subsystems with more species the procedure is described in section 3.1.4. For the moment, the focus will be on the evaluation of the binary terms within a ternary subsystem.

Owing to the symmetric nature of the preceding equation, the equations for partial molar excess Gibbs energies can be derived for a single binary subsystem and the contribution from each subsystem can be summed together. Considering the contribution of the $i - j$ binary subsystem:

$$\text{KO } g_{ij}^{\text{ex}} = (x_i + x_j)^2 \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right), \quad (\text{Eq 27})$$

the integral excess Gibbs energy of mixing contribution of the subsystem can be written as follows:

$$\begin{aligned} & \text{KO } G_{ij}^{\text{ex}} = n \cdot \text{KO } g_{ij}^{\text{ex}} \\ &= \frac{(n_i + n_j)^2}{n} \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right) \quad (\text{Eq 28}) \end{aligned}$$

The interpolated integral excess Gibbs energy of the binary subsystem is weighted such that:

$$\begin{aligned} & \text{SP } G_{ij}^{\text{ex}}(\{n_i; n_j\}, n_i + n_j) = (n_i + n_j) \\ & \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right), \quad (\text{Eq 29}) \end{aligned}$$

and the equation then becomes:

$$\begin{aligned} & \text{KO } G_{ij}^{\text{ex}} = \frac{(n_i + n_j)}{n} \\ & \cdot \text{SP } G_{ij}^{\text{ex}}(\{n_i; n_j\}, n_i + n_j). \quad (\text{Eq 30}) \end{aligned}$$

Taking the partial derivative of Eq 30 with respect to n_i :

$$\begin{aligned} & \text{KO } \mu_{i(ij)}^{\text{ex}} \\ &= \frac{(n_i + n_j)}{n} \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right) \\ &+ \frac{(n_i + n_j)}{n} \cdot \text{SP } \mu_{i(ij)}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right) \quad (\text{Eq 31}) \\ &- \frac{(n_i + n_j)^2}{n^2} \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right). \end{aligned}$$

The previous equation simplifies to the following expression, which is applicable to both species of the binary subsystem¹:

$$\begin{aligned} & \text{KO } \mu_{i(ij)}^{\text{ex}} \\ &= \left[\text{SP } \mu_{i(ij)}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right) + (1 - x_i - x_j) \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right) \right] (x_i + x_j), \quad (\text{Eq 32}) \end{aligned}$$

where the term $\text{SP } \mu_{i(ij)}^{\text{ex}}$ is the chemical potential of species i in binary subsystem $i - j$ and can be calculated using Eq 25. For any remaining species (i.e., the species not part of the binary subsystem):

$$\begin{aligned} & \text{KO } \mu_{k(ij)}^{\text{ex}} = -(x_i + x_j)^2 \\ & \cdot \text{SP } g_{ij}^{\text{ex}} \left(\frac{x_i}{x_i + x_j}; \frac{x_j}{x_i + x_j} \right). \quad (\text{Eq 33}) \end{aligned}$$

In Eq 31, 32 and 33, the definitions of $\text{SP } g_{ij}^{\text{ex}}$ and $\text{SP } \mu_{i(ij)}^{\text{ex}}$ given in Eq 24 and 25 can be used directly. Therefore, in a ternary phase evaluated using Kohler interpolation, the total of the binary contributions to the chemical potential of species i will be:

$$\begin{aligned} & \text{KO } \mu_{i(ijk)}^{\text{ex}} = \text{KO } \mu_{i(ij)}^{\text{ex}} \\ &+ \text{KO } \mu_{i(ik)}^{\text{ex}} + \text{KO } \mu_{i(jk)}^{\text{ex}}. \quad (\text{Eq 34}) \end{aligned}$$

3.1.3 Derivation of Ternary Phase from Binary Subsystems of a Substitutional Solution Model Using Kohler-Toop Interpolation

When modelling the ternary phase of a three species subsystem by geometrically interpolating binary subsystems

¹ Unless specified otherwise, all the expressions for chemical potentials account for the chain rule and the expressions from the referenced equations can be directly substituted.

using Kohler–Toop interpolation (indicated in the following by the left-superscript KT), the expression shown in Eq 16 is obtained:

$$\begin{aligned} {}^{\text{KT}}g_{ijk}^{\text{ex}} &= \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &+ (1-x_i)^2 \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right), \end{aligned} \quad (\text{Eq } 35)$$

where the binary subsystems are evaluated as mentioned in section 2. Since the model is asymmetric, the expression for the partial molar excess Gibbs energy will depend on the choice of the Kohler component, which has been selected to be species i in the previous equation.

Expressing the previous equation in terms of molar quantities and multiplying by the molar amount of the phase, n , the following ternary contribution to the integral Gibbs energy is obtained:

$$\begin{aligned} {}^{\text{KT}}G_{ijk}^{\text{ex}} &= n \left[\frac{n_j}{n-n_i} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \right. \\ &+ \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &\left. + \left(\frac{n-n_i}{n}\right)^2 \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \right]. \end{aligned} \quad (\text{Eq } 36)$$

The integral excess Gibbs energy of mixing contribution of the ij pair and non-Kohler subsystems can be written as follows:

$${}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n-n_i\}, n) = n \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i), \quad (\text{Eq } 37)$$

making use of this plus the earlier definition in Eq 29

$$\begin{aligned} {}^{\text{KT}}G_{ijk}^{\text{ex}} &= \frac{n_j}{n-n_i} \cdot {}^{\text{SP}}G_{ij}^{\text{ex}}(\{n_i; n-n_i\}, n) \\ &+ \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}G_{ik}^{\text{ex}}(\{n_i; n-n_i\}, n) \\ &+ \frac{(n-n_i)^2}{n \cdot (n_j+n_k)} \cdot {}^{\text{SP}}G_{jk}^{\text{ex}}(\{n_i; n_j\}, n_i+n_j). \end{aligned} \quad (\text{Eq } 38)$$

The partial molar excess Gibbs energy of species j can be calculated by taking the partial derivative of Eq 36 with respect to n_j :

$$\begin{aligned} {}^{\text{KT}}\mu_{j(ijk)}^{\text{ex}} &= n \left(\frac{1}{n-n_i} - \frac{n_j}{(n-n_i)^2} \right) \\ &\cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{n_j}{n-n_i} \cdot {}^{\text{SP}}\mu_{j(ij)}^{\text{ex}}(x_i; 1-x_i) \\ &- n \frac{n_k}{(n-n_i)^2} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}\mu_{j(ik)}^{\text{ex}}(x_i; 1-x_i) \\ &+ \left(\frac{2}{n-n_i} - \frac{1}{n} - \frac{1}{n_j+n_k} \right) \left(\frac{(n-n_i)^2}{n} \right) \\ &\cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\ &+ \frac{(n-n_i)^2}{n \cdot (n_j+n_k)} \\ &\cdot {}^{\text{SP}}\mu_{j(jk)}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\ &= \left(\frac{1}{1-x_i} - \frac{x_j}{(1-x_i)^2} \right) \\ &\cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}\mu_{j(ij)}^{\text{ex}}(x_i; 1-x_i) \\ &- \frac{x_k}{(1-x_i)^2} \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\ &+ \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}\mu_{j(ik)}^{\text{ex}}(x_i; 1-x_i) \\ &+ \left(2(1-x_i) - (1-x_i)^2 - \frac{(1-x_i)^2}{x_j+x_k} \right) \\ &\cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\ &+ \frac{(1-x_i)^2}{x_j+x_k} \\ &\cdot {}^{\text{SP}}\mu_{j(jk)}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right). \end{aligned} \quad (\text{Eq } 39)$$

Similarly, the partial molar excess Gibbs energy of mixing of species k can be calculated by taking the partial derivative of Eq 36 with respect to n_k :

$$\begin{aligned}
& {}^{\text{KT}}\mu_{k(ijk)}^{\text{ex}} \\
&= -\frac{x_j}{(1-x_i)^2} \cdot {}^{\text{SP}}g_{ij}^{\text{ex}}(x_i; 1-x_i) \\
&\quad + \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}\mu_{k(ij)}^{\text{ex}}(x_i; 1-x_i) \\
&\quad + \left(\frac{1}{1-x_i} - \frac{x_k}{(1-x_i)^2} \right) \\
&\quad \cdot {}^{\text{SP}}g_{ik}^{\text{ex}}(x_i; 1-x_i) \\
&\quad + \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}\mu_{k(ik)}^{\text{ex}}(x_i; 1-x_i) \\
&\quad + \left(2(1-x_i) - (1-x_i)^2 - \frac{(1-x_i)^2}{x_j+x_k} \right) \\
&\quad \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\
&\quad + \frac{(1-x_i)^2}{x_j+x_k} \\
&\quad \cdot {}^{\text{SP}}\mu_{k(jk)}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right).
\end{aligned} \tag{Eq 40}$$

Finally, the partial molar excess Gibbs energy of species i can be calculated by taking the partial derivative of Eq 36 with respect to n_i :

$$\begin{aligned}
& {}^{\text{KT}}\mu_{i(ijk)}^{\text{ex}} \\
&= \frac{n_j}{n-n_i} \cdot {}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}(x_i; 1-x_i) \\
&\quad + \frac{n_k}{n-n_i} \cdot {}^{\text{SP}}\mu_{i(ik)}^{\text{ex}}(x_i; 1-x_i) \\
&\quad - \frac{(n-n_i)^2}{n^2} \\
&\quad \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right) \\
&= \frac{x_j}{1-x_i} \cdot {}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}(x_i; 1-x_i) \\
&\quad + \frac{x_k}{1-x_i} \cdot {}^{\text{SP}}\mu_{i(ik)}^{\text{ex}}(x_i; 1-x_i) \\
&\quad - (1-x_i)^2 \\
&\quad \cdot {}^{\text{SP}}g_{jk}^{\text{ex}}\left(\frac{x_j}{x_j+x_k}; \frac{x_k}{x_j+x_k}\right).
\end{aligned} \tag{Eq 41}$$

In the previous equations, the definitions of ${}^{\text{SP}}g_{ij}^{\text{ex}}$ and ${}^{\text{SP}}\mu_{i(ij)}^{\text{ex}}$ given in Eq 24 and 25 can be used directly.

3.1.4 Derivation of Terms of a Ternary Subsystem Using Kohler Interpolation

A multi-species phase can be extrapolated from the ternary phase following the same principle used for extrapolating the ternary from a binary. The molar excess Gibbs energy of mixing of such a phase can be represented as:

$$\begin{aligned}
g^{\text{ex}} &= \sum_{i,j,k \geq 0} (x_i + x_j + x_k)^3 \\
&\quad \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}}\left(\frac{x_i}{x_i + x_j + x_k}; \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k}\right),
\end{aligned} \tag{Eq 42}$$

and expanding this expression in terms of molar quantities instead of mole fractions:

$$\begin{aligned}
g^{\text{ex}} &= \sum_{i,j,k \geq 0} \left(\frac{n_i + n_j + n_k}{n}\right)^3 \\
&\quad \cdot \frac{{}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k)}{n_i + n_j + n_k}.
\end{aligned} \tag{Eq 43}$$

Evidently, the integral excess Gibbs energy of mixing of the phase is defined as:

$$\begin{aligned}
G^{\text{ex}} &= \sum_{i,j,k \geq 0} \left(\frac{n_i + n_j + n_k}{n}\right)^2 \\
&\quad \cdot {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k).
\end{aligned} \tag{Eq 44}$$

As before, the focus can be on a single ternary subsystem for finding the relevant partial molar quantities. The partial molar excess Gibbs energy of mixing of species i due to the ijk ternary subsystem is the following:

$$\begin{aligned}
& {}^{\text{SP}}\mu_{i(ijk)}^{\text{ex}} \\
&= 2\left(\frac{n_i + n_j + n_k}{n^2}\right) \\
&\quad \cdot {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k) \\
&\quad + \left(\frac{n_i + n_j + n_k}{n}\right)^2 \\
&\quad \cdot {}^{\text{SP}}\mu_{i(ijk)}^{\text{ex}}\left(\frac{x_i}{x_i + x_j + x_k}; \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k}\right) \\
&\quad - 2\frac{(n_i + n_j + n_k)^2}{n^3} \\
&\quad \cdot {}^{\text{SP}}G_{ijk}^{\text{ex}}(\{n_i; n_j; n_k\}, n_i + n_j + n_k).
\end{aligned} \tag{Eq 45}$$

In a simplified form, the previous equation can be written as follows:

$$\begin{aligned} \mu_{i(ijk)}^{\text{ex}} &= (x_i + x_j + x_k)^2 \left[{}^{\text{SP}}\mu_{i(ijk)}^{\text{ex}} \left(\frac{x_i}{x_i + x_j + x_k}; \right. \right. \\ &\quad \left. \left. \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k} \right) \right. \\ &\quad \left. + 2(1 - x_i - x_j - x_k) \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}} \right. \\ &\quad \left. \left(\frac{x_i}{x_i + x_j + x_k}; \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k} \right) \right] \end{aligned} \quad (\text{Eq } 46)$$

The partial molar excess Gibbs energy of mixing of species m ($m \neq i, j, k$) is:

$$\begin{aligned} \mu_{m(ijk)}^{\text{ex}} &= -2(x_i + x_j + x_k)^3 \\ &\quad \cdot {}^{\text{SP}}g_{ijk}^{\text{ex}} \left(\frac{x_i}{x_i + x_j + x_k}; \frac{x_j}{x_i + x_j + x_k}; \frac{x_k}{x_i + x_j + x_k} \right) \end{aligned} \quad (\text{Eq } 47)$$

In the preceding equations, the definitions of ${}^{\text{SP}}g_{ijk}^{\text{ex}}$ and ${}^{\text{SP}}\mu_{i(ijk)}^{\text{ex}}$ given in Eq 17 and 22 can be used directly.

4 Redlich–Kister Polynomial Model with Muggiano Interpolation

The substitutional solution model employing a Redlich–Kister polynomial formulation has several advantages over the simple polynomial formulation. These advantages have already been mentioned in the previous section. Starting with the Redlich–Kister formalism, the Muggiano interpolation is the simplest higher-order interpolation scheme and the resultant formalism, often called Redlich–Kister–Muggiano polynomial formalism, is widely used in thermodynamic modelling of symmetric phases. The derivations of the relevant terms for computing the chemical potential of a phase modelled using a Redlich–Kister polynomial with Muggiano interpolation are presented in the following discussion.

4.1 Derivation of Partial Excess Gibbs Energy of Mixing

4.1.1 Derivation of Terms of a Multi-species Phase with only Binary Excess Mixing Terms

If Redlich–Kister polynomials are used to represent interaction parameters, then the binary contribution to the molar excess Gibbs energy of mixing of a multi-species phase is simply:

$$g_{\text{bin}}^{\text{ex}} = \sum_i \sum_{j > i} x_i x_j \sum_v {}^v L_{ij}(x_i - x_j)^v. \quad (\text{Eq } 48)$$

The equations are simplified in comparison to the Kohler–Toop scheme, which requires special consideration when relating binary interaction parameters for the molar Gibbs energy of a phase.

The integral excess Gibbs energy of the phase, considering only binary contributions, is defined as follows:

$$\begin{aligned} G_{\text{bin}}^{\text{ex}} &= n \sum_i \sum_{j > i} x_i x_j \sum_v {}^v L_{ij}(x_i - x_j)^v \\ &= \sum_i \sum_{j > i} \frac{n_i n_j}{n} \sum_v {}^v L_{ij} \left(\frac{n_i - n_j}{n} \right)^v. \end{aligned} \quad (\text{Eq } 49)$$

For deriving the partial molar excess Gibbs energy of mixing of species k in a multi-species phase, the binary contribution to the integral Gibbs energy of mixing can be subdivided into three cases based on the presence or absence of species k in the binary subsystems. This results in the following form of Eq 49:

$$\begin{aligned} G_{\text{bin}}^{\text{ex}} &= \underbrace{\sum_{j > k} \frac{n_i n_j}{n} \sum_v {}^v L_{kj} \left(\frac{n_k - n_j}{n} \right)^v}_{i=k} \\ &\quad + \underbrace{\sum_{i < k} \frac{n_i n_k}{n} \sum_v {}^v L_{ik} \left(\frac{n_i - n_k}{n} \right)^v}_{j=k} \\ &\quad + \underbrace{\sum_i \sum_{j > i} \frac{n_i n_j}{n} \sum_v {}^v L_{ij} \left(\frac{n_i - n_j}{n} \right)^v}_{i,j \neq k}. \end{aligned} \quad (\text{Eq } 50)$$

Taking the partial derivative of Eq 50 with respect to n_k , the partial molar excess Gibbs energy of mixing can be given as follows:

$$\begin{aligned} \mu_{k(\text{bin})}^{\text{ex}} &= \sum_{j > k} \left[\left(\frac{n_j}{n} - \frac{n_k n_j}{n^2} \right) \sum_v {}^v L_{kj} \left(\frac{n_k - n_j}{n} \right)^v + \frac{n_k n_j}{n} \sum_v {}^v L_{kj} v \left(\frac{n_k - n_j}{n^2} \right)^{v-1} \left(\frac{1}{n} - \frac{n_k - n_j}{n^2} \right) \right] \\ &\quad + \underbrace{\sum_{i < k} \left[\left(\frac{n_i}{n} - \frac{n_k n_i}{n^2} \right) \sum_v {}^v L_{ik} \left(\frac{n_i - n_k}{n} \right)^v + \frac{n_k n_i}{n} \sum_v {}^v L_{ik} v \left(\frac{n_i - n_k}{n^2} \right)^{v-1} \left(-\frac{1}{n} - \frac{n_i - n_k}{n^2} \right) \right]}_{j=k} \\ &\quad + \underbrace{\sum_i \sum_{j > i} \left[-\frac{n_i n_j}{n^2} \sum_v {}^v L_{ij} \left(\frac{n_i - n_j}{n} \right)^v - \frac{n_i n_j}{n} \sum_v {}^v L_{ij} v \left(\frac{n_i - n_j}{n^2} \right)^{v-1} \left(\frac{n_i - n_j}{n^2} \right) \right]}_{i,j \neq k}, \end{aligned} \quad (\text{Eq } 51)$$

which simplifies to the following expression for the partial molar excess Gibbs energy of mixing of species k when considering only binary contributions:

$$\begin{aligned} \mu_{k(\text{bin})}^{\text{ex}} &= \sum_{j>k} \left[(x_j - x_k x_j) \underbrace{\sum_v {}^v L_{kj}(x_k - x_j)^v}_{i=k} + x_k x_j (1 - (x_k - x_j)) \sum_v {}^v L_{kj} v (x_k - x_j)^{v-1} \right] \\ &+ \sum_{i<k} \left[(x_i - x_i x_k) \underbrace{\sum_v {}^v L_{ik}(x_i - x_k)^v}_{j=k} - x_i x_k (1 + (x_i - x_k)) \sum_v {}^v L_{ik} v (x_i - x_k)^{v-1} \right] \\ &- \underbrace{\sum_i \sum_{j>i} \left[x_i x_j \sum_v {}^v L_{ij}(1+v)(x_i - x_j)^v \right]}_{i,j \neq k}. \end{aligned} \quad (\text{Eq } 52)$$

4.1.2 Derivation of Terms of a Multi-species Phase with only Ternary Excess Mixing Terms

Using Muggiano interpolation, the ternary contribution to the molar Gibbs energy of a multi-species solution phase can be represented by the following expression^[13]:

$$\begin{aligned} g_{\text{ter}}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \sum_l {}^0 L_{l(ijk)} \left(\frac{1 - x_i - x_j - x_k}{3} + x_l \right), \end{aligned} \quad (\text{Eq } 53)$$

where the interaction parameter ${}^0 L_{l(ijk)}$ is only temperature dependent (i.e., only a zeroth-order interaction term, independent of composition) and the right superscript $l = i, j$ and k denotes the species for which the parameter has been established.

The integral excess Gibbs energy of mixing is given as the following:

$$\begin{aligned} G_{\text{ter}}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} \frac{n_i n_j n_k}{n^3} \sum_l {}^0 L_{l(ijk)} \\ &\quad \left(\frac{n - n_i - n_j - n_k}{3} + n_l \right). \end{aligned} \quad (\text{Eq } 54)$$

For a general species w of the multi-species phase, the partial molar excess Gibbs energy can be derived by taking the partial derivative of Eq 54 with respect to the molar quantity of w , n_w

$$\begin{aligned} \mu_{w(\text{ter})}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} \left[\left\{ \frac{1}{n^3} (\delta_{iw} n_j n_k + \delta_{jw} n_i n_k + \delta_{kw} n_i n_j) \right. \right. \\ &\quad - \frac{3n_i n_j n_k}{n^4} \left. \sum_l {}^0 L_{ijk}^l \left(\frac{n - n_i - n_j - n_k}{3} + n_l \right) \right. \\ &\quad \left. + \frac{n_i n_j n_k}{n^3} \sum_l {}^0 L_{l(ijk)} \left(\frac{1 - \delta_{iw} - \delta_{jw} - \delta_{kw}}{3} + \delta_{lw} \right) \right], \end{aligned} \quad (\text{Eq } 55)$$

where the Kronecker delta function δ_{ij} is defined as:

$$\delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j. \end{cases}$$

Equation 55 simplifies into the following form valid for any species:

$$\begin{aligned} \mu_{w(\text{ter})}^{\text{ex}} &= \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \\ &\quad \left[\left(\sum_u \frac{\delta_{uw}}{x_u} - 3 \right) \sum_l {}^0 L_{l(ijk)} \left(\frac{1 - x_i - x_j - x_k}{3} + x_l \right) \right. \\ &\quad \left. + \sum_l {}^0 L_{ijk}^l \left(\frac{1 - \delta_{iw} - \delta_{jw} - \delta_{kw}}{3} + \delta_{lw} \right) \right], \end{aligned} \quad (\text{Eq } 56)$$

where the species index $u = i, j$ and k .

4.1.3 Derivation of Terms of a Multi-species Phase with only Quaternary Excess Mixing Terms

In a multi-species phase modelled by the Redlich–Kister polynomials with Muggiano interpolation, the quaternary contribution to the molar Gibbs energy can be represented with the following equation:

$$g_{\text{qua}}^{\text{ex}} = \sum_i \sum_{j>i} \sum_{k>j} \sum_{l>k} x_i x_j x_k x_l L_{ijkl}, \quad (\text{Eq } 57)$$

where the interaction parameter L_{ijkl} is only temperature dependent (i.e. only a zeroth-order interpolation term, independent of composition).^[13]

The integral excess Gibbs energy of the phase can then be written as follows:

$$G_{\text{qua}}^{\text{ex}} = \sum_i \sum_{j>i} \sum_{k>j} \sum_{l>k} \left(\frac{n_i n_j n_k n_l}{n^3} \right) L_{ijkl}. \quad (\text{Eq } 58)$$

For a general species v of the multi-species phase, the quaternary contribution to the partial molar excess Gibbs energy of mixing can be derived by taking the partial derivative of the previous equation with respect to the molar quantity of v , n_v :

$$\begin{aligned} \mu_{w(qua)}^{\text{ex}} &= \sum_i \sum_j \sum_k \sum_l \left[\frac{1}{n^3} (\delta_{iw} n_j n_k n_l + \delta_{jw} n_i n_k n_l \right. \\ &\quad \left. + \delta_{kw} n_i n_j n_l + \delta_{lw} n_i n_j n_k) - \frac{3 n_i n_j n_k n_l}{n^4} \right] L_{ijkl}, \end{aligned} \quad (\text{Eq } 59)$$

The previous expression can be simplified using the definition of mole fractions:

$$\begin{aligned} \mu_{w(qua)}^{\text{ex}} &= \sum_i \sum_j \sum_k \sum_l x_i x_j x_k x_l \left(\sum_u \frac{\delta_{uw}}{x_u} - 3 \right) L_{ijkl}, \end{aligned} \quad (\text{Eq } 60)$$

where the species index $u = i, j, k$ and l .

5 Compound Energy Formalism

The CEF was developed to account for the existence of multiple sublattices and the mixing of constituents within a sublattice. The CEF is applicable to an arbitrary number of sublattices with any number of constituents on each sublattice. It has been widely applied to the modelling of a variety of phases, such as interstitial solutions, intermetallic phases, etc.

Following the nomenclature of Hillert,^[16] while there can be multiple sets of species with the same chemical formula, they can be distinguished as compound end members with different constituents on the sublattices. To reiterate earlier definitions, in the context of the CEF, a *compound end member* refers to a unique combination of constituents formed by picking one constituent from each sublattice. The total number of end members of a phase modelled by the CEF is the product of the number of constituents on each sublattice. The CEF is based on the principle that each compound end member has its own Gibbs energy of formation.

5.1 Gibbs Energy of Compound Energy Formalism Phases

In CEF, the molar Gibbs energy expressions are defined for each compound end member and excess Gibbs energy of mixing parameters are defined for interactions between the constituents. The molar Gibbs energy, g , of a solution phase modelled using the CEF model is generally given as^[16]:

$$\begin{aligned} g &= \sum_{k=1}^N g_k^{\circ} \prod_{s=1}^{N_s} y_{k(s)} \\ &\quad + RT \left(\sum_{s=1}^{N_s} v_s \sum_{j=1}^{C_s} y_{j(s)} \ln(y_{j(s)}) \right) + g^{\text{ex}}, \end{aligned} \quad (\text{Eq } 61)$$

where g_k° is the reference molar Gibbs energy of the compound end member k , $y_{j(s)}$ represents the site fraction on sublattice s corresponding to constituent j , N and N_s denote the number of compound end members and number of sublattices in the solution phase, respectively. The site fractions of constituents of an end member can be related to the mole fraction of the end member as $x_k = \prod_{s=1}^{N_s} y_{j(s)}$. The stoichiometry coefficient for sublattice s is represented by v_s , the number of constituents on sublattice s is C_s . Finally, the molar excess Gibbs energy of mixing of the solution phase is g^{ex} and is generally defined as follows:

$$g^{\text{ex}} = \sum_{p=1}^{N_p} y_{j_p(s_p)} y_{k_p(s_p)} \left(\prod_{\substack{s=1 \\ s \neq s_p}}^{N_s} y_{l_p(s)} \right) \sum_{v=0}^{V_p} {}^v L_{j_p(s_p)k_p(s_p)} (y_{j_p(s_p)} - y_{k_p(s_p)})^v, \quad (\text{Eq } 62)$$

where N_p denotes the number of excess mixing terms, s_p is the sublattice on which mixing is taking place, $j_p(s_p)$ and $k_p(s_p)$ are the constituents being mixed on that sublattice, $l_p(s)$ are the constituents corresponding to the mixed end members on all sublattices other than s_p , and ${}^v L_{jk}$ denotes the interaction parameter of order v . V_p denotes the number of interaction parameters corresponding to the excess mixing term p .

Equation 61 can be represented in the following form which is more conducive to the subsequent mathematics and explicitly states the meaning of the first term in the previous equation:

$$\begin{aligned} g &= \sum_{k=1}^N g_k^{\circ} \prod_{s=1}^{N_s} \sum_{j=1}^{C_s} \delta_{k(s)j(s)} y_{j(s)} \\ &\quad + RT \left(\sum_{s=1}^{N_s} v_s \sum_{j=1}^{C_s} y_{j(s)} \ln(y_{j(s)}) \right) + g^{\text{ex}}, \end{aligned} \quad (\text{Eq } 63)$$

where $\delta_{k(s)j(s)}$ is a Kronecker delta term that is equal to unity when the constituent j on sublattice s matches that of end member k on sublattice s and is otherwise equal to zero.

5.2 Derivation of Chemical Potential

In models with multiple sublattices including the CEF, the chemical potentials are defined for the compound end members—not the species or constituents—because the reference Gibbs energies are defined for the compound end members.^[16] Applying Eq 3 in this context, the chemical potential of compound end member i in the solution phase represented by the CEF model is generally given as^[17]:

$$\mu_i = g + \underbrace{\sum_{s=1}^{N_s} \sum_{j=1}^{C_s} \delta_{i(s)j(s)} \frac{\partial g}{\partial y_{j(s)}}}_{\text{constituents in end member}} + \underbrace{\sum_{s=1}^{N_s} \sum_{j=1}^{C_s} y_{j(s)} \frac{\partial g}{\partial y_{j(s)}}}_{\text{all constituents}}. \quad (\text{Eq 64})$$

5.2.1 Derivation of Partial Molar Reference Gibbs Energy and Partial Molar Ideal Gibbs Energy of Mixing Contributions to Chemical Potential

Defining the derivative of the site fraction of constituent k on a sublattice a with respect to the site fraction of constituent j on a sublattice s as:

$$\frac{\partial y_{k(a)}}{\partial y_{j(s)}} = \delta_{as} \delta_{j(s)k(s)}, \quad (\text{Eq 65})$$

one can compute the partial derivative of Eq 63 with respect to $y_{j(s)}$ for all constituents j of compound end member i . Neglecting the partial excess Gibbs energy contribution, the following is obtained for a particular constituent:

$$\begin{aligned} \frac{\partial(g - g^{\text{ex}})}{\partial y_{j(s)}} &= \sum_{k=1}^{N_s} g_k^{\circ} \left(\frac{\delta_{k(s)j(s)}}{y_{k(s)}} \right) \prod_{a=1}^{N_s} y_{k(a)} + RT v_s (1 + \ln(y_{j(s)})). \end{aligned} \quad (\text{Eq 66})$$

Substituting Eq 66 into Eq 64 yields the reference and ideal mixing contributions to the chemical potential of compound end member i ^[17]:

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= (g - g^{\text{ex}}) + \sum_{s=1}^{N_s} \sum_{j=1}^{C_s} \delta_{i(s)j(s)} \left(\sum_{k=1}^{N_s} g_k^{\circ} \left(\frac{\delta_{k(s)j(s)}}{y_{k(s)}} \right) \right. \\ &\quad \left. \prod_{a=1}^{N_s} y_{k(a)} + RT v_s (1 + \ln(y_{j(s)})) \right) \\ &\quad - \sum_{s=1}^{N_s} \sum_{j=1}^{C_s} y_{j(s)} \left(\sum_{k=1}^{N_s} g_k^{\circ} \left(\frac{\delta_{k(s)j(s)}}{y_{k(s)}} \right) \right) \prod_{a=1}^{N_s} y_{k(a)} \\ &\quad + RT v_s (1 + \ln(y_{j(s)})), \end{aligned} \quad (\text{Eq 67})$$

which simplifies to the following:

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= (g - g^{\text{ex}}) + \sum_{s=1}^{N_s} \sum_{k=1}^{N_s} g_k^{\circ} x_k \left(\frac{\delta_{i(s)k(s)}}{y_{k(s)}} \right) \\ &\quad + RT \sum_{s=1}^{N_s} v_s (1 + \ln(y_{i(s)})) \\ &\quad - N_s \sum_{k=1}^{N_s} g_k^{\circ} x_k - RT \sum_{s=1}^{N_s} v_s \left(1 + \sum_{j=1}^{C_s} y_{j(s)} \ln(y_{j(s)}) \right). \end{aligned} \quad (\text{Eq 68})$$

Replacing the expression for $g - g^{\text{ex}}$ from Eq 61 into the preceding equation, the following is obtained:

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= \sum_{k=1}^{N_s} g_k^{\circ} x_k \\ &\quad + RT \left(\sum_{s=1}^{N_s} v_s \sum_{j=1}^{C_s} y_{j(s)} \ln(y_{j(s)}) \right) + \sum_{s=1}^{N_s} \sum_{k=1}^{N_s} g_k^{\circ} x_k \left(\frac{\delta_{i(s)k(s)}}{y_{k(s)}} \right) \\ &\quad + RT \sum_{s=1}^{N_s} v_s (1 + \ln(y_{i(s)})) \\ &\quad - N_s \sum_{k=1}^{N_s} g_k^{\circ} x_k - RT \sum_{s=1}^{N_s} v_s \left(1 + \sum_{j=1}^{C_s} y_{j(s)} \ln(y_{j(s)}) \right), \end{aligned} \quad (\text{Eq 69})$$

which simplifies to the following expression for reference and ideal mixing contributions to chemical potential of compound end member i :

$$\begin{aligned} \mu_i^{\circ} + \mu_i^{\text{id}} &= \sum_{k=1}^{N_s} g_k^{\circ} x_k \left(1 - N_s + \sum_{s=1}^{N_s} \frac{\delta_{i(s)k(s)}}{y_{i(s)}} \right) \\ &\quad + RT \sum_{s=1}^{N_s} v_s \ln(y_{i(s)}). \end{aligned} \quad (\text{Eq 70})$$

The chemical potential of a compound end member therefore includes contributions from the reference molar Gibbs energies of all compound end members in that phase and the ideal mixing contribution to μ_i only considers the constituents associated with the compound end member i .

5.2.2 Derivation of Partial Molar Excess Gibbs Energy of Mixing Contribution to Chemical Potential

Considering only the composition-independent interaction parameters, Sundman and Ågren gave an expression for the partial molar excess Gibbs energy of mixing of an end member in a CEF phase.^[17] However, a full derivation of partial molar excess Gibbs energy of mixing requires considering composition-dependent terms as well. Accounting for these interaction terms results in the following general expression:

$$\begin{aligned} \mu_i^{\text{ex}} = & \sum_{p=1}^{N_p} y_{j_p(s_p)} y_{k_p(s_p)} \left(\prod_{\substack{s=1 \\ s \neq s_p}}^{N_s} y_{l_p(s)} \right) \sum_{v=0}^{V_p} {}^v L_{j_p(s_p)k_p(s_p)}(y_{j_p(s_p)} \right. \\ & \left. - y_{k_p(s_p)})^v \cdot \left(-(N_s + v) + \frac{\delta_{i(s_p)j_p(s_p)}}{y_{j_p(s_p)}} + \frac{\delta_{i(s_p)k_p(s_p)}}{y_{k_p(s_p)}} \right. \right. \\ & \left. + \sum_{s=1}^{N_s} \frac{\delta_{i(s)l_p(s)}}{y_{l_p(s)}} + \frac{v(\delta_{i(s_p)j_p(s_p)} - \delta_{i(s_p)k_p(s_p)})}{(y_{j_p(s_p)} - y_{k_p(s_p)})} \right) \\ & s \neq s_p \end{aligned} \quad (\text{Eq 71})$$

where terms such as $\delta_{i(s_p)j_p(s_p)}$ are Kronecker deltas equal to unity when the constituent associated with compound end member i on the mixing sublattice s_p is the same as the corresponding constituent of mixing parameter p , $j_p(s_p)$. Equation 71 depends only on the constituents j_p and k_p , and compound end member i . Therefore, this computation does not require looping over other end members and their constituents. Also, note that the indexing scheme used here differs from that of Sundman and Ågren.^[17] Sundman et al. use the variables $z > 0$ and b to represent the order of mixing where $z = b + 1$. To minimise confusion, $v \geq 0$ is used here.

6 Conclusion

Chemical potentials play a key role in the calculation of thermodynamic equilibrium of an isothermal, isobaric system. Explicit expressions for chemical potentials of the

independent variables are required by Gibbs energy minimisers for the formulation of the constraint vector associated with the Hessian matrix of the undetermined Lagrange multipliers and to update the system. A large number of classes of thermodynamic models have been proposed to describe the excess Gibbs energy of mixing for a wide variety of solution phases. While several papers are available in the literature that have described the development of those classes of models, derivations of the chemical potentials ready for implementation in a Gibbs energy minimiser have been absent from the literature. This paper provides full derivations of the chemical potentials of the species in several commonly-used classes of thermodynamic models, such as the substitutional solution model with Kohler–Toop and Muggiano interpolation schemes, and compound energy formalism. These derivations will enable researchers in developing new thermodynamic equilibrium solvers and in integrating the models described in this paper into their pre-existing software.

7 Supplementary Materials

To aid the readers in exploring and verifying the equations presented, Mathematica notebooks are available as supplementary material. Readers without a Mathematica license can use the free Wolfram Player (<https://www.wolfram.com/player/>) to view and interact with the notebooks. A sample PDF output from the notebooks is also attached.

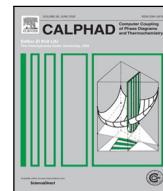
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Recent developments for molten salt systems in ThermoChimica

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ABSTRACT

The modified quasi-chemical model in the quadruplet approximation has been implemented in the open-source equilibrium thermodynamics library ThermoChimica, enabling single point equilibrium calculations and sophisticated multi-physics simulations of molten salt nuclear reactor systems. Here, the derivations necessary to obtain the chemical potentials of the quadruplet species required for Gibbs energy minimization are provided. The implementation is verified via code-to-code benchmarking against FactSage. A scheme to increase computational efficiency of multi-physics simulations including ThermoChimica is described and its effectiveness for molten salt systems demonstrated. Finally, a multi-physics simulation of a molten salt nuclear fuel system is presented as a demonstration problem: ORIGEN-S is used to calculate the isotopic evolution of a fuel-loaded FLiBe mixture with fission and activation products as ThermoChimica predicts the phase evolution and number of moles of Cs in various phases.

1. Introduction

With the recent increase in world-wide interest in Molten Salt (nuclear) Reactor (MSR) designs [1], the need for efficient and accurate chemical thermodynamics calculations involving molten salts has grown rapidly. The MSR concept is being actively explored as a next generation nuclear reactor design in Canada, United States, Europe, and several other nation states in both large scale (e.g., approximately 1000 GWe) and small modular reactor platforms. Molten salts are also used in other engineering applications, including solar technologies. The Modified Quasi-chemical Model (MQM) [2–4] in the Quadruplet Approximation (MQMQA) [5,6] has proven to be an effective model for representing fluoride [7–12] and chloride [8,11–14] salt systems. Use of the MQMQA specifically within the FactSage [15] software in which it was first made available has been extremely popular in recent years [16–21]. Unlike other classes of thermodynamic models that focus on the mixing of constituents, the MQMQA focuses on the mixing of pairs (or quadruplets) of constituents to capture short-range ordering.

As a result of this rapidly growing interest, the MQMQA has been implemented in ThermoChimica [22]. ThermoChimica offers two features that distinguish it from other software: ThermoChimica is a free, open-source library, and ThermoChimica may be readily coupled to other software for the purposes of multi-physics simulations. In particular, ThermoChimica has a history of use in multi-physics simulations of nuclear fuel materials [23–28]. Thus, implementation of MQMQA in

ThermoChimica enables the integration of ThermoChimica into multi-physics simulations of MSRs. Due to widespread concerns over possible corrosion of MSR components by the salts themselves [29], thermochemical predictions for these systems are of particularly high importance. Through the use of ThermoChimica, designers of MSR systems may be able to predict when corrosion of reactor components and formation of precipitate or gaseous species may occur, and seek combinations of chemistry and operating conditions that minimize these occurrences.

A critical step in implementing the MQMQA into ThermoChimica, or any other Gibbs energy minimizer that uses explicit expressions for the chemical potentials, is the derivation of equations to represent the chemical potentials of individual species as input to the Hessian matrix. These equations have not been previously presented in the literature and are not trivial to derive. One objective of this paper is to provide a derivation of these equations, which will be helpful to others in implementing this model into their own programming. Another objective of this work is to demonstrate capabilities in using such calculations in a multi-physics code for subsequent engineering analyses.

In Section 2, the equations required to implement the MQMQA in thermodynamic software are derived. In Section 3, the implementation of these equations in ThermoChimica is verified. In Section 4, a method for accelerating multi-physics simulations employing ThermoChimica through re-initialization is described. In Section 5 an application of the

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MQMQA in Thermochimica to a multi-physics simulation of a molten salt nuclear fuel system is demonstrated. In Section 6 concepts for improvement and future applications are laid out.

2. Derivation of chemical potentials within the modified quasichemical model

Thermochimica [22] is an open-source equilibrium thermodynamics software library that solves for a unique combination of phases and concentrations that minimizes the Gibbs energy of an input system. This is performed using the Gibbs Energy Minimization (GEM) method [30]. The approach of the GEM method is to optimize the system such that the residuals in mass balance equations and the total Gibbs energy are simultaneously minimized, subject to the constraints of the Gibbs Phase Rule and conservation of mass [30,31]. Upon successful optimization of the chemical system, many thermochemical properties are available, including the mass of stable phases, the concentrations of all species in every stable solution phase, the Gibbs energy of the system, and the chemical potentials of all system components and stable species in the system. Some of these quantities may be used directly in the context of multi-physics simulations, while others might feed into parametrizations of necessary thermophysical properties.

The Gibbs energy of a solution phase depends on its composition, and a number of models and parameters have been proposed to model different phases. These models include ideal solution models, models for a single sublattice and models for multiple sublattices (e.g., Compound Energy Formalism (CEF) [32]). Despite the large number of models available to represent the Gibbs energy of a phase, the general representative expression is as follows:

$$G = G^\circ + G^{\text{id}} + G^{\text{ex}} + G^{\text{phys}}, \quad (1)$$

where the Gibbs energy of the phase, G , is a sum of the reference Gibbs energy of its species, G° , which depends only on temperature, hydrostatic pressure and composition of individual species, the ideal mixing term of Gibbs energy, $G^{\text{id}} = -TS^{\text{id}}$, which assumes random mixing of constituents with S^{id} denoting the entropy of mixing, and a term to account for non-ideal mixing energy, G^{ex} . The term G^{phys} captures the various physical phenomena that contribute to the Gibbs energy of the phase (e.g., magnetic contributions), and is not used within the existing MQMQA formalism.

The chemical potential of species i is by definition the partial derivative of the integral Gibbs energy of the system with respect to the number of moles of that species at constant temperature, T , and pressure, P . Mathematically, this is represented as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq i}, \quad (2)$$

where n_i represents the number of moles of species i . One can obtain an expanded expression for chemical potential of i by substituting Eq. (1) into Eq. (2) above, which gives the following:

$$\mu_i = \underbrace{\left(\frac{\partial G^\circ}{\partial n_i} \right)_{T,P,n_j \neq i}}_{\mu_i^\circ} + \underbrace{\left(\frac{\partial G^{\text{id}}}{\partial n_i} \right)_{T,P,n_j \neq i}}_{\mu_i^{\text{id}}} + \underbrace{\left(\frac{\partial G^{\text{ex}}}{\partial n_i} \right)_{T,P,n_j \neq i}}_{\mu_i^{\text{ex}}}, \quad (3)$$

where the contributions to the integral Gibbs energy are obtained as the product of number of moles of a phase and the respective molar Gibbs energy contribution (i.e., $G^\circ = ng^\circ$, $G^{\text{id}} = ng^{\text{id}}$ and $G^{\text{ex}} = ng^{\text{ex}}$), with g° , g^{id} and g^{ex} denoting the molar reference Gibbs energy, the molar ideal Gibbs energy of mixing and the molar excess Gibbs energy of mixing, respectively. The partial derivative terms are referred to as the partial reference molar Gibbs energy, partial molar ideal Gibbs energy of mixing and partial molar excess Gibbs energy of mixing and are denoted by μ_i° , μ_i^{id} , and μ_i^{ex} respectively.

The MQMQA is a thermodynamic model for treating Short-Range Order (SRO) with two sublattices. The MQMQA is fundamentally different from other classes of thermodynamic models in that the focus

is not on the mixing of chemical species or constituents on a lattice, but rather the mixing of species as quadruplets to capture SRO of both First-Nearest-Neighbors (FNN) and Second-Nearest-Neighbors (SNN) in liquid or solid solutions. The details of the evolution of the modified quasichemical model from pair approximation for species mixing on only one sublattice to the current quadruplet approximation on two sublattices are provided by Pelton et al. [2,3,5], Chartrand et al. [4], and Lambotte et al. [6].

2.1. Gibbs energy of modified quasichemical model phases

The integral Gibbs energy of a solution phase modeled by MQMQA can be expanded in terms of the site fractions of constituents, X_i , equivalent site fractions of constituents, Y_i , FNN pair fractions, $X_{i/k}$, SNN quadruplet fractions, $X_{ij/kl}$, and the molar quantities corresponding to these fractions. As the quadruplets are taken to be independent components of the phase, it is necessary to express all of these quantities in terms of the molar quantities of the quadruplets, $n_{ij/kl}$. In the subscript notation used throughout, a single subscript (i.e. i) indicates a cation or anion constituent, a subscript pair (i/k) indicates a pair consisting of cation constituent i and anion constituent k , and a quartet (ij/kl) indicates a quadruplet composed of cation constituents i and j , and anion constituents k and l . The quadruplet fractions are:

$$X_{ij/kl} = \frac{n_{ij/kl}}{\sum_{ab/xy} n_{ab/xy}}. \quad (4)$$

The molar quantity of a pair i/k is:

$$n_{i/k} = \sum_{ab/xy} n_{ab/xy} \frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{\zeta_{i/k}}, \quad (5)$$

where δ is the Kronecker delta function, and $\zeta_{i/k}$ is the FNN to SNN ratio for the pair i/k . Then, the mole fraction of a pair is:

$$X_{i/k} = \frac{n_{i/k}}{\sum_{a/x} n_{a/x}}. \quad (6)$$

Next are the site molar quantities, n_i . Since the site fractions are specific to each sublattice, the calculation of each is explicitly shown (i.e. $n_i^{1\text{st}}$ and $n_k^{2\text{nd}}$). In the following discussion, the distinction will not be carried through, and the convention will be that if a constituent i is on the first sublattice, then X_i is implicitly $X_i^{1\text{st}}$. That said,

$$n_i^{1\text{st}} = \sum_{ab/xy} n_{ab/xy} \left(\frac{\delta_{ai}}{Z_{ab/xy}^a} + \frac{\delta_{bi}}{Z_{ab/xy}^b} \right), \quad (7)$$

where $Z_{ij/kl}^i$ is the coordination number of constituent i within the quadruplet ij/kl , and

$$n_k^{2\text{nd}} = \sum_{ab/xy} n_{ab/xy} \left(\frac{\delta_{xk}}{Z_{ab/xy}^x} + \frac{\delta_{yk}}{Z_{ab/xy}^y} \right). \quad (8)$$

Then, the site fractions are:

$$X_i^{1\text{st}} = \frac{n_i^{1\text{st}}}{\sum_a n_a^{1\text{st}}}, \quad (9)$$

and

$$X_k^{2\text{nd}} = \frac{n_k^{2\text{nd}}}{\sum_x n_x^{2\text{nd}}}. \quad (10)$$

The site-equivalent fractions (Y_i) are calculated similar to the site molar quantities (n_i), and the same convention will be used here to distinguish between sublattices. They are then:

$$Y_i^{1\text{st}} = \sum_{ab/xy} X_{ab/xy} \left(\frac{\delta_{ai} + \delta_{bi}}{2} \right), \quad (11)$$

and

$$Y_k^{2\text{nd}} = \sum_{ab/xy} X_{ab/xy} \left(\frac{\delta_{xk} + \delta_{yk}}{2} \right). \quad (12)$$

The coordination-equivalent fractions (F_i), which are identical to the site-equivalent fractions (Y_i) when all $\zeta_{i/k}$ are equal, are defined as [6]:

$$F_i^{1\text{st}} = \sum_{a/x} \delta_{ai} X_{a/x}, \quad (13)$$

and

$$F_k^{2\text{nd}} = \sum_{a/x} \delta_{xk} X_{a/x}. \quad (14)$$

The reference Gibbs energy term is given as follows:

$$G^\circ = \sum_{ij/kl} n_{ij/kl} g_{ij/kl}^\circ, \quad (15)$$

where $g_{ij/kl}^\circ$ denotes the reference molar Gibbs energy of the quadruplet. The configurational entropy terms can be written as the following:

$$\Delta S = -R \left[\sum_i n_i \ln(X_i) + \sum_{i/k} n_{i/k} \ln \left(\frac{X_{i/k}}{F_i F_k} \right) + \sum_{ij/kl} n_{ij/kl} \ln \left(\frac{X_{ij/kl}}{C_{ij/kl} (X_{i/k} X_{l/i} X_{j/k} X_{l/j})^\phi / (Y_i Y_j Y_k Y_l)^\psi} \right) \right], \quad (16)$$

where R is the ideal gas constant, $C_{ij/kl} = (2 - \delta_{ij})(2 - \delta_{kl})$ with δ being the Kronecker delta function, and the exponents ϕ and ψ take the values 1 and 1, or $3/4$ and $1/2$, depending on whether the original or the updated implementation of MQMQA is used [6]. The excess Gibbs energy term takes the following form:

$$G^{\text{ex}} = \frac{1}{2} \left[\sum_{ij/kl} n_{ij/kl} \Delta g_{ij/kl} + \sum_{\substack{ij/kl \\ l=k}} \left(\frac{Z_{ij/kl}^k}{2} \sum_m \frac{n_{ij/km}}{Z_{ij/km}^k} \right) \Delta g_{ij/kl} + \sum_{\substack{ij/kl \\ j=i}} \left(\frac{Z_{ij/kl}^i}{2} \sum_m \frac{n_{im/kl}}{Z_{im/kl}^i} \right) \Delta g_{ij/kl} \right]. \quad (17)$$

In the preceding expressions, sums over i are for all constituents, sums over i/k are for all FNN pairs, and sums over ij/kl are for all FNN quadruplets. The empirical mixing parameter used to fit the Gibbs energy of formation of quadruplets, $\Delta g_{ij/kl}$, can take a variety of forms, and indeed even be composed of many of these forms. Because each $\Delta g_{ij/kl}$ contains an unknown number (possibly zero) of terms of various forms, which eventually will be summed, it is convenient to handle each of these terms independently. It should be noted that by definition for quadruplets with $i = j$ and $k = l$, the excess mixing energy is necessarily zero (as no mixing is occurring). For all other quadruplets:

$$\Delta g_{ij/kl} = \sum_{\alpha=1}^{N_{ij/kl}^{\text{ex}}} \Delta g_{ij/kl,\alpha}, \quad (18)$$

where $N_{ij/kl}^{\text{ex}}$ is the number of excess energy terms corresponding to the ij/kl quadruplet.

As described by Pelton [33], the calculation of excess mixing energy terms within the MQMQA depends on the symmetry of the ternary subsystems. These calculations are aided by the use of the variables $\xi_{ij/k}$ and $\chi_{ij/kl}$. They have been generalized to allow for the existence in the system of multiple constituents on both sublattices and to specify which of these constituents the mixing term corresponds to. $\xi_{ij/k}$ is defined as follows:

$$\xi_{ij/k} = \sum_{a=\{i,v\}} Y_{a/k}, \quad (19)$$

where v represents all constituents that form asymmetrical $i - j - v$ ternary subsystems in which j is the asymmetric constituent. $Y_{i/k}$ is

a modification of Y_i from Eq. (11) such that only contributions from quadruplets containing species k on the second sublattice are included, such that:

$$Y_{i/k} = \sum_{ab/xy} X_{ab/xy} \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right). \quad (20)$$

$\chi_{ij/kl}$ is defined as follows in the original implementation [5]:

$$\begin{aligned} \chi_{ij/kl} &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} X_{ab/kl}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} X_{ab/kl}} \\ &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} n_{ab/kl}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} n_{ab/kl}}, \end{aligned} \quad (21)$$

or in the updated implementation [6,33]:

$$\begin{aligned} \chi_{ij/kl} &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} \sum_x \sum_y \frac{\delta_{xk} + \delta_{yk}}{2} X_{ab/xy}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} \sum_x \sum_y \frac{\delta_{xk} + \delta_{yk}}{2} X_{ab/xy}} \\ &= \frac{\sum_{a=\{i,v\}} \sum_{b=\{i,v\}} \sum_x \sum_y \frac{\delta_{xk} + \delta_{yk}}{2} n_{ab/xy}}{\sum_{a=\{i,j,v,\gamma\}} \sum_{b=\{i,j,v,\gamma\}} \sum_x \sum_y \frac{\delta_{xk} + \delta_{yk}}{2} n_{ab/xy}}, \end{aligned} \quad (22)$$

where γ represents all constituents that form asymmetrical $i - j - \gamma$ ternary subsystems in which i is the asymmetric constituent. The sums over x and y are for all constituents on the second sublattice. These equations can be reversed to apply to the second sublattice, but for the sake of brevity from here on only mixing on the first sublattice will be shown explicitly. In Eq. (21), it can be observed that because the numerator and denominator involve the same powers of $X_{ij/kl}$, the mole fractions can be replaced with the molar quantities.

There are numerous possibilities for the form of each $\Delta g_{ij/kl,\alpha}$. These include binary mixing terms proportional to the quadruplet fractions:

$$\Delta g_{ij/kl,\alpha} = g_{ij/kl,\alpha} \cdot \chi_{ij/kl}^{\rho_\alpha} \chi_{ji/kl}^{q_\alpha}, \quad (23)$$

binary mixing proportional to equivalent site fractions:

$$\Delta g_{ij/kl,\alpha} = g_{ij/kl,\alpha} \cdot \frac{\xi_{ij/k}^{\rho_\alpha} \xi_{ji/k}^{q_\alpha}}{(\xi_{ij/k} + \xi_{ji/k})^{\rho_\alpha + q_\alpha}}, \quad (24)$$

ternary mixing proportional to the quadruplet fractions:

$$\Delta g_{ij(m)/kl,\alpha} = g_{ij(m)/kl,\alpha} \cdot \chi_{ij/kl}^{\rho_\alpha} \chi_{ji/kl}^{q_\alpha} \cdot \begin{cases} \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ij/k}} \right)^{r_\alpha-1} & m \in \gamma \\ \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha-1} & m \in v \\ Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_\alpha-1} & m \notin \{v, \gamma\}, \end{cases} \quad (25)$$

and ternary mixing proportional to equivalent site fractions:

$$\begin{aligned} \Delta g_{ij(m)/kl,\alpha} &= g_{ij(m)/kl,\alpha} \cdot \frac{\xi_{ij/k}^{\rho_\alpha} \xi_{ji/k}^{q_\alpha}}{(\xi_{ij/k} + \xi_{ji/k})^{\rho_\alpha + q_\alpha}} \\ &\cdot \begin{cases} \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ij/k}} \right)^{r_\alpha-1} & m \in \gamma \\ \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha-1} & m \in v \\ Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_\alpha-1} & m \notin \{v, \gamma\}, \end{cases} \end{aligned} \quad (26)$$

where in the above equations p_α , q_α , and r_α are integer exponents chosen for the excess mixing term α .

In the types of mixing terms described in Eqs. (23)–(26), there is a restriction of having only one constituent involved on either the first or second sublattice. Expressions for mixing on the first sublattice are shown. Note that the terms preceding the cases in Eqs. (25) and (26) correspond to Eqs. (23) and (24), and that the terms within the cases are identical for the two forms of ternary mixing. The cases $m \in \gamma$, $m \in v$, and $m \notin \{v, \gamma\}$ correspond to the ternary system $i - j - m$ being

asymmetric with i as the asymmetric constituent, asymmetric with j as the asymmetric constituent, and either asymmetric with m as the asymmetric constituent or symmetric, respectively. m cannot be equal to either of i and j , as this would not indicate a ternary subsystem.

2.2. Derivation of chemical potential equations

In the MQMQA, the chemical potentials are defined as partial derivatives in terms of the molar quantities of the various quadruplets (analogous to the compound end members in the CEF). Following the procedure employed to compute the Gibbs energies, the chemical potentials are computed as sums of derivatives of the various energetic contributions:

$$\begin{aligned}\mu_{ij/kl} &= \left(\frac{\partial G}{\partial n_{ij/kl}} \right)_{T,P,n_{(ab/xy)} \neq (ij/kl)} \\ &= \left(\frac{\partial G^\circ}{\partial n_{ij/kl}} - T \frac{\partial \Delta S}{\partial n_{ij/kl}} + \frac{\partial G^{\text{ex}}}{\partial n_{ij/kl}} \right)_{T,P,n_{(ab/xy)} \neq (ij/kl)}.\end{aligned}\quad (27)$$

The following sub-sections will derive each of the terms in Eq. (27).

2.2.1. Derivation of the reference Gibbs energy and entropic contributions to chemical potential equations

The partial molar reference Gibbs energy is defined as follows:

$$\frac{\partial G^\circ}{\partial n_{ij/kl}} = g_{ij/kl}^\circ. \quad (28)$$

The entropic contributions to chemical potentials are greatly simplified by the cancellation of the derivatives of the terms within logarithms, which results in:

$$\begin{aligned}\frac{\partial \Delta S}{\partial n_{ij/kl}} &= R \left[\sum_m \frac{\partial n_m}{\partial n_{ij/kl}} \ln(X_m) + \sum_{m/z} \frac{\partial n_{m/z}}{\partial n_{ij/kl}} \ln \left(\frac{X_{m/z}}{F_m F_z} \right) \right. \\ &\quad \left. + \ln \left(\frac{X_{ij/kl}}{C_{ij/kl} (X_{i/l} X_{j/k} X_{j/l})^\phi / (Y_i Y_j Y_k Y_l)^\psi} \right) \right],\end{aligned}\quad (29)$$

where the sum over m is over all constituents, and the sum over m/z is over all pairs. This leaves only the values of the partial derivatives $\frac{\partial n_m}{\partial n_{ij/kl}}$ and $\frac{\partial n_{m/z}}{\partial n_{ij/kl}}$ to be determined as follows:

$$\frac{\partial n_m}{\partial n_{ij/kl}} = \frac{\delta_{im}}{Z_{ij/kl}^i} + \frac{\delta_{jm}}{Z_{ij/kl}^j} + \frac{\delta_{km}}{Z_{ij/kl}^k} + \frac{\delta_{lm}}{Z_{ij/kl}^l}. \quad (30)$$

While the previous expression is general, it is worth noting that m can never be equal to i or j and k or l at the same time, as the constituent is on either the first sublattice or the second. Finally,

$$\frac{\partial n_{m/z}}{\partial n_{ij/kl}} = \frac{(\delta_{im} + \delta_{jm})(\delta_{kj} + \delta_{lj})}{\zeta_{m/z}}, \quad (31)$$

where $\zeta_{m/z}$ is the ratio of FNN to SNN for the FNN pair m/z .

2.2.2. Derivation of the partial molar excess Gibbs energy contribution to chemical potential

Due to the dependence of excess mixing Gibbs energy terms on the mole fractions of phase components, the derivative of each term with respect to molar amounts of all quadruplets are non-zero, unless if all exponents are zero. This results in many cases for the derivatives, as within each form there are cases for the quadruplets explicitly involved in the mixing, and for the rest that are implicitly involved. Fortunately, as will be shown, these derivatives can be written compactly in terms of the excess mixing energies themselves. It is crucial not to forget the product rule resulting from Eq. (17), in which molar quantities are

multiplied by the sums of individual excess mixing terms:

$$\begin{aligned}\frac{\partial G^{\text{ex}}}{\partial n_{ab/xy}} &= \frac{1}{2} \left[\sum_{ij/kl} \left\{ \frac{\partial n_{ij/kl}}{\partial n_{ab/xy}} \Delta g_{ij/kl} + n_{ij/kl} \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right. \\ &\quad + \sum_{\substack{ij/kl \\ l=k}} \left\{ \left(\frac{Z_{ij/kl}^k}{2} \sum_m \frac{\partial n_{ij/km}}{\partial n_{ab/xy}} \right) \Delta g_{ij/kl} \right. \\ &\quad \left. + \left(\frac{Z_{ij/kl}^k}{2} \sum_m \frac{n_{ij/km}}{Z_{ij/km}^k} \right) \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \\ &\quad + \sum_{\substack{ij/kl \\ j=i}} \left\{ \left(\frac{Z_{ij/kl}^i}{2} \sum_m \frac{\partial n_{im/kl}}{\partial n_{ab/xy}} \right) \Delta g_{ij/kl} \right. \\ &\quad \left. + \left(\frac{Z_{ij/kl}^i}{2} \sum_m \frac{n_{im/kl}}{Z_{im/kl}^i} \right) \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \left. \right].\end{aligned}\quad (32)$$

$\frac{\partial n_{ij/kl}}{\partial n_{ab/xy}}$ is equal to 1 if $i = a$, $j = b$, $k = x$, and $l = y$, and is 0 otherwise. Thus, the foregoing expression simplifies to the following:

$$\begin{aligned}\frac{\partial G^{\text{ex}}}{\partial n_{ab/xy}} &= \frac{1}{2} \left[\Delta g_{ab/xy} + \sum_{ij/kl} \left\{ n_{ij/kl} \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right. \\ &\quad + \left(\frac{Z_{ab/xx}^x}{2Z_{ab/xy}^x} + \frac{Z_{ab/yy}^y}{2Z_{ab/xy}^y} \right) \Delta g_{ab/xy} \\ &\quad + \sum_{\substack{ij/kl \\ l=k}} \left\{ \left(\frac{Z_{ij/kl}^k}{2} \sum_m \frac{n_{ij/km}}{Z_{ij/km}^k} \right) \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \\ &\quad + \left(\frac{Z_{aa/xy}^a}{2Z_{ab/xy}^a} + \frac{Z_{bb/xy}^b}{2Z_{ab/xy}^b} \right) \Delta g_{ab/xy} \\ &\quad \left. + \sum_{\substack{ij/kl \\ j=i}} \left\{ \left(\frac{Z_{ij/kl}^i}{2} \sum_m \frac{n_{im/kl}}{Z_{im/kl}^i} \right) \frac{\partial \Delta g_{ij/kl}}{\partial n_{ab/xy}} \right\} \right].\end{aligned}\quad (33)$$

By substituting Eq. (18) into Eq. (33), $\Delta g_{ij/kl}$ can be replaced by $\frac{\sum_{\alpha=1}^{N_{ij/kl}^{\text{ex}}} \Delta g_{ij/kl,\alpha}}{\partial \Delta g_{ij/kl,\alpha}} \Delta g_{ij/kl,\alpha}$. Thus, in all cases, the quantity of interest remains $\frac{\partial \Delta g_{ij/kl,\alpha}}{\partial n_{ab/xy}}$. The possible forms for $\Delta g_{ij/kl,\alpha}$ will be approached in the same order as before. Starting with binary mixing based on quadruplet fractions:

$$\begin{aligned}\frac{\partial (\Delta g_{ij/kk,\alpha})}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij/kk,\alpha}}{\sum_{cd/vv} n_{cd/vv}} \cdot \frac{\delta_{xk} \delta_{yk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} X_{cd/kk}} \\ &\quad \times \left[\frac{(\sum_{e=i,v} \delta_{ae}) (\sum_{e=i,v} \delta_{be}) p_\alpha}{\chi_{ij/kk}} \right. \\ &\quad \left. + \frac{(\sum_{e=j,y} \delta_{ae}) (\sum_{e=j,y} \delta_{be}) q_\alpha}{\chi_{ji/kl}} \right] \\ &\quad - \left(\sum_{e=i,v} \delta_{ae} + \sum_{e=j,y} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} + \sum_{e=j,y} \delta_{be} \right) \\ &\quad \times (p_\alpha + q_\alpha).\end{aligned}\quad (34)$$

In these equations, advantage has been taken of the equal powers of the mole fractions $X_{ij/kl}$ terms in the numerator and denominator to transform these to the molar quantities $n_{ij/kl}$ prior to differentiation.

Eq. (34) is convenient for computational purposes because the derivative of the excess energy term can be expressed relatively compactly in terms of the excess energy term itself. Furthermore, all quantities can be written in terms of $X_{ij/kl}$ except the denominator of the leading fraction, which will cancel with a similar term in Eq. (33).

Next, one can apply the same procedure to binary mixing based on equivalent site fractions:

$$\begin{aligned} \frac{\partial(\Delta g_{ij/kk,\alpha})}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \left[\left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\ &\quad \times \left(\frac{p_\alpha}{\xi_{ij/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \\ &\quad \left. + \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\ &\quad \left. \times \left(\frac{q_\alpha}{\xi_{ji/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \right], \end{aligned} \quad (35)$$

which has similar properties to Eq. (34).

As shown in Eqs. (25) and (26), the ternary mixing terms include three possible cases. To compute the derivatives of Eqs. (25) and (26), one must first differentiate these three cases. First, the case in which $m \in \gamma$ results in:

$$\begin{aligned} \frac{\partial}{\partial n_{ab/xy}} &\left[\left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_\alpha-1} \right] \\ &= \left(\frac{1}{\sum_{cd/vw} n_{cd/vw}} \right) \left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_\alpha-1} \\ &\quad \cdot \left[\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right. \\ &\quad \left. - \left(\frac{r_\alpha - 1}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \right. \\ &\quad \left. \left. - Y_{j/k} \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right\} \right] \end{aligned} \quad (36)$$

Similarly, the case in which $m \in v$ results in:

$$\begin{aligned} \frac{\partial}{\partial n_{ab/xy}} &\left[\left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha-1} \right] \\ &= \left(\frac{1}{\sum_{cd/vw} n_{cd/vw}} \right) \left(\frac{Y_{m/k}}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{r_\alpha-1} \\ &\quad \cdot \left[\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right. \\ &\quad \left. - \left(\frac{r_\alpha - 1}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \right. \\ &\quad \left. \left. - Y_{i/k} \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right\} \right] \end{aligned} \quad (37)$$

The case in which $m \notin \{v, \gamma\}$ results in:

$$\begin{aligned} \frac{\partial}{\partial n_{ab/xy}} &\left[Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_\alpha-1} \right] = \left(\frac{Y_{m/k} (1 - \xi_{ij/k} - \xi_{ji/k})^{r_\alpha-1}}{\sum_{cd/vw} n_{cd/vw}} \right) \\ &\quad \cdot \left[-(r_\alpha) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) \right. \\ &\quad \left. + (r_\alpha - 1) \{1 - \xi_{ij} - \xi_{ji}\}^{-1} \right. \\ &\quad \cdot \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \\ &\quad \left. - \sum_{e=\{j,\gamma\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \right] \end{aligned} \quad (38)$$

With all the necessary pieces in place, the derivatives for ternary excess energy terms can be formed by combining Eqs. (36), (37), and (38) with Eq. (34) (for the quadruplet fraction formulation) and with Eq. (35) (for the site fraction formulation). Taking the quadruplet fraction case first: Eq. (37) is given in **Box I** where the cases in the last term were described below equation (26). In the second line of Eq. (39), the term $\delta_{xk}\delta_{yk}$ is replaced with $\frac{1}{2}(\delta_{xk} + \delta_{yk})$ for the updated implementation of MQMQA [6,33]. Finally, the site fraction case: Eq. (38) is given in **Box II**.

The equations presented here are in a form suitable for direct implementation into software, and have been incorporated in Thermochemica in as similar a manner as is possible within the Fortran language. This is intended to enhance readability of the Thermochemica source code to enable verification, modification, use, and comparison with other software in which the MQMQA is implemented. In the following sections, we will demonstrate verification, modification, and use of the MQMQA in Thermochemica.

$$\begin{aligned}
\frac{\partial \Delta g_{ij(m)/kk,\alpha}}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij(m)/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \\
&\cdot \left[\frac{\delta_{xk} \delta_{yk}}{\sum_{e=\{i,j,v,\gamma\}} \sum_{d=\{i,j,v,\gamma\}} X_{cd/kk}} \left[\frac{\left(\sum_{e=i,v} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} \right) p_\alpha}{\chi_{ij/kk}} + \frac{\left(\sum_{e=j,\gamma} \delta_{ae} \right) \left(\sum_{e=j,\gamma} \delta_{be} \right) q_\alpha}{\chi_{ji/kk}} \right. \right. \\
&- \left(\left(\sum_{e=i,v} \delta_{ae} \right) + \left(\sum_{e=i,j,\gamma} \delta_{ae} \right) \right) \left(\left(\sum_{e=i,v} \delta_{be} \right) + \left(\sum_{e=j,\gamma} \delta_{be} \right) \right) (p_\alpha + q_\alpha) \\
&\left. \left. - \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right. \right. \\
&- \left(\frac{r_\alpha - 1}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{j/k} \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right\} \quad m \in \gamma \\
&+ \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \\
&- \left(\frac{r_\alpha - 1}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{i/k} \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right\} \quad m \in v \\
&- (r_\alpha) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) + (r_\alpha - 1) \left\{ 1 - \xi_{ij} - \xi_{ji} \right\}^{-1} \\
&\left. \left. \cdot \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) - \sum_{e=\{j,\gamma\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \quad m \notin \{v, \gamma\} \right] \right. \end{aligned} \tag{39}$$

Box I.

$$\begin{aligned}
\frac{\partial \Delta g_{ij(m)/kk,\alpha}}{\partial n_{ab/xy}} &= \frac{\Delta g_{ij(m)/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \\
&\cdot \left[\left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{p_\alpha}{\xi_{ij/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \right. \\
&+ \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{q_\alpha}{\xi_{ji/k}} - \frac{p_\alpha + q_\alpha}{\xi_{ij/k} + \xi_{ji/k}} \right) \\
&\left. - \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right. \\
&- \left(\frac{r_\alpha - 1}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{j/k} \left(\sum_{e=\{j,\gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right\} \quad m \in \gamma \\
&+ \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \\
&- \left(\frac{r_\alpha - 1}{\xi_{ij/k}} \right) \left(1 - \frac{Y_{i/k}}{\xi_{ij/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{ai} + \delta_{bi})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{i/k} \left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ij/k}} \right) \right\} \quad m \in v \\
&- (r_\alpha) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) + (r_\alpha - 1) \left\{ 1 - \xi_{ij} - \xi_{ji} \right\}^{-1} \\
&\left. \left. \cdot \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) - \sum_{e=\{j,\gamma\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \quad m \notin \{v, \gamma\} \right] \right. \end{aligned} \tag{40}$$

Box II.

Eq. (35) is given in Box III.

Eq. (36) is given in Box IV.

Eq. (38):

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

A.1. Extended derivations

Some steps omitted from the derivations in the main text are included below for curious readers.

Eq. (34):

$$\begin{aligned} \frac{\partial g_{ij/kk,\alpha}}{\partial n_{ab/xy}} &= g_{ij/kk,\alpha} \frac{\partial}{\partial n_{ab/xy}} \left[\chi_{ij/kk}^{p_a} \chi_{ji/kk}^{q_a} \right] \\ &= g_{ij/kk,\alpha} \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} X_{cd/kk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} X_{cd/kk}} \right)^{p_a} \right. \\ &\quad \times \left. \left(\frac{\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} X_{cd/kk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} X_{cd/kk}} \right)^{q_a} \right] \\ &= g_{ij/kk,\alpha} \frac{\partial}{\partial n_{ab/xy}} \left[\frac{\left(\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} n_{cd/kk} \right)^{p_a} \left(\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} n_{cd/kk} \right)^{q_a}}{\left(\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk} \right)^{p_a+q_a}} \right] \\ &= g_{ij/kk,\alpha} \delta_{xk} \delta_{yk} \left[\frac{\left(\sum_{e=i,v} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} \right) p_a + \left(\sum_{e=j,y} \delta_{ae} \right) \left(\sum_{e=j,y} \delta_{be} \right) q_a}{\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} n_{cd/kk}} + \frac{\left(\sum_{e=j,y} \delta_{ae} \right) \left(\sum_{e=j,y} \delta_{be} \right) p_a + \left(\sum_{e=i,v} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} \right) q_a}{\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} n_{cd/kk}} \right. \\ &\quad - \left. \frac{\left(\sum_{e=i,v} \delta_{ae} + \sum_{e=j,y} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} + \sum_{e=j,y} \delta_{be} \right) (p_a + q_a)}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk}} \right] \\ &\quad \cdot \left[\frac{\left(\sum_{c=\{i,v\}} \sum_{d=\{i,v\}} n_{cd/kk} \right)^{p_a} \left(\sum_{c=\{j,y\}} \sum_{d=\{j,y\}} n_{cd/kk} \right)^{q_a}}{\left(\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk} \right)^{p_a+q_a}} \right] \quad (\text{A.1}) \end{aligned}$$

$$\begin{aligned} &= \Delta g_{ij/kk,\alpha} \frac{\delta_{xk} \delta_{yk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} n_{cd/kk}} \left[\frac{\left(\sum_{e=i,v} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} \right) p_a}{\chi_{ij/kk}} \right. \\ &\quad + \left. \frac{\left(\sum_{e=j,y} \delta_{ae} \right) \left(\sum_{e=j,y} \delta_{be} \right) q_a}{\chi_{ji/kk}} - \left(\sum_{e=i,v} \delta_{ae} + \sum_{e=j,y} \delta_{ae} \right) \right. \\ &\quad \times \left. \left(\sum_{e=i,v} \delta_{be} + \sum_{e=j,y} \delta_{be} \right) (p_a + q_a) \right] \\ &= \frac{\Delta g_{ij/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \cdot \frac{\delta_{xk} \delta_{yk}}{\sum_{c=\{i,j,v,y\}} \sum_{d=\{i,j,v,y\}} X_{cd/kk}} \left[\frac{\left(\sum_{e=i,v} \delta_{ae} \right) \left(\sum_{e=i,v} \delta_{be} \right) p_a}{\chi_{ij/kk}} \right. \\ &\quad + \left. \frac{\left(\sum_{e=j,y} \delta_{ae} \right) \left(\sum_{e=j,y} \delta_{be} \right) q_a}{\chi_{ji/kk}} - \left(\sum_{e=i,v} \delta_{ae} + \sum_{e=j,y} \delta_{ae} \right) \right. \\ &\quad \times \left. \left(\sum_{e=i,v} \delta_{be} + \sum_{e=j,y} \delta_{be} \right) (p_a + q_a) \right]. \end{aligned}$$

$$\begin{aligned} &\frac{\partial}{\partial n_{ab/xy}} \left[Y_{m/k} \left(1 - \xi_{ij/k} - \xi_{ji/k} \right)^{r_a-1} \right] \\ &= \frac{\partial}{\partial n_{ab/xy}} \left[Y_{m/k} \left(1 - \sum_{e=\{i,v\}} Y_{e/k} - \sum_{e=\{j,y\}} Y_{e/k} \right)^{r_a-1} \right] \\ &= \frac{\partial}{\partial n_{ab/xy}} \left[\left(\sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{cm} + \delta_{dm})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right. \\ &\quad \left. - \left(\sum_{e=\{j,y\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right]^{r_a-1} \\ &= \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{1}{\sum_{cd/vw} n_{cd/vw}} \right)^{r_a} \left(\sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{cm} + \delta_{dm})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right. \\ &\quad \left. - \left(\sum_{e=\{j,y\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right) \right]^{r_a-1} \\ &= \left(\frac{Y_{m/k} \left(1 - \xi_{ij/k} - \xi_{ji/k} \right)^{r_a-1}}{\sum_{cd/vw} n_{cd/vw}} \right) \\ &\quad \cdot \left[-(r_a) + \left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{1}{Y_{m/k}} \right) \right. \\ &\quad \left. + (r_a - 1) \left\{ 1 - \xi_{ij} - \xi_{ji} \right\}^{-1} \right. \\ &\quad \left. - \left\{ 1 - \sum_{e=\{i,v\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right. \right. \\ &\quad \left. \left. - \sum_{e=\{j,y\}} \left(\frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \right\} \right] \quad (\text{A.4}) \end{aligned}$$

Appendix B. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.calphad.2021.102341>.

$$\begin{aligned}
\frac{\partial(\Delta g_{ij/kk,\alpha})}{\partial n_{ab/xy}} &= g_{ij/kk,\alpha} \frac{\partial}{\partial n_{ab/xy}} \left[\frac{\xi_{ij/j/k}^{q_a} \xi_{ji/k}^{q_a}}{(\xi_{ij/j/k} + \xi_{ji/k})^{p_a+q_a}} \right] \\
&= g_{ij/kk,\alpha} \frac{\partial}{\partial n_{ab/xy}} \left[\frac{\left(\sum_{e=\{i,v\}} Y_{e/k} \right)^{p_a} \left(\sum_{e=\{j,y\}} Y_{e/k} \right)^{q_a}}{\left(\sum_{e=\{i,v\}} Y_{e/k} + \sum_{e=\{j,y\}} Y_{e/k} \right)^{p_a+q_a}} \right] \\
&= g_{ij/kk,\alpha} \frac{\partial}{\partial n_{ab/xy}} \left[\left(\sum_{e=\{i,v\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right)^{p_a} \cdot \left(\sum_{e=\{j,y\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right)^{q_a} \right. \\
&\quad \left. / \left(\sum_{e=\{i,v\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) + \sum_{e=\{j,y\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right)^{p_a+q_a} \right] \\
&= g_{ij/kk,\alpha} \frac{\partial}{\partial n_{ab/xy}} \left[\left(\sum_{e=\{i,v\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right)^{p_a} \cdot \left(\sum_{e=\{j,y\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right)^{q_a} \right. \\
&\quad \left. / \left(\sum_{e=\{i,v\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) + \sum_{e=\{j,y\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) \right)^{p_a+q_a} \right] \\
&= \Delta g_{ij/kk,\alpha} \left[\left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{p_a}{\sum_{e=\{i,v\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right)} - \frac{p_a + q_a}{\sum_{e=\{i,v\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) + \sum_{e=\{j,y\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right)} \right) \right. \\
&\quad \left. + \left(\sum_{e=\{j,y\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{q_a}{\sum_{e=\{j,y\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right)} - \frac{p_a + q_a}{\sum_{e=\{i,v\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right) + \sum_{e=\{j,y\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{vk} + \delta_{wk})}{4} \right)} \right) \right] \\
&= \frac{\Delta g_{ij/kk,\alpha}}{\sum_{cd/vw} n_{cd/vw}} \left[\left(\sum_{e=\{i,v\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{p_a + q_a}{\xi_{ij/j/k} - \xi_{ij/j/k} + \xi_{ji/k}} \right) + \left(\sum_{e=\{j,y\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4} \right) \left(\frac{q_a}{\xi_{ji/j/k}} - \frac{p_a + q_a}{\xi_{ij/j/k} + \xi_{ji/k}} \right) \right],
\end{aligned}$$

Box III.

$$\begin{aligned}
& \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_a-1} \right] = \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{Y_{m/k}}{\sum_{e \in \{j, \gamma\}} Y_{e/k}} \right) \left(1 - \frac{Y_{j/k}}{\sum_{e \in \{j, \gamma\}} Y_{e/k}} \right)^{r_a-1} \right] \\
&= \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{\sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{cm} + \delta_{bm})(\delta_{ck} + \delta_{wk})}{4} \right)}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right) \cdot \left(1 - \frac{\sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{cj} + \delta_{dj})(\delta_{ek} + \delta_{wk})}{4} \right)}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} X_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right)^{r_a-1} \right] \\
&= \frac{\partial}{\partial n_{ab/xy}} \left[\left(\frac{\sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{cm} + \delta_{bm})(\delta_{ck} + \delta_{wk})}{4} \right)}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right) \cdot \left(1 - \frac{\sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{cj} + \delta_{dj})(\delta_{ek} + \delta_{wk})}{4} \right)}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right)^{r_a-1} \right] \\
&= \left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_a-1} \left[\left(\frac{\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4}}{\sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right) - \left(\frac{\sum_{e \in \{j, \gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4}}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right) - \left(\frac{r_a - 1}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right) \right. \\
&\quad \left. \left(1 - \frac{\sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{cj} + \delta_{dj})(\delta_{xk} + \delta_{yk})}{4} \right)}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right)^{-1} \times \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) - \left(\sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{cj} + \delta_{dj})(\delta_{ek} + \delta_{wk})}{4} \right) \right) \cdot \left(\frac{\sum_{e \in \{j, \gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4}}{\sum_{e \in \{j, \gamma\}} \sum_{cd/vw} n_{cd/vw} \left(\frac{(\delta_{ce} + \delta_{de})(\delta_{ek} + \delta_{wk})}{4} \right)} \right) \right\} \right] \\
&= \left(\frac{1}{\sum_{cd/vw} n_{cd/vw}} \right) \left(\frac{Y_{m/k}}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{r_a-1} \times \left[\left(\frac{(\delta_{am} + \delta_{bm})(\delta_{xk} + \delta_{yk})}{4Y_{m/k}} \right) - \left(\sum_{e \in \{j, \gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right. \\
&\quad \left. - \left(\frac{r_a - 1}{\xi_{ji/k}} \right) \left(1 - \frac{Y_{j/k}}{\xi_{ji/k}} \right)^{-1} \left\{ \left(\frac{(\delta_{aj} + \delta_{bj})(\delta_{xk} + \delta_{yk})}{4} \right) - Y_{j/k} \left(\sum_{e \in \{j, \gamma\}} \frac{(\delta_{ae} + \delta_{be})(\delta_{xk} + \delta_{yk})}{4\xi_{ji/k}} \right) \right\} \right]
\end{aligned}$$

Box IV

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5

Equilibrium Thermodynamics

The foundations of thermodynamic equilibrium calculations were laid down by American chemical physicist Josiah Willard Gibbs who originally published his work *On the Equilibrium of Heterogeneous Substances* in a relatively obscure American journal, the Transactions of the Connecticut Academy of Arts and Sciences, in several parts, during the years 1875 to 1878. Thermodynamic equilibrium computations in isothermal, isobaric systems are aimed at identifying a unique combination of phases and species which minimises the integral Gibbs energy of the system while satisfying the necessary underlying conditions. Thermodynamics requires that a favourable change in a system must decrease the Gibbs energy of the system while respecting the mass constraints of the system components and the Gibbs' phase rule must be satisfied.

5.1. Phase Equilibrium in Heterogeneous Systems

A heterogeneous system is defined as one where the thermodynamic properties may have different values in different parts of the system when the system is at equilibrium. While a continuous variation of these properties is possible, equilibrium thermodynamics in the context of this work only concerns discontinuous variations where the properties have different values in different portions of the systems but are homogenous within each portion. A practical example of such a scenario is that of multiple phases being present in a system with the properties in phase being homogenous and the different phases are in equilibrium with each other [158].

In a system at equilibrium, with C components, there are $C + 2$ natural variables with 2 representing the variables temperature, T , and pressure, P . For an isothermal, isobaric system,

the equilibrium conditions result in:

$$dG_{\text{sys}} = -SdT - Vd(-P) + \sum_i \mu_j dn_j = 0. \quad (5.1)$$

As a result, the equilibrium state is defined by a minimum in the integral Gibbs energy of the system at constant T , P and n_i . In doing so one must respect the mass balance and charge neutrality constraints. In the present context, this also implies that the chemical potential of each component must be homogenous in all phases stable at equilibrium and gives the common tangent construction for phases at equilibrium:

$$\mu_i^{\phi_1} = \mu_i^{\phi_2} = \mu_i^{\phi_3} = \dots, \quad (5.2)$$

where ϕ_1 , ϕ_2 , etc. denote the phases stable at equilibrium. The above arguments can be generalised into the necessary and sufficient conditions for equilibrium which are used in the development of the Gibbs energy minimiser.

5.2. Conditions of Phase Equilibrium

A thermodynamic equilibrium solver must meet both the necessary and sufficient conditions for thermodynamic equilibrium. Rooted in the fundamental laws of thermodynamics, the necessary and sufficient conditions together ensure that the Gibbs energy of the system is at a local equilibrium while respecting the constraints.

5.2.1. Necessary conditions

The necessary conditions for thermodynamic equilibrium require satisfaction of mass conservation and the Gibbs' phase rule in addition to satisfying the Gibbs' criterion which is a generalisation of the common tangent construction. These condition can be summarised as follows.

1. Conservation of mass

The law of conservation of mass requires that the linear equations representing mass constraints be satisfied. For component j , the mass balance equation can be written as:

$$b_j = \sum_{\phi=1}^{\Phi} n_{\phi} \sum_{i=1}^{N_{\phi}} \nu_{ij} x_i, \quad (5.3)$$

where ν_{ij} represents the stoichiometric coefficient of element j in phase species i . In an electrochemical system where the electrons form a system component with zero moles

overall in the system, the mass balance constraint includes the charge neutrality constraint but it can be explicitly written as:

$$b_{e^-} = \sum_{i=1}^{N_\phi} x_i \nu_{ie^-} = 0. \quad (5.4)$$

2. Gibbs' phase rule

Thermodynamic equilibrium conditions also require that the Gibbs' phase rule be satisfied. Gibbs' phase rule determines the *degree of freedom* of the system, i.e., the number of phases that can be stable at equilibrium in relation to the state variables [147]. In general, the phase rule can be written as:

$$F = C - \Phi + 2 + \Xi, \quad (5.5)$$

where F represents the degrees of freedom, C denotes the number of components in the system, Φ denotes the number of phases and Ξ denotes the number of ionic phases. However, for isothermal, isobaric systems with no charged species, the phase rule takes the following simplified form :

$$F = C - \Phi, \quad (5.6)$$

which implies that the number of phases that can co-exist at equilibrium cannot exceed the number of components in a closed isothermal, isobaric system.

3. Gibbs' criterion

Ensuring that the Gibbs phase rule and mass balance constraints are satisfied is relatively straightforward but special attention must be paid to ensuring that the integral Gibbs energy of the system is at a minimum. The equilibrium criteria established by Gibbs requires that at equilibrium $dG_{\text{sys}} = 0$ [147]. Thus, differentiating equation (4.24):

$$dG_{\text{sys}} = \sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_\phi} (dn_i \mu_i + n_i d\mu_i) = 0. \quad (5.7)$$

The chemical potentials are related through the *Gibbs-Duhem equation* which, at constant temperature and pressure, can be written as [159]:

$$\sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_\phi} (n_i d\mu_i) = 0. \quad (5.8)$$

Substituting the Gibbs-Duhem equation in equation (5.8) gives:

$$dG_{\text{sys}} = \sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} (dn_i \mu_i) = 0. \quad (5.9)$$

The chemical potentials of the species can be written in terms of the chemical potentials of the system components. Therefore, substituting equation (5.3) into equation (4.25), differentiating with respect to n_i at constant temperature and pressure and equating to zero gives:

$$dG_{\text{sys}} = \sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} dn_i \sum_{j=1}^C \nu_{ij} \Gamma_j = 0, \quad (5.10)$$

and rearranging the above results in:

$$\sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} dn_i \left(\mu_i - \sum_{j=1}^C \nu_{ij} \Gamma_j \right) = 0. \quad (5.11)$$

Since both ν_{ij} and μ_i are unique for every species, the chemical potentials of species or phase in the system can be related to chemical potentials of system component at equilibrium through the following equation [44]:

$$\mu_{i(\phi)} = \sum_{j=1}^C \nu_{ij} \Gamma_j. \quad (5.12)$$

Equation (4.22) is known as *Gibbs' criterion* and ensuring that it is satisfied for all species in the system is equivalent to satisfying the equilibrium criterion that the Gibbs energy of the system be at a local minimum. This is useful in developing a convergence criterion for thermodynamic equilibrium calculations.

5.2.2. Sufficient conditions

The linear equality in equation (4.22) justifies the selection of stable species and making sure that no metastable species gets added to the system. However, satisfying the linear equation is insufficient to conclude that the system is at a *global* minimum since g_{ϕ}^{ex} can be non-convex [4]. The driving force of a phase, ΔG_{ϕ} , is used to determine whether a system involving that

phase is more stable than the previous system, which is defined as:

$$\Delta G_\phi = \min_{\lambda} \sum_{i=1}^{N_\lambda} x_i \left(\mu_i - \sum_{j=1}^C \nu_{ij} \Gamma_j \right), \quad (5.13)$$

which is subject to the following linear equality and inequality constraints:

$$\sum_{i=1}^{N_\phi} x_i = 1, \quad x_i > 0, \quad \forall i \in \phi. \quad (5.14)$$

5.3. Computing Phase Equilibria

Accurate and computationally efficient determination of equilibrium from the conditions mentioned in the previous section require careful consideration of the numerical method employed in the solver. Over the years, numerous strategies have been developed to solve the equilibrium thermodynamics problems but the two most relevant methods are the *Gibbs Energy Minimisation* by White, Johnson and Dantzig [45] which is based on the method of steepest descent of second order and the *Partitioning of Free Energy* which was also proposed by White [60] but is substantially different from Gibbs energy minimisation.

The goal of both Gibbs energy minimisation (GEM) and partitioning of Gibbs energy (PGE) approaches is to predict a unique combination of phases and species that minimise the integral Gibbs energy of an isothermal, isobaric system at a given composition. As in equation (4.24), the integral Gibbs energy of a multicomponent multiphase system can be represented as:

$$G = RT \left(\sum_{\lambda=1}^{\Lambda} n_\lambda \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \tilde{\mu}_{i(\lambda)} + \sum_{\omega=1}^{\Omega} n_\omega \tilde{\mu}_\omega \right), \quad (5.15)$$

where the symbols represent their usual variables mentioned before. As the conditions that must be satisfied at thermodynamic equilibrium have already been mentioned, the numerical procedures for both the approaches can now be elaborated.

5.3.1. Method of Lagrange multipliers

White et al. [45] established a second order steepest descent method for Gibbs energy minimisation which is based on the method of Lagrange multipliers for constrained optimisation. The GEM approach simultaneously optimises mass balance constraint and Gibbs' criterion while fixing the system size through the Gibbs phase rule. The dimensionless form of Gibbs energy of the system can be expressed as a quadratic approximation obtained by the Taylor series

expansion as follows:

$$\begin{aligned}
\tilde{Q}^{m+1} &= \tilde{G}^m + \sum_{\omega=1}^{\Omega} \Delta_{\omega} \frac{\partial \tilde{G}^m}{\partial n_{\omega}^m} \Big|_{n_{\omega}^m = n_{\omega}^{m+1}} \\
&\quad + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \Delta_i \frac{\partial \tilde{G}^m}{\partial n_{i(\lambda)}^m} \Big|_{n_{i(\lambda)}^m = n_{i(\lambda)}^{m+1}} \\
&\quad + \frac{1}{2} \sum_{\omega=1}^{\Omega} \Delta_{\omega}^2 \frac{\partial^2 \tilde{G}^m}{\partial (n_{\omega}^m)^2} \Big|_{n_{\omega}^m = n_{\omega}^{m+1}} \\
&\quad + \frac{1}{2} \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \sum_{l=1}^{N_{\lambda}} \Delta_i \Delta_l \frac{\partial^2 \tilde{G}^m}{\partial n_{i(\lambda)}^m \partial n_{l(\lambda)}^m} \Big|_{n_{i(\lambda)}^m = n_{i(\lambda)}^{m+1}},
\end{aligned} \tag{5.16}$$

where the superscript m and $m+1$ denote the iteration at which the Gibbs energy is calculated and the deltas can be represented as follows:

$$\Delta_i = n_{i(\lambda)}^{m+1} - n_{i(\lambda)}^m, \tag{5.17}$$

$$\Delta_{\lambda} = n_{\lambda}^{m+1} - n_{\lambda}^m, \tag{5.18}$$

$$\Delta_{\omega} = n_{\omega}^{m+1} - n_{\omega}^m. \tag{5.19}$$

While the first order partial derivatives are equal to the chemical potentials as shown in equation (4.20), the second order derivatives are as follows:

$$\frac{\partial^2 \tilde{G}^m}{\partial (n_{\omega}^m)^2} = 0, \tag{5.20}$$

$$\frac{\partial^2 \tilde{G}^m}{\partial (n_{i(\lambda)}^m)^2} = \frac{1}{n_{i(\lambda)}^m} - \frac{1}{n_{\lambda}^m}, \tag{5.21}$$

$$\frac{\partial^2 \tilde{G}^m}{\partial n_{i(\lambda)}^m \partial n_{l \neq i(\lambda)}^m} = -\frac{1}{n_{\lambda}^m}. \tag{5.22}$$

Substituting equations (4.20) and (5.20)–(5.22) into the second order approximation of Gibbs energy given by equation (5.16), one gets the following objective function:

$$\tilde{Q}^{m+1} = \tilde{G}^m + \sum_{\omega=1}^{\Omega} \tilde{\mu}_{\omega}^m + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \Delta_i \tilde{\mu}_{i(\lambda)}^m + \frac{1}{2} \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)}^m \left(\frac{\Delta_i}{n_{i(\lambda)}^m} - \frac{\Delta_{\lambda}}{n_{\lambda}^m} \right)^2, \tag{5.23}$$

which must be minimised subject to the mass balance constraint. In order to solve the constrained optimisation problem, the method of Lagrange multipliers can be used and the resulting Lagrangian function is defined as:

$$\mathcal{L} = \tilde{Q}^{m+1} - \sum_{j=1}^C \pi_j^{m+1} (b_j - b_j^m), \quad (5.24)$$

where π_j denote the dimensionless undetermined Lagrange multipliers¹. The Gibbs energy of the system and the mass balance residuals can be simultaneously minimised by equating the gradient of the Lagrangian function to zero:

$$\nabla \mathcal{L} = 0. \quad (5.25)$$

The elements of the gradient vector are found by taking the partial derivatives of equation (5.24) with respect to the number of moles of species $n_{i(\lambda)}$ and n_ω :

$$\frac{\partial \mathcal{L}}{\partial n_{i(\lambda)}} = \tilde{\mu}_{i(\lambda)} - \sum_{j=1}^C \nu_{ij} \pi_j^{m+1} + \left(\frac{n_{i(\lambda)}^{m+1}}{n_{i(\lambda)}^m} - \frac{n_\lambda^{m+1}}{n_\lambda^m} \right), \quad (5.26)$$

$$\frac{\partial \mathcal{L}}{\partial n_\omega} = \tilde{\mu}_\omega - \sum_{j=1}^C \nu_{\omega j} \pi_j^{m+1}, \quad (5.27)$$

$$\frac{\partial \mathcal{L}}{\partial \pi_j} = b_j - b_j^m. \quad (5.28)$$

By rearranging the preceding equations and substituting the mass balance constraint, the following equation is obtained:

$$b_j = \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_\lambda} \left(-\tilde{\mu}_{i(\lambda)}^m + \frac{n_\lambda^{m+1}}{n_\lambda^m} + \sum_{k=1}^C \nu_{ik} \pi_k^{m+1} \right) n_{i(\lambda)}^m \nu_{ij} + \sum_{\omega=1}^{\Omega} n_\omega^m \nu_{ij}. \quad (5.29)$$

¹While λ is commonly used to denote Lagrange multipliers, π is used here to avoid confusion with the solution phase index λ .

Upon rearranging, the commonly used form proposed by Eriksson and Rosén [51] is obtained:

$$\begin{aligned} & \sum_{j=1}^C \underbrace{\sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)} \nu_{ij} \nu_{ik} \pi_j^{m+1}}_{r_{jk}} + \underbrace{\sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)} \nu_{ij}}_{\phi_{j\lambda}^m} \underbrace{\left(\frac{n_{\lambda}^{m+1}}{n_{\lambda}^m} - 1 \right)}_{\pi_{\lambda}^{m+1}} \\ & + \sum_{\omega=1}^{\Omega} n_{\omega}^{m+1} \nu_{\omega j} = b_j + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} (\tilde{\mu}_{i(\lambda)}^{m+1} - 1) n_{i(\lambda)}^m \nu_{ij}. \quad (5.30) \end{aligned}$$

The chemical potentials of the species in solution phases can be related to system component potentials by the following:

$$\sum_{j=1}^C \pi_j^{m+1} \phi_{j\lambda}^m = \sum_{i=1}^{N_{\lambda}} \tilde{\mu}_{i(\lambda)}^m n_{i(\lambda)}^m, \quad (5.31)$$

and the chemical potentials of stoichiometric phases constrain the system component potentials through the following relationship:

$$\tilde{\mu}_{\omega} = \sum_{j=1}^C \nu_{\omega j} \pi_j^{m+1}. \quad (5.32)$$

Together, equations (5.30)–(5.32) results in the following system of linear equations:

$$\mathbf{H}\mathbf{u} = \boldsymbol{\kappa} \quad (5.33)$$

where the unknown vector $\mathbf{u} \in \mathbb{R}^N$ and the vector of constraints $\boldsymbol{\kappa} \in \mathbb{R}^N$ with the number of unknowns $N = E + \Lambda + \Omega$. The two can be expanded as:

$$\mathbf{u} = \begin{bmatrix} \pi_{j=1}^{m+1} \\ \vdots \\ \pi_{j=E}^{m+1} \\ \pi_{\lambda=1}^{m+1} \\ \vdots \\ \pi_{\lambda=\Lambda}^{m+1} \\ n_{\omega=1}^{m+1} \\ \vdots \\ n_{\omega=\Omega}^{m+1} \end{bmatrix}, \boldsymbol{\kappa} = \begin{bmatrix} b_{j=1} + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} (\tilde{\mu}_{i(\lambda)}^m - 1) n_{i(\lambda)}^m \nu_{ij=1} \\ \vdots \\ b_{j=E} + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} (\tilde{\mu}_{i(\lambda)}^m - 1) n_{i(\lambda)}^m \nu_{ij=E} \\ \sum_{i=1}^{N_{\lambda}} \tilde{\mu}_{i(\lambda=1)}^m n_{i(\lambda=1)}^m \\ \vdots \\ \sum_{i=1}^{N_{\lambda}} \tilde{\mu}_{i(\lambda=\Lambda)}^m n_{i(\lambda=\Lambda)}^m \\ \tilde{\mu}_{\omega=1} \\ \vdots \\ \tilde{\mu}_{\omega=\Omega} \end{bmatrix}. \quad (5.34)$$

The Hessian matrix, \mathbf{H} , is given as follows:

$$\mathbf{H} = \begin{bmatrix} r_{11} & \dots & r_{1E} & \phi_{11} & \dots & \phi_{1\Lambda} & \nu_{11} & \dots & \nu_{1\Omega} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ r_{E1} & \dots & r_{EE} & \phi_{E1} & \dots & \phi_{E\Lambda} & \nu_{E1} & \dots & \nu_{E\Omega} \\ \phi_{11} & \dots & \phi_{1E} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \phi_{\Lambda 1} & \dots & \phi_{\Lambda E} & 0 & \dots & 0 & 0 & \dots & 0 \\ \nu_{11} & \dots & \nu_{1E} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \nu_{\Omega 1} & \dots & \nu_{\Omega E} & 0 & \dots & 0 & 0 & \dots & 0 \end{bmatrix}, \quad (5.35)$$

where the terms r_{jk} and $\phi_{j\lambda}$ are defined in equation (5.30) and $\nu_{\omega j}$ represents the stoichiometric coefficient of system component j in stoichiometric compound ω .

While solving equation (5.33) gives the mole numbers of stoichiometric phases directly, the mole numbers of the species of solution phases must be computed using the following rearranged form of equation (5.26):

$$n_{i(\lambda)}^{m+1} = n_{i(\lambda)}^{m+1} \left(-\tilde{\mu}_{i(\lambda)}^m + \frac{n_\lambda^{m+1}}{n_\lambda^m - \sum_{j=1}^C \nu_{ij} \pi_j^{m+1}} \right). \quad (5.36)$$

5.3.2. Partitioning of Gibbs energy

PGE is based on finding the roots of the mass balance residual by expressing the mole fraction as a function of system component potentials. The expression for chemical potential of a species from equation (4.22) can be substituted into equation (5.12) and upon rearranging one gets:

$$x_{i(\lambda)} = \exp \left(-\tilde{\mu}_{i(\lambda)}^\circ - \tilde{\mu}_{i(\lambda)}^{\text{ex}} + \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right). \quad (5.37)$$

Substituting the previous equation into the mass balance equation (5.3), one can formally relate the mass balance equations to the element potentials and results in the following:

$$b_k^m = \sum_{\lambda=1}^{\Lambda} n_\lambda^m \sum_{i=1}^{N_\lambda} \nu_{ik} \exp \left(-\tilde{\mu}_{i(\lambda)}^\circ - \tilde{\mu}_{i(\lambda)}^{\text{ex}} + \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j^m \right) + \sum_{\omega=1}^{\Omega} n_\omega^m \nu_{\omega k}, \quad (5.38)$$

where the superscript m denotes that the mass of element k is the estimated mass at iteration m and not the true total amount of the element in the system which will be denoted by b_k

without the iteration index. At convergence, the two will be equal and the sum of the mole fractions of the species $x_{i(\lambda)}$ will be equal to unity.

The PGE method surmises to partitioning the Gibbs energy of the system among elements by manipulating $\tilde{\Gamma}_j^m$ together with n_λ^m and n_ω^m in order to reduce the residuals of the mass balance equations to zero. While doing this, one must ensure that the Gibbs criterion given by equation (5.12) is always satisfied. Mathematically this is equivalent to finding the roots of the system of non-linear equations of mass balance. The residual of mass balance Δb_k^m at iteration m can be defined as:

$$\Delta b_k^m = \sum_{\lambda=1}^{\Lambda} n_\lambda^m \sum_{i=1}^{N_\lambda} \nu_{ik} \exp \left(-\tilde{\mu}_{i(\lambda)}^\circ - \tilde{\mu}_{i(\lambda)}^{\text{ex}} + \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j^m \right) + \sum_{\omega=1}^{\Omega} n_\omega^m \nu_{\omega k} - b_k. \quad (5.39)$$

The subsidiary condition satisfying the requirement for the sum of all mole fraction to be equal to unity results in the following residual for each phase λ :

$$\Delta x_\lambda^m = x_\lambda^m - 1, \quad (5.40)$$

where x_λ^m denotes the sum of mole fractions of all species of phase λ at iteration m (i.e. $x_\lambda^m = \sum_{i=1}^{N_\lambda} x_{i(\lambda)}$).

Finally, the chemical potentials of the stoichiometric phases constrain the adjustments applied to the element potentials through the Gibbs criterion and results in the following residual equation:

$$\Delta \tilde{\mu}_\omega = \sum_{k=1}^C \nu_{\omega k} \tilde{\Gamma}_k - \tilde{\mu}_\omega^\circ. \quad (5.41)$$

Together, the residual equations (5.39)–(5.41) result in the following system of equation with the objective of finding roots \mathbf{u} of the residual vector ϵ :

$$\epsilon(\mathbf{u}) = 0, \quad (5.42)$$

where $\epsilon \in \mathbb{R}^N$, $\mathbf{u} \in \mathbb{R}^N$ and N is the number of non-linear equations and corresponding unknown variables ($N = E + \Lambda + \Omega$). The residual vector, ϵ , can be expanded as:

$$\epsilon(\mathbf{u}) = \begin{bmatrix} \Delta b_{k=1}^m & \dots & \Delta b_{k=E}^m & \Delta x_{\lambda=1}^m & \dots & \Delta x_{\lambda=\Lambda}^m & \Delta \tilde{\mu}_{\omega=1} & \dots & \Delta \tilde{\mu}_{\omega=\Omega} \end{bmatrix}^T, \quad (5.43)$$

where superscript T denotes the transpose. The unknown system variable vector takes the

following form:

$$\mathbf{u} = \left[\tilde{\Gamma}_{k=1}^m \dots \tilde{\Gamma}_{k=E}^m \ n_{\lambda=1}^m \dots n_{\lambda=\Lambda}^m \ n_{\omega=1}^m \dots n_{\omega=\Omega}^m \right]^T. \quad (5.44)$$

The roots of equation (5.42) can be found using the Newton-Raphson method. Given $\epsilon : \mathbb{R}^N \rightarrow \mathbb{R}^N$ continuously differentiable and starting with an initial estimate \mathbf{u}^0 , the Newton-Raphson method for a system of nonlinear equations requires solving the following at each iteration m [160]:

$$\mathbf{J}(\mathbf{u}^m)\mathbf{s}^m = -\epsilon(\mathbf{u}^m), \quad (5.45)$$

$$\mathbf{u}^{m+1} = \mathbf{u}^m + \alpha^m \mathbf{s}^m, \quad (5.46)$$

where α^m is a scaling factor selected using an appropriate line search algorithm and \mathbf{s}^m is the Newton step representing the adjustment to the system variables and is given by:

$$\mathbf{s}^m = \left[d\tilde{\Gamma}_{k=1}^m \dots d\tilde{\Gamma}_{k=E}^m \ dn_{\lambda=1}^m \dots dn_{\lambda=\Lambda}^m \ dn_{\omega=1}^m \dots dn_{\omega=\Omega}^m \right]^T. \quad (5.47)$$

The Jacobian matrix² is defined as:

$$\mathbf{J} = \begin{bmatrix} \partial b_1^m / \partial \tilde{\Gamma}_1^m & \dots & \partial b_1^m / \partial \tilde{\Gamma}_E^m & \partial b_1^m / \partial n_{\lambda=1}^m & \dots & \partial b_1^m / \partial n_{\lambda=\Lambda}^m & \partial b_1^m / \partial n_{\omega=1}^m & \dots & \partial b_1^m / \partial n_{\omega=\Omega}^m \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \partial b_E^m / \partial \tilde{\Gamma}_1^m & \dots & \partial b_E^m / \partial \tilde{\Gamma}_E^m & \partial b_E^m / \partial n_{\lambda=1}^m & \dots & \partial b_E^m / \partial n_{\lambda=\Lambda}^m & \partial b_E^m / \partial n_{\omega=1}^m & \dots & \partial b_E^m / \partial n_{\omega=\Omega}^m \\ \partial b_1^m / \partial n_{\lambda=1}^m & \dots & \partial b_1^m / \partial n_{\lambda=\Lambda}^m & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \partial b_E^m / \partial n_{\lambda=1}^m & \dots & \partial b_E^m / \partial n_{\lambda=\Lambda}^m & 0 & \dots & 0 & 0 & \dots & 0 \\ \partial b_1^m / \partial n_{\omega=1}^m & \dots & \partial b_E^m / \partial n_{\omega=1}^m & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \partial b_1^m / \partial n_{\omega=\Omega}^m & \dots & \partial b_E^m / \partial n_{\omega=\Omega}^m & 0 & \dots & 0 & 0 & \dots & 0 \end{bmatrix} \quad (5.48)$$

²It must be noted the Jacobian matrix from the partitioning of Gibbs energy method is equivalent to the Hessian matrix resulting from the Gibbs energy minimisation approach.

where, the partials derivatives are defined as follows:

$$\frac{\partial b_j^m}{\partial \tilde{\Gamma}_k^m} = \sum_{\lambda=1}^{\Lambda} n_{\lambda}^m \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)}^m \nu_{ij} \nu_{ik} \quad (5.49)$$

$$\frac{\partial b_j^m}{\partial n_{\lambda}^m} = \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)}^m \nu_{ij} \quad (5.50)$$

$$\frac{\partial b_j^m}{\partial n_{\omega}^m} = \nu_{\omega j}. \quad (5.51)$$

At every iteration step, the direction vector is computed and the system is adjusted until the convergence criteria are achieved.

5.3.3. Convergence criteria

A number of different methods can be proposed to judge the convergence of a thermodynamic equilibrium solver, the most obvious being ensuring that the relative change in Gibbs energy between two iterations is within a specified tolerance. Another approach that makes better use of principles of thermodynamic equilibrium is based on equation (4.22) and requires that the chemical potentials of all species lie on or above the Gibbs plane formed by chemical potentials of system components.

1. Tolerance of G_{sys}^m

The most obvious method of ensuring convergence is to ensure that the normalised absolute difference of Gibbs energy, Ψ_G , between subsequent iterations is within a specified tolerance. Mathematically, this can be expressed as:

$$\Psi_G = \left| \frac{G_{\text{sys}}^m - G_{\text{sys}}^{m-1}}{G_{\text{sys}}^m} \right| < \epsilon, \quad (5.52)$$

where ϵ denotes the specified tolerance and the superscripts refer to iteration m and $m-1$ respectively. Using the interpretation of Lagrange multipliers in the Gibbs Energy Minimisation (GEM) method proposed by White et al. [110], we can obtain a similar estimate of convergence. Since the Lagrange multipliers, π_j , denote the chemical potentials, they can be related to Gibbs energy of the system, G_{sys} . This can be mathematically expressed as:

$$\Psi_{\pi} = \left| \frac{\pi_j^m - \pi_j^{m-1}}{\pi_j^m} \right| < \epsilon. \quad (5.53)$$

Though intuitive, this approach to judging convergence suffers from two potential is-

sues. The first issue is commonly observed in iterative solutions of non-linear systems where numerical stagnation can occur when significant numerical dampening is required to maintain the stability of numerical algorithm. In GEM for large chemical components, numerical dampening is often required and false convergence can result when the approach to minimum Gibbs energy becomes extremely slow. The second issue relates to insignificant contribution to the Gibbs energy of the system by minor species. These minor species can often be incorrect by several orders of magnitude and though they don't contribute to Gibbs energy significantly, they might be of significant chemical or radiological importance and the false sense of convergence can then lead to significant problems [3].

2. Gibbs' Criterion

The Gibbs criteria for judging convergence relies on the relationship between chemical potentials and Gibbs energies. To utilise this concept, the chemical potentials can be expressed per gram-atom as:

$$\hat{\mu}_i = \frac{\mu_i}{a_{i(T)}}, \quad (5.54)$$

where $\hat{\mu}_i$ [J/g – at] is the chemical potential and $a_{i(T)}$ is the total number of atoms in the formula mass. This method of defining chemical potentials allows an equivalent comparison of chemical potentials of compounds with different numbers of atoms per molar mass.

At equilibrium, all $\hat{\mu}_i$ must lie on a hyper-plane at equilibrium in the C -dimensional Euclidean space, where C represents the number of system components. This plane is called the *Gibbs plane* and an example of it is shown in figure 5.1 for a three dimensional space.

The chemical potential of any point on the Gibbs plane can be expressed as a linear combination of chemical potentials of system components and this interpolated potential can be denoted by $\hat{\mu}_{i(\phi)}(\Gamma)$. The absolute difference between $\hat{\mu}_{i(\phi)}(\Gamma)$ and $\hat{\mu}_{i(\phi)}$, Ψ_Γ can then be used as convergence criterion:

$$\Psi_\Gamma = |\hat{\mu}_{i(\phi)}(\Gamma) - \hat{\mu}_{i(\phi)}| < \epsilon, \quad (5.55)$$

i.e., all the species in equilibrium must lie on the Gibbs plane. If a phase lies below the Gibbs plane, adding it to the phase assemblage would yield a lower Gibbs energy of the system and such a system would not be at a global minimum. The Gibbs criteria is easily extendable to electrochemical equilibrium and can be conveniently implemented in

a thermodynamic equilibrium solver [3].

5.3.4. Choice of numerical algorithm

Both GEM and PGE have advantages and disadvantages and the choice of the algorithm must be based on the applications and excess mixing models used in them. For Yellowjacket–GEM, the Gibbs energy minimisation method was selected and the reasoning behind it has been explained by Bajpai et al. [161]. While the paper, presented on the following pages, was written primarily for the thermochemistry library ThermoChimica, the goal was also to pre-emptively justify the choice of the algorithm for Yellowjacket–GEM.



Corrigendum

Corrigendum to “The thermochemistry library Thermochimica”

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ABSTRACT

The CALPHAD method has been highly relied upon for material design and development and a number of software packages have been developed for computing thermodynamic equilibrium. While Gibbs Energy Minimisation (GEM) has been the most commonly used algorithm for thermodynamic equilibrium calculations, an alternative technique namely Partitioning of Gibbs Energy Minimisation (PGE) was advanced and applied to the thermochemistry library Thermochimica due to some of its numerical advantages. The PGE approach, however, has considerable convergence issues when applied to highly non-ideal solution phases and therefore was eventually abandoned in Thermochimica. This corrigendum illustrates the convergence issues and their underlying cause with the aim of informing the readers about the reasoning for adopting GEM in place of PGE in Thermochimica and may help their own decision making in selecting an algorithm for their own software.

1. Introduction

Recent trends in material design and development have relied heavily on the CALPHAD method [1] and over the years a number of software packages have been developed for computing thermodynamic equilibrium, such as Thermo-Calc [2], FactSage [3], PANDAT [4], pyCalphad [5], OpenCalphad [6], Thermochimica [7], Yellowjacket [8], etc. While most thermochemical equilibrium solvers rely on the Gibbs Energy Minimisation (GEM) approach, originally developed by White et al. [9], Piro et al. advanced a numerical procedure called the Partitioning of Gibbs Energy (PGE) in Thermochimica, which built upon the concepts presented by White [10] in combination with that of Eriksson and Thompson [11]. In initial developments of Thermochimica, the PGE method was applied in place of the GEM method due to some numerical advantages that improved the rate of convergence and reduced numerical instabilities for some applications. These advantages include the fact that PGE does not require any numerical dampening to ensure that the mole fractions of the various solution species remain positive as compared to GEM where numerical dampening becomes necessary. This issue will become clearer in the next section. GEM also requires additional corrections to be applied in order to improve the estimates of mole fractions of dilute species. While such corrections can compromise the mass balance constraints in GEM, they are inherently satisfied in PGE, thereby simplifying the numerical process.

Despite its numerical advantages, a significant challenge is experienced when PGE is applied to a broader range of applications that results in considerable convergence issues. Ultimately, the PGE method was abandoned in Thermochimica in favour of the more widely used GEM technique, which offers greater robustness over a wide range of applications. This corrigendum is intended to better inform the readers about the reasoning behind adopting the GEM method in place of PGE, which may help their own decision making in developing their own software. In the current context, for the sake of simplicity, the discussion will focus on species in single-sublattice phases. However, the concepts readily apply to the compound end members and/or quadruplets in multi-sublattice phases.

2. Discussion

From a theoretical point view, both GEM and PGE methods should yield the same set of predictions of thermodynamic equilibria: a unique combination of phases and species that are stable in a closed isothermal-isobaric system of fixed composition. The distinction between GEM and PGE lies not in the mathematical content of the equilibrium conditions but rather in the numerical algorithms adopted to solve the problem. At a high level, GEM is an optimisation method, whereas the PGE approach is based on finding the roots of a system of nonlinear equations [12]. To highlight the differences between the two approaches, the conditions for

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thermodynamic equilibrium are first summarized:

1. The conservation of mass must be satisfied:

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \nu_{ij} + \sum_{\omega=1}^{\Omega} n_{\omega} \nu_{\omega j} \quad (1)$$

where b_j denotes the molar amount of component j in the system¹, n_{λ} and n_{ω} are the molar amounts of solution phase λ and stoichiometric phase ω , respectively. $x_{i(\lambda)}$ represents the mole fraction of species i in solution phase λ , and ν_{ij} and $\nu_{\omega j}$ are the stoichiometry coefficients of component j in species i and stoichiometric phase ω , respectively. Note that this equation also applies to ionic charge to ensure charge neutrality constraints are respected.

2. The Gibbs phase rule must be respected:

$$F = C - \Phi + 2 - \Xi \quad (2)$$

where F denotes the degree of freedom of the system, C represents the number of system components and $\Phi = \lambda + \Omega$ is the number of phases present at equilibrium. Ξ represents the number of ionic phases². Under isothermal-isobaric conditions, the Gibbs phase rule is reduced to $F = C - \Phi - \Xi$, where $F \geq 0$.

3. The Gibbs energy of the system must be at a global minimum. The *necessary condition* corresponding to a local minimum requires that the chemical potentials of any species must be represented by a linear function of the system component potentials as [12–14]:

$$\tilde{\mu}_{i(\lambda)} = \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j, \quad (3)$$

where $\tilde{\mu}_{i(\lambda)}$ represents the dimensionless chemical potential of species i and $\tilde{\Gamma}_j$ represents the dimensionless chemical potential³ of component j . The *sufficient condition* for global minimum requires that all the metastable phases abide by the following condition [15–17]:

$$\pi_{\lambda} = \min_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) \geq 0, \quad (4)$$

that is, the driving force of all the phases believed to be metastable must be positive and all stable phases are zero.

In addition to the above conditions, the following constraints must be respected:

- A. The number of moles of any phase cannot be negative.
- B. The sum of mole fractions of all species in a solution phase must equal unity.

It must be mentioned that both GEM and PGE are methods for computing local minima and to compute the global minimum, they must be coupled with a global optimisation routine, some of which have been analysed by Piro and Simunovic [17].

The fundamental premise of GEM is to define the quantities of all species and phases as the *independent* variables, and their corresponding chemical potentials as *dependent* variables (i.e., $\mu_i = f(\mathbf{x})$). In contrast,

the PGE method defines the chemical potentials as *independent* variables, and the quantities of species and phases as the *dependent* variables (i.e., $x_i = f(\boldsymbol{\mu})$). In GEM, the estimated quantities of all species and phases are iteratively altered to progressively minimize the Gibbs energy of the system. In other words, the GEM approach optimises equilibrium conditions 1 and 3 while constraining equilibrium condition 2 [9,18,19].

Thus, the mass balance residuals and residuals of chemical potentials of each phase with respect to the system components are simultaneously minimised in GEM [7]. The number of moles of each solution species is updated with a linear function, which is then used to compute the conjugate chemical potential terms. One must often dampen this calculation to prevent the computation of the logarithm of a negative number. In contrast, the PGE method defines the chemical potentials of all species and phases by a set chemical potentials of the system components, which are then used to compute the mole fractions of individual species and iteratively attempts to satisfy the mass balance equations in Eq. (1). Thus, PGE constrains equilibrium conditions 2 and 3 while iteratively satisfying equilibrium condition 1 [7]. Furthermore, since the PGE method defines the mole fraction as an exponential function, rather than a linear function involving the natural logarithm, it will always be positive as long as the chemical potentials are real. This feature reduces the need for numerical dampening in PGE.

The distinguishing feature of PGE is in solving a system of non-linear equations to find the roots of the mass balance equations, which requires representing the mole fraction of any species as an exponential function involving the system component potentials. One can formulate an explicit function for species in an ideal solution phase; however, for non-ideal solution phases requiring an excess Gibbs energy of mixing contribution, this is not always a straightforward mathematical operation. The Gibbs energy of a non-ideal solution phase is generally given as:

$$G_{\lambda} = G_{\lambda}^{\circ} + G_{\lambda}^{\text{id}} + G_{\lambda}^{\text{ex}}, \quad (5)$$

where G_{λ} is the Gibbs energy of the solution phase λ and the superscripts \circ , id and ex denote the reference, ideal mixing and excess mixing contributions, respectively. The chemical potential of species i in solution phase λ is generally given as:

$$\mu_{i(\lambda)} = \left(\frac{\partial G_{\lambda}}{\partial n_{i(\lambda)}} \right)_{T, P, n_{j \neq i}} \quad (6)$$

For a species in an ideal solution phase, the reference and ideal mixing contributions result in linear contributions to the chemical potentials, yielding:

$$\tilde{\mu}_{i(\lambda)} = \tilde{\mu}_{i(\lambda)}^{\circ} + \ln(x_{i(\lambda)}) \quad (7)$$

Recall that $\tilde{\mu}_{i(\lambda)}$ represents the dimensionless chemical potential, which is why RT is not used in the foregoing equation.

Substituting Eq. 3 for $\tilde{\mu}_{i(\lambda)}$ in Eq. (7), and re-arranging to solve for $x_{i(\lambda)}$ gives:

$$x_{i(\lambda)} = \exp \left(-\tilde{\mu}_{i(\lambda)}^{\circ} + \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) \quad (8)$$

For the case of a non-ideal solution phase, an excess Gibbs energy of mixing term is added, which is a model-specific function that involves mole fractions of the species within that phase, $x_{i(\lambda)}$ [20]. Similar to Eq. (8), the mole fraction of a species in a non-ideal phase is represented in PGE as a function of the system component potentials as follows:

$$x_{i(\lambda)} = \exp \left(-\tilde{\mu}_{i(\lambda)}^{\circ} - \tilde{\mu}_{i(\lambda)}^{\text{ex}} + \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) \quad (9)$$

Technically, the equation for $x_{i(\lambda)}$ in Eq. (9) is *not a function* because $\tilde{\mu}_{i(\lambda)}^{\text{ex}}$ is itself a function of $x_{j(\lambda)}$, $\forall j$. Therefore, one can only define an

¹ Note that a system component may be a chemical element, an integer combination of chemical elements, or an electron corresponding to an ionic phase.

² Note that Ξ is the conjugate variable to the increase in C corresponding to ionic phases.

³ Dividing by RT , where R is the ideal constant and T the absolute temperature, reduces computational expense and is standard practice.

explicit function for $x_{i(\lambda)}$ in PGE when solution phase λ is ideal; however, this cannot be done when λ is non-ideal. For any non-ideal solution phase λ , replacing the expressions of chemical potentials in Eq. (9), one gets an implicit expression of the form $x_{i(\lambda)} = f(\mu(x))$. In PGE, the preceding expression is used to construct the mass balance residuals, which must be near zero (within tolerance) when the conditions of equilibrium are satisfied [7]. The roots, including $x_{i(\lambda)}$, of the non-linear system of equations so formed must then be solved, which significantly impacts the performance and stability of PGE. At this stage, one faces a difficult choice of options due to several reasons.

Firstly, since the residual equations are not explicit, solving the system of equations in order to find the mole fractions of the species requires solving an additional non-linear problem within PGE. One is faced with the question of how to evaluate the roots of an implicit expression in a closed-form sense. In ThermoChimica, multiple approaches were explored to find the roots. One of these approaches was to solve for the mole fractions, $x_{i(\lambda)}$, at each step while computing the partial molar excess terms using the mole fractions from the previous global iteration. Though the use of this approach temporarily makes the residual equation explicit, it does not guarantee convergence especially in highly non-linear phases. Another approach was to use a linear averaged approximation of the mole fraction ($x^{m+1} = 0.5(x^m + x^{\text{temp}})$) or a non-linear averaged approximation ($x^{m+1} = \sqrt{x^m x^{\text{temp}}}$) but without any assurance of convergence. A more involved attempt used a nested non-linear root finding algorithm but it was often unfruitful despite adding significantly to the computational expense.

Secondly, and more critically, there might be cases where the residual equations result in a system with no roots. Such a situation cannot be dealt with using any algorithm and causes the PGE method to fail. Finally, the last issue relates to existence of multiple roots. Such a scenario can arise, for example, in systems with miscibility gaps and the roots calculated using the PGE algorithm are virtually indistinguishable and can therefore result in misleading predictions of equilibrium conditions. These predicaments are further amplified as one moves to more complicated non-linear models and higher order systems. In general, such models act as significant impediments to the applicability of PGE for determining phase equilibrium in systems where highly non-linear non-ideal phases are involved.

GEM, on the other hand, does not require a set of explicit functions of the mole fractions of the species $x_{i(\lambda)}$. Since the Gibbs energy and mass balance residual are simultaneously minimised in GEM, it instead requires an explicit function of chemical potentials as a function of $x_{i(\lambda)}$. Even without any rearrangement, the chemical potentials of species are explicit functions of mole fractions ($\tilde{\mu}_{i(\lambda)} = f(x)$). As a result, the roots of the resulting system of linearised equations⁴ can be directly evaluated. Therefore, GEM does not suffer from the shortcomings of PGE and is directly applicable to all sorts of mixing models. While applying GEM, one does not need to focus on sidestepping the numerous hurdles faced by PGE when dealing with highly non-linear phases and despite the numerical disadvantages discussed by Piro et al. [7], it is much more robust and with the aid of a good initial estimate and proper line search methods it converges easily for a much broader range of models compared to PGE.

3. Summary

In summary, the PGE method has been found to offer marginal benefits to GEM in handling systems containing stoichiometric and ideal solution phases. However, PGE experiences a great predicament when

involving non-ideal solution phases whereby one can no longer define mole fractions as explicit functions of chemical potentials because excess Gibbs energy expressions are also functions of mole fractions. In contrast, the GEM method avoids this shortfall as it reverses the selection of dependent and independent variables, whereby the chemical potentials of solution species can be written as explicit functions of the mole fraction of solution species. In practice, the GEM method has proven to be quite robust in a number of complex thermodynamic systems involving highly non-linear excess Gibbs energy models.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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⁴ The linearised system follows from the method of Lagrange multipliers used to solve the constrained optimisation problem and derivation of such a system of equations has been presented by, for example, White et al. [9], Eriksson and Rosen [18], etc.

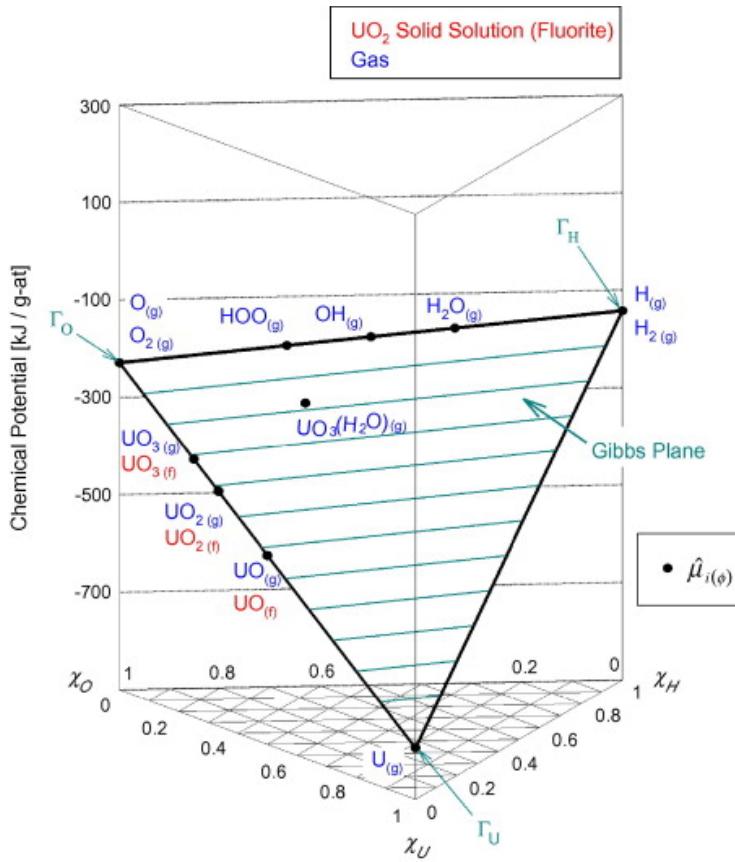


Figure 5.1: The Gibbs criteria is satisfied when the chemical potentials for all species represented per gram-atom lie on the Gibbs Plane within an acceptable tolerance [3].

5.4. Global Energy Minimisation

Global minimisation of Gibbs energy is crucial to accurately predicting the stable phase assemblage using equilibrium thermodynamic softwares. An example application is the detection of miscibility gaps in phases containing regions of compositional instability. In a miscibility gap, the same phase can appear with different compositions and finding the global minimum from among the many local minima can be a daunting challenge. For multi-component systems, the topology of the energy surfaces tends to become quite complex particularly when there are multiple non-ideal phases in the system. This significantly complicates the interaction of the Gibbs energy surface with the Gibbs hyperplane and an inadequate numerical approach may lead to a false sense of thermodynamic equilibrium despite being far from the true equilibrium. To illustrate how an inadequate solver may yield a false equilibrium, the following scenarios can be considered:

1. In the fictive binary system shown in figure 5.2, a solution phase α and a stoichiometric phase A_3B_2 can possibly coexist. While the stoichiometric phase A_3B_2 and solution phase

α are predicted to be stable, as represented by the dashed tangent line, they are in fact metastable and a miscibility gap would yield a lower value of the integral Gibbs energy of the system, G_{sys} .

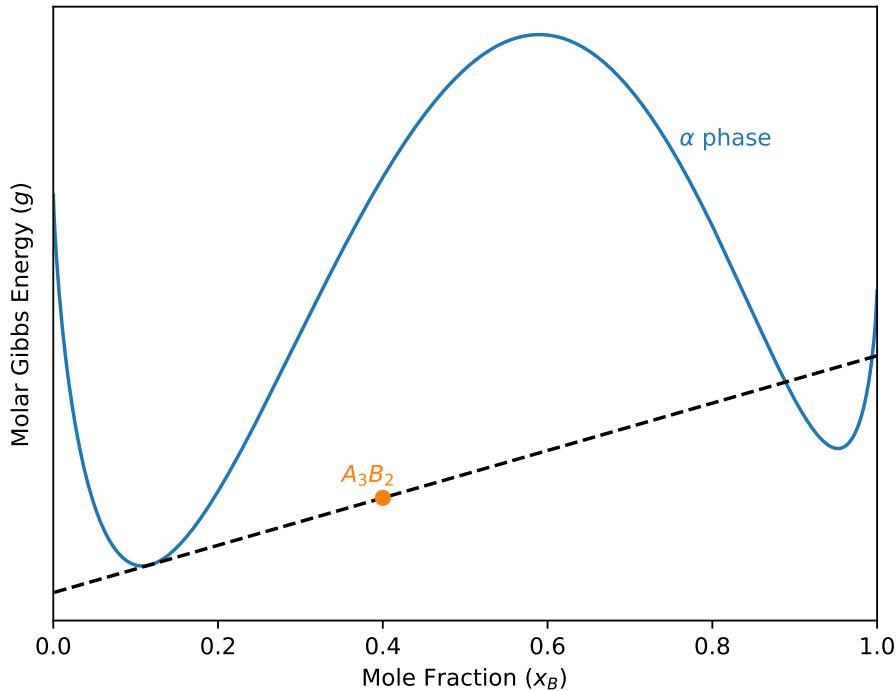


Figure 5.2: Fictive system with miscibility gap showing a possible false positive from thermodynamic equilibrium (after Piro and Simunovic [4]).

2. In the fictive binary system shown in figure 5.3 which can have three possible solution phases, the δ phase is believed to be metastable but one must confirm that the combination of β and γ is most stable or if a different combination is more stable. However, it can be seen that inserting the δ phase into the system and replacing one of the other two phases would yield a lower value of the integral Gibbs energy of the system, G_{sys} .

As previously mentioned in section 5.2, satisfying the necessary conditions, specifically the Gibbs' Criterion, is equivalent to finding a local minimum but one must demonstrate that the driving force, ΔG , is non-negative for all phases to be metastable. Throughout the iterative process, the driving force for all the metastable phases should be calculated to determine if a particular phase needs to be added to the system. At this point, two similar but distinct approaches to the problem of identifying phases with negative driving force can be adopted. In the first approach, the goal is only to find out whether or not a phase has a negative driving force while in the second approach the goal is to determine the minimum value of the driving force

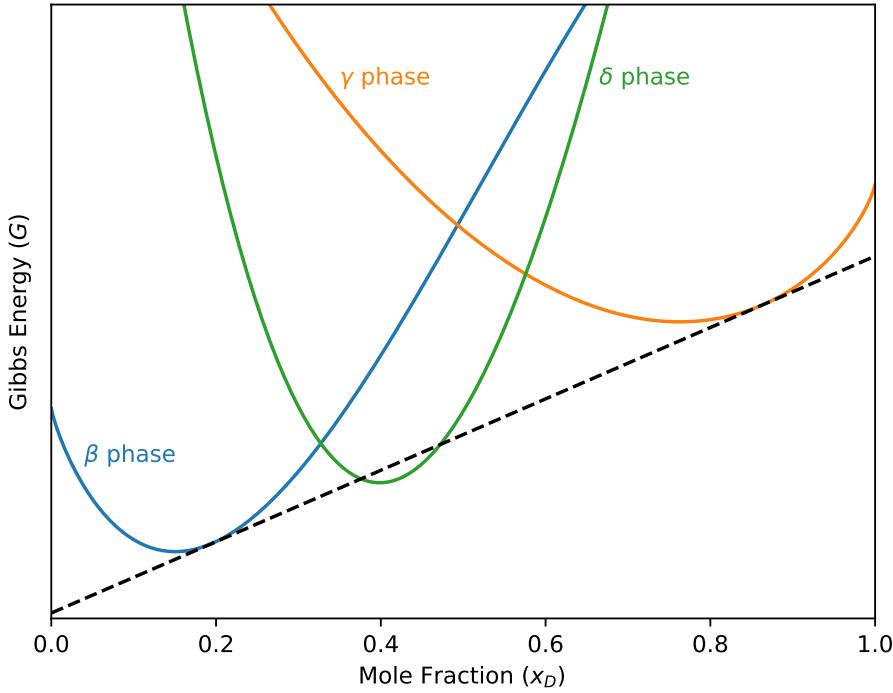


Figure 5.3: Fictive system with three possible phases showing a false positive from thermodynamic equilibrium solver wherein a wrong phase is believed to be present at equilibrium (after Piro and Simunovic [4]).

subject to the equality and inequality constraints mentioned previously. While the first approach can be computationally cheaper, the second approach can provide additional information about the state of the system. For instance, when multiple phases have a negative driving force, the phase with the most negative driving force can be added to the system.

Since the driving force function can be non-convex, finding the most negative driving force is essentially a constrained global optimisation problem. The domain space of the problem is defined by the number of species in the solution phase and, because the mole fractions of the species must lie in $(0, 1)$, the search space is box constrained. Using the sufficient conditions previously mentioned, the Lagrangian function of the driving force of solution phase ϕ can be defined as:

$$\mathcal{L}_\phi = \sum_{i=1}^{N_\phi} x_i \left(\tilde{\mu}_i - \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) - \lambda_\phi \left(\sum_{i=1}^{N_\phi} x_i - 1 \right) - \lambda_{e^-} \left(\sum_{i=1}^{N_\phi} \nu_{ie^-} x_i - 1 \right), \quad (5.56)$$

where the first Lagrange multiplier, λ_{ph} , imposes the constraint on mole fractions and the second multiplier, λ_{e^-} , extends the constraints to handle ionic phases where the charge neutrality constraint must also be satisfied. The natural constraint on mole fractions implies $x_i \in (0, 1)$ and the unknowns in the above expression, x_i , λ_ϕ and λ_{e^-} , must lie in $\mathbb{R}^{N_\phi+2}$. For phases

without any ionic components, the dimension of the above problem reduces by one. The Lagrangian function has a minimum value when $\nabla \mathcal{L} = 0$. Differentiating \mathcal{L} with respect to x_i :

$$\frac{\partial \mathcal{L}}{\partial x_i} = \tilde{\mu}_i - \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j - \lambda_\phi, \quad (5.57)$$

which shows that the undetermined Lagrange multiplier, λ_ϕ , is the same as the driving force of the phase, ΔG_ϕ . Differentiating with respect to λ_ϕ yields:

$$\frac{\partial \mathcal{L}}{\partial \lambda_\phi} = 1 - \sum_{i=1}^{N_\phi} x_i, \quad (5.58)$$

and taking the derivative with respect to λ_{e^-} results in:

$$\frac{\partial \mathcal{L}}{\partial \lambda_{e^-}} = 1 - \sum_{i=1}^{N_\phi} \nu_{ie^-} x_i. \quad (5.59)$$

The system of non-linear equations above can be solved using many different non-linear solution methods such as by taking the second order Taylor expansion of the Lagrangian function. The global optimisation algorithms used in Yellowjacket–GEM will be discussed in further details in chapter 6.

5.5. Summary

Based on the fundamental laws of thermodynamics, achieving thermochemical equilibrium in a system requires satisfaction of several conditions which are as follows:

1. *Conservation of mass* requires that the mass of element j , b_j , must satisfy the following mass balance equation:

$$b_j = \sum_{\lambda=1}^{\Lambda} n_\lambda \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \nu_{ij} + \sum_{\omega=1}^{\Omega} n_\omega \nu_\omega,$$

where ν_{ij} and ν_ω represent the stoichiometric coefficients of element j in solution phase species j and stoichiometric phase ω respectively.

2. *Gibbs' phase rule* which defines the thermodynamic degrees of freedom of the system must also be satisfied:

$$F = C - \Phi + 2 + \Xi,$$

where F represents the degrees of freedom, C denotes the number of components in the system, Φ denotes the number of phases and Ξ denotes the number of ionic phases.

3. *Gibbs' criteria* for equilibrium requires that the Gibbs energy of a system be at a global equilibrium. In equivalent terms, the chemical potential for each system component must have the same value in all stable phases within the system [162], where the chemical potential of any constituent in a stable phase can be defined as a linear function of the element potentials, Γ_j , as:

$$\mu_i = \sum_{j=1}^C \nu_{i,j} \Gamma_j.$$

The necessary conditions for thermodynamic equilibrium require that the chemical potentials of all stable solution phase species and stoichiometric phases abide by the above equality, which is equivalent to Gibbs energy of the system being at a local minimum, and that the conservation of mass and the Gibbs phase rule are satisfied. The sufficient condition requires that all the metastable phases abide by the following conditions

$$\Delta G_\phi = \min_x \sum_{i=1}^{N_\phi} x_i \left(\mu_i - \sum_{j=1}^C \nu_{i,j} \Gamma_j \right),$$

i.e., there must exist a Gibbs' plane such that the element potentials lie on the plane and the chemical potentials of all the species lie on or above the plane and the mole fraction of the species must satisfy the following constraints

$$\begin{aligned} \sum_{i=1}^{N_\phi} x_i &= 1, \\ x_i &\geq 0 \quad \forall i, \end{aligned}$$

i.e., the sum of mole fraction of all the species in a phase ϕ must be unity and that the individual mole fractions must be greater than or equal to zero.

The aforementioned conditions are used in Gibbs energy minimisers to find a unique combination of phases that are stable in the system. In such solvers, one must also carefully consider the role of the numerical algorithm and the convergence criteria to be adopted as these choices can have a significant impact on both computational performance and robustness of the solver.

6

Computational Implementation

The principles of thermodynamic equilibrium set the background for solving phase equilibrium problem in multicomponent system but being able to solve the resulting optimisation problem requires the use of high-quality software implementations. Though several such softwares exists, most of them do not meet the requirements for direct integration with MOOSE framework. The commercial softwares do not provide source codes and the application programming interfaces (APIs) provided by a few of such codes are usually very difficult to modify to meet the needs of multiphysics implementations. The open-source softwares on the other hand do have readily available source codes but often lack in terms of quality of code implementation and software quality assurance (SQA). To overcome the challenges and to provide readily usable thermodynamic equilibrium framework in MOOSE, a new Gibbs energy minimiser was developed. While many of the algorithms employed in Yellowjacket–GEM embody the concepts previously presented in open literature, there remains a scope for improving the efficiency and capabilities of some of these algorithms through careful implementation and/or building upon them. The top level architecture of the thermodynamic equilibrium solver has been outlined in figure 6.1. The program essentially consists of parsing and input modules to read the required thermodynamic data and system information followed by initialisation routines which provide the initial assemblage to a non-linear solver. The assemblage from the non-linear solver is then checked to ensure global minimum is achieved at which stage the outputs are produced.

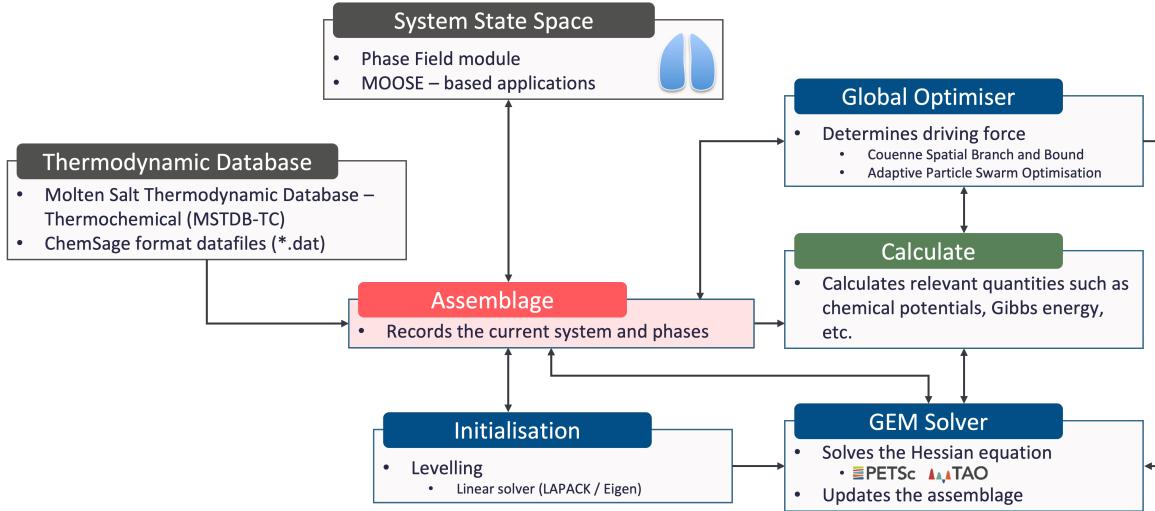


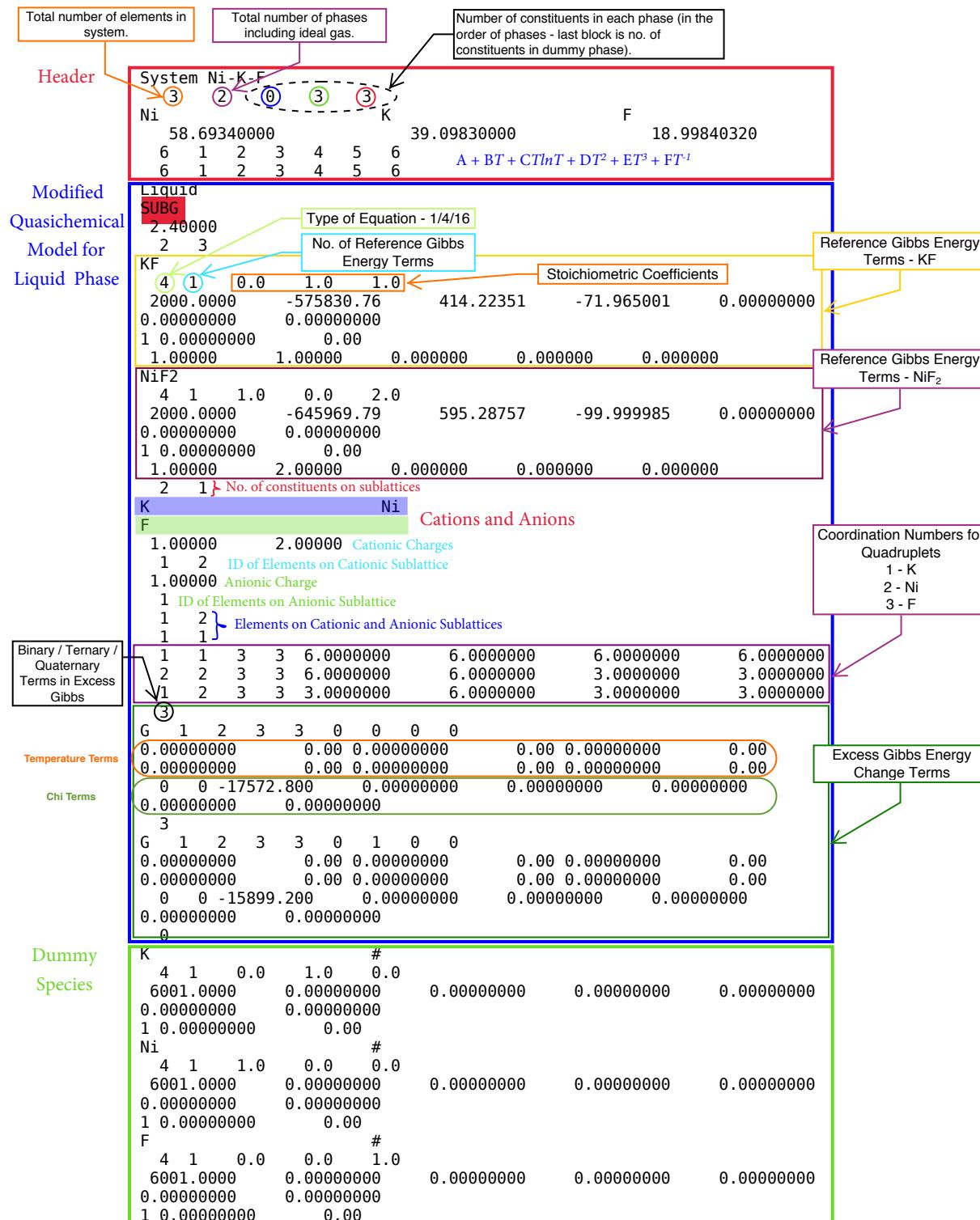
Figure 6.1: Top-level architecture of Yellowjacket–GEM.

6.1. Thermodynamic Database

Calculation of thermodynamic equilibrium requires a thermodynamic database, which includes Gibbs energy functions of the different phases and species that can exist in the system. These thermodynamic databases are developed using the well established CALPHAD method [158] and are available in different formats, the most commonly used being ThermoCalc (*.tdb) and ChemSage (*.dat) data file formats, which are generated by the commercial software ThermoCalc and FactSage, respectively. An example of a typical ChemSage data file is shown in figure 6.2 and consists of a header block followed by information blocks for every possible phase in the system.

A data file parser for Yellowjacket–GEM has been developed in C++ and it performs the extraction of Gibbs energy functions from ChemSage format (*.dat) thermodynamic files (ChemSage format) and creates an in-memory thermodynamic database class, Database, that can be conveniently accessed by any part of the code throughout rest of the solve. All the data structure objects inherit from a single base class allowing the rest of the code to track the phases conveniently without having to track the model-specific details. Moreover, in multiphysics simulations, it allows a single database instance to be created at the start of the simulations instead of the need of reading the datafile every time the information is needed. In Yellowjacket–GEM, the Molten Salt Thermodynamic Database - Thermochemical [? ?], is natively supported but any ChemSage format datafile can be supplied by the user.

The Database class includes a number of utility functions for post-processing and cleaning up the raw database constructed after parsing. A peculiarity of ChemSage datafiles is how they denote phases that can have a miscibility gap. In ChemSage, such phases are denoted by



adding a duplicate entry for a phase that is considered to have miscibility gaps. This has several disadvantages. First, this creates unnecessary duplication of thermodynamic data and can have memory and performance implications for large databases. Second, the decision for miscibility gap should be enforced using physical rules rather than basing them upon the database or user inputs. As an example, since a phase with more than one miscibility gap is not only plausible but also observed in many physical systems, a phase being duplicated once doesn't reveal any information about the number of such possible gaps and can be a source of confusion. In post-processing, such duplicate entries are deleted, but to not lose the information completely, a flag is raised in the thermodynamic phase whose duplicate was deleted. For multi-sublattice phases, the post-processor also maps all the sublattice constituents to the system components, and, for phase represented by MQM, it calculates the default coordination numbers for the quadruplets that are not included in the datafile.

6.2. System State-Space

Thermochemical equilibrium calculations are isothermal, isobaric point calculations and require the temperature, pressure as well as the composition of the system to be specified. In Yellowjacket-GEM, this information is provided by MOOSE or MOOSE-based applications such as the Phase Field module. To facilitate such data transfer, a MOOSE UserObject, namely GEMUserObject, has been developed. The MOOSE UserObject system is built for developing and running custom algorithms that may not fit well within any other system in MOOSE. Examples include complex calculations that may result in values that don't associate in a one to one manner with elements, nodes, or sides. GEMUserObject allows the thermodynamic equilibrium solver to be called by other codes and the invocation requires that the temperature, pressure and composition be specified as required parameters. The UserObject is also responsible for passing back the return values to the calling code and some of the common variables that are often requested include the Gibbs energy, chemical potentials, stable phases and their speciation.

6.3. Initialisation

Much like any other optimisation problem, the choice of initial estimate plays a critical role in reducing the amount of computational time required for the solution to converge to a minimum. This requirement of initial estimates of the stable phases and their speciation creates a significant challenge. Many early softwares created for the purpose of estimating thermodynamic equilibrium, for example SOLGASMIX, required the user to input an initial estimate but this relied on the user's intuition and was often very inconvenient for them, especially when working

with complex systems and/or systems where finding estimates from intuition was not straightforward. A bigger problem was that it could often result in initial estimates which were far from the real stable assemblage of phases and would increase the computational cost substantially, often even compromising the convergence itself.

To overcome the need for user prescribed initial estimates, Eriksson and Thompson [59] proposed an initialisation algorithm called *levelling* that has found widespread application in thermodynamic equilibrium softwares. Yellowjacket–GEM implements this algorithm as the standard initialisation routine and the it is described in the following text.

6.3.1. Levelling

The levelling algorithm was developed to accelerate the rate of convergence by eliminating the phases and species that have an insignificant contribution in the final phase assemblage. The algorithm is based on a temporary treatment of all species and phases in the system as pure stoichiometric phases. Mathematically, this amounts to temporarily converting the non-linear optimisation problem into a linear optimisation problem and the algorithm for the computational implementation has been illustrated in figure 6.3.

Since the Gibbs energy is a relative thermodynamic function and the Gibbs energies of each component element are not related to one another [59], it is possible to numerically alter the Gibbs energy of each phase while preserving the elemental differences. Levelling is performed by representing the set of Gibbs energies relative to the collection of phases assumed to be most stable and uses a relative Gibbs energy function called the *absolute Gibbs energy* by Eriksson and Thompson and is the Gibbs energy of the pure species per atom in the species as shown in equation (6.1)

$$\hat{G}_i = \frac{G_j}{\sum_{j=1}^C \nu_{ij}} \quad (6.1)$$

The levelling process determines the combination of phases yielding the lowest Gibbs energy by evaluating a combination of Gibbs energies on a relative basis. A phase that has a negative relative Gibbs energy with respect to the assemblage indicates that a phase in the assemblage must be replaced by the current phase to achieve a lower integral Gibbs energy.

Mathematically, levelling is achieved through an iterative process that systematically adjusts fixed combinations of phases, subject to the linear equality and inequality mass balance constraints, to progressively minimise the Gibbs energy of the system [164]. At iteration $m + 1$,

the adjustment to be applied to the relative Gibbs energy of phase i is defined by [59]:

$$\begin{aligned} d\hat{G}_i^{m \rightarrow m+1} &= \sum_{j=1}^C c_{ij} d\Gamma_j^{m \rightarrow m+1} \\ \hat{G}_i^{m+1} &= \hat{G}_i^m - d\hat{G}_i^{m \rightarrow m+1} \end{aligned} \quad (6.2)$$

where, c_{ij} denotes the atomic fraction of element j in species i and $d\Gamma_j^{m \rightarrow m+1}$ is the adjustment applied to the chemical potential of element j , which in turn is determined by the most stable phases found at iteration m .

In matrix form, the overall mass balance constraint can be represented as [164]

$$\mathbf{A}^T \mathbf{n} = \mathbf{b} \quad (6.3)$$

where $\mathbf{A} \in \mathbb{R}^{E \times \Phi}$ represents the stoichiometric matrix, $\mathbf{n} \in \mathbb{R}^\Phi$ denotes the column vector of the number of moles of each phase, and $\mathbf{b} \in \mathbb{R}^E$ is the column vector with the total mass of each element in the system. When equation 6.3 is used in levelling, $\Phi = E$.

The initial guess for the levelling method is the most chemically stable form of each element and the stoichiometric matrix \mathbf{A}^T in equation (6.3) becomes a diagonal matrix. Subsequently, provided all elements of vector \mathbf{b} are positive, all the elements of \mathbf{n} must also be positive. However, the diagonality of the stoichiometric matrix is not preserved over subsequent iteration and it assumes a non-symmetric sparse form. In fact, the matrix \mathbf{A}^T might become rank deficient if proper care is not taken while selecting the phase assemblage.

In levelling, since the number of phases in the system is equal to the number of elements, the element potentials can then be uniquely determined from the current estimated phase assemblage by solving the following system of linear equations:

$$\mathbf{A}^T \boldsymbol{\Gamma} = \boldsymbol{\mu} \quad (6.4)$$

where $\boldsymbol{\Gamma} \in \mathbb{R}^E$ and $\boldsymbol{\mu} \in \mathbb{R}^\Phi$.

The next step in levelling is updating the phase assemblage in accordance with equation (6.2). A species with a positive \hat{G}_i^{m+1} would yield a thermodynamically less stable assemblage and is left out along with phases with insignificant contributions to final equilibrium while the phase with the most negative \hat{G}_i^{m+1} is introduced into the assemblage by replacing a phase in the previous assemblage. The phase assemblage at this stage must meet three requirements. First, the number of moles of all phase in \mathbf{n} must be non-negative and real. Second, all the elements of the vector $\boldsymbol{\Gamma}$ must be real. Finally, the phase assemblage must not have been

previously considered. If the phase assemblage does not meet any of these requirements, the phase with the second lowest relative Gibbs energy must be considered, and so on.

While the criteria for the phase to be added in the system was well established by Eriksson and Thompson, a criterion to select the phase to be replaced wasn't proposed and, typically, local iterations were performed to systematically traverse through the candidate phases until a particular combination yielded an entire set of non-negative and real mole numbers [59]. The number of these local iterations rapidly grows with the number of elements in the system and an alternative named *Euclidean norm* was proposed by Piro and Simunovic [164]. This method has been described in section 6.3.2.

Once the new phase has been exchanged with one of the existing phases and its acceptability has been determined, levelling step is repeated until no phases with negative absolute Gibbs energy remain in the system. At this stage, the assemblage can be passed on to a non-linear solver as the initial estimate.

An example of the levelling method is presented in figure 6.4. In the illustration, in the first iteration, the phase with the most negative Gibbs energy is paired with another phase that together has non-negative molar quantities. At the end of iteration 0, choosing solid UO_2 as the phase with the most negative relative Gibbs energy and arbitrarily choosing solid UO_3 to pair it with, the equivalent Gibbs energies of pure uranium and pure oxygen are computed and followed by the element potentials Γ_U and Γ_O (represented by the dashed red line). The levelling procedure is then applied and the relative Gibbs energies of the terms are calculated.

At the start of iteration 1, the relative Gibbs energy of solid U_3O_8 is negative with respect to the combination of solid UO_2 and solid UO_3 , indicating it must be introduced in the assemblage. The internal linear solver then determines the phase that must be replaced and the iterative process continues with the updated phase assemblage.

At the end of the levelling procedure, the assemblage has the lowest Gibbs energy with all other phases being positive with respect to the assemblage. The Gibbs energy of the pure stoichiometric system is thereby minimised. For the example presented in figure 6.4, the levelling solver converges in only 3 iterations. According to Eriksson and Thompson [59], the computational expense using levelling can be up to two to five times lower than the general equilibrium calculations.

Mathematically, the levelling process always respects the Gibbs phase rule, mass balance and the Gibbs' criterion and the number of iterations required to achieve convergence is typically close to the number of elements. This results in significant computational advantage when considering exceeding large number of possible phase combinations as the number of elements in the system grow making levelling an excellent choice as an initialisation routine.

6.3.2. Euclidean norm

The Euclidean norm method was proposed by Piro and Simunovic [164], to strategically rank the best candidate phases to accommodate a new phase change. The Gibbs phase rule requires that when the thermodynamic degree of freedom F equals zero, a phase must be removed in order to introduce a new phase. Determining whether a candidate phase is feasible is the most expensive task within the global iteration cycles as it requires solution of a simultaneous equation to ensure that the Hessian matrix is non-singular [164]. If there are multiple candidate phases, this iterative process must be repeated for each candidate.

The Euclidean norm method systematically ranks the best candidates to be withdrawn from the system without having to perform an exhaustive search. The method is based on the principle that the best candidate phase to be withdrawn from the current assemblage has the most similar atomic composition to the phase that has to be added to the system.

The atomic fraction of element j in a pure stoichiometric phase ω is represented as:

$$c_{\omega j} = \frac{c_{\omega j}}{\sum_{k=1}^E x_{i(\omega)} \nu_{\omega k}} \quad (6.5)$$

Similarly, in the solution phase λ , the atomic fraction of element j is computed by

$$c_{\lambda j} = \frac{\sum_{i=1}^{N_\lambda} \nu_{ij}}{\sum_{i=1}^{N_\lambda} \sum_{k=1}^E x_{i(\lambda)} \nu_{ik}} \quad (6.6)$$

Denoting the atom fraction of the element j in the new phase that is to be introduced into the system with $c_{\phi j}^*$, the difference between this phase and the phases currently in the assemblage is given by the Euclidean norm of each phase ϕ

$$\|c_\phi\|_2 = \sqrt{\sum_{j=1}^E (c_{\phi,j} - c_{\phi,j}^*)^2} \quad (6.7)$$

The phase with the lowest Euclidean norm has the most similar composition to the phase to be introduced in the assemblage. In case the resulting assemblage does not meet the criterion to be a valid assemblage, the phase with the second lowest Euclidean norm can be introduced and so on.

6.4. Non-linear solver

The linear solver can often provide estimates close to the final assemblage of the system and in certain circumstances, such as for systems with only pure stoichiometric species, it might be able to predict the equilibrium assemblage. However, almost always, further computations are required to arrive at the final assemblage especially in cases where the phases have more than one species with significant contribution to the Gibbs energy. This situation arises more often than not and a non-linear solver is required to handle the non-linearities arising from the logarithmic term in the compositional component of the chemical potentials.

For the sake of completeness of the argument, the conditions for equilibrium are restated below:

1. The mass balance constraint must be satisfied.
2. The Gibbs' phase rule must be satisfied.
3. The integral Gibbs energy must be at a global minimum.

The following subsidiary conditions arise from the constraints

- A. The number of moles of any species must be positive.
- B. The sum of mole fractions must be one (inherent in the Gibbs energy method).

6.4.1. Numerical implementation

The system of non-linear equations can be solved using the Newton-Raphson method. Newton-Raphson method depends on solving equation (??) and is an $O(N^3)$ operation where N is the size of the system. An integral component of the solver is an appropriate line-search algorithm to determine how far the system should progress along the direction vectors. The functional norm of the Lagrangian is an effective choice to ensure convergence and is defined as [6]:

$$\|f\|^2 = \sum_{j=1}^C \left(\sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \nu_{ij} + \sum_{\omega=1}^{\Omega} n_{\omega} \nu_{\omega,j} - b_j \right)^2 + \sum_{\lambda=1}^{\Lambda} \left(\sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \left| \mu_{i(\lambda)} - \sum_{j=1}^C \nu_{ij} \Gamma_j \right| \right)^2 + \sum_{\omega=1}^{\Omega} \left(g_{\omega} - \sum_{j=1}^C \nu_{\omega,j} \Gamma_j \right)^2 \quad (6.8)$$

where the first term on the right represents the mass balance residuals, the second represents the absolute sum of chemical potential residuals of solution species and the third represents the

chemical potential residuals of stoichiometric phases. By enforcing the Wolfe/Armijo condition [58], a sufficient step length is decided.

Each iteration step in the minimisation problem involves approximately solving the subproblem:

$$\min_{\alpha} f(\mathbf{x}^m + \alpha \mathbf{p}^m) \quad (6.9)$$

where \mathbf{x}^m is the best estimate at iteration m , \mathbf{p}^m denotes the search direction vector and α represents the step size.

The Wolfe conditions are a set of inequalities for performing inexact line search and provide an efficient way of computing an acceptable step length α that reduces the objective function sufficiently, rather than minimising the objective function over $\alpha \in \mathbb{R}^+$ exactly.

A step length α^m is said to satisfy the Wolfe conditions, restricted to the direction \mathbf{p}^m , if the following two inequalities hold:

$$f(\mathbf{x}^m + \alpha^m \mathbf{p}^m) \leq f(\mathbf{x}^m) + c_1 \alpha^m (\mathbf{p}^m)^T \nabla f(\mathbf{x}^m) \quad (6.10)$$

$$-(\mathbf{p}^m)^T \nabla f(\mathbf{x}^m + \alpha^m \mathbf{p}^m) \leq -c_2 (\mathbf{p}^m)^T \nabla f(\mathbf{x}^m) \quad (6.11)$$

with $0 < c_1 < c_2 < 1$. The first inequality, known as the Armijo condition ensures that the step length α^m decreases f sufficiently, and the second inequality known as the curvature condition ensures that the slope has been reduced sufficiently. Together, the two inequalities provide upper and lower bounds for the step lengths [58].

Yellowjacket–GEM uses the state-of-the-art non-linear solvers in PETSc to solve the non-linear system. The SNESNEWTONLS is a Newton based nonlinear solver that uses line search and has been used as the default solver in this work.

6.4.2. Adding/Removing phases

Updating the estimated assemblage plays a significant role in the convergence of thermodynamic solvers. Inadequate strategies for updating the assemblage might lead to inefficient global iterations (i.e., iterations in which changes are made to the system such as addition/removal of phases while the Newton iterations described above can be referred to as local iteration since they are aimed at finding the minimum of a problem with a fixed system) and might even prevent convergence. Though the number of phases that can be added into or removed from the system is constrained by the Gibbs' phase rule, proper care must be taken to ensure that any change to the system drives it towards convergence and not hold it back. To ensure that the phase assemblage updating does not result in undesired behaviour, the strategy proposed

by Piro [6] has been adopted. This strategy has been illustrated in figure 6.5.

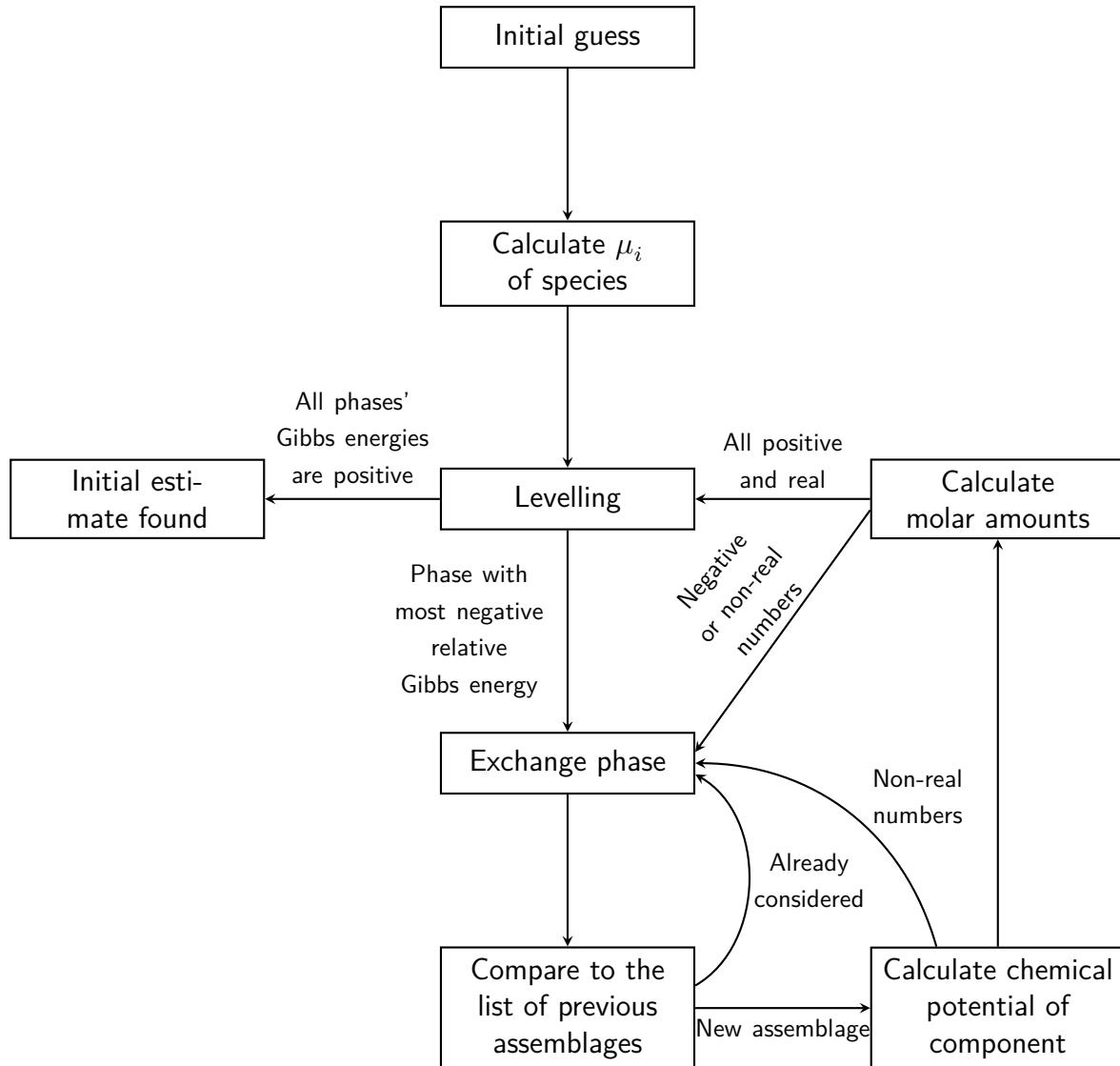


Figure 6.3: Levelling algorithm for finding the initial estimate of stable phase assemblage. After Loukusa [99].

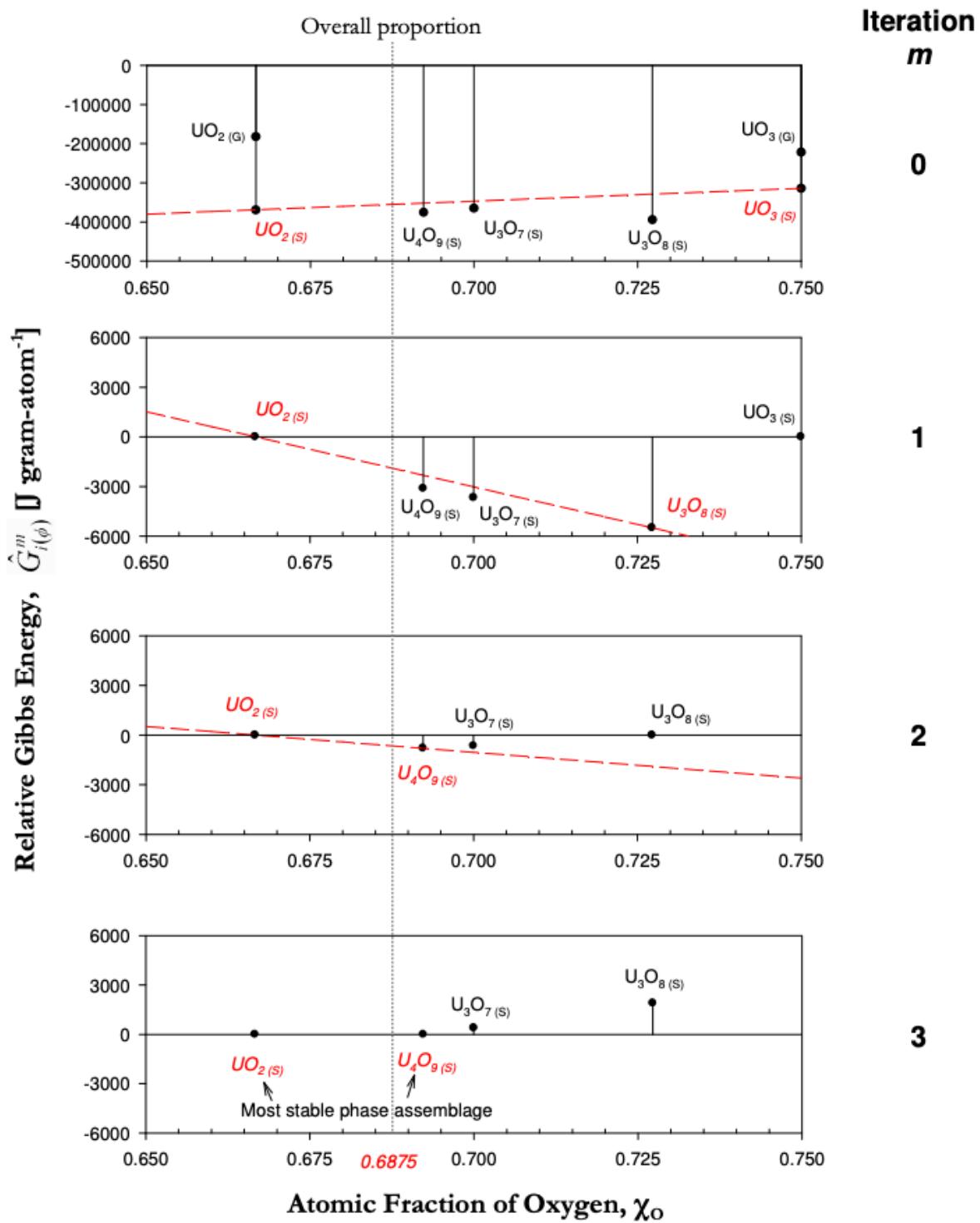


Figure 6.4: Illustration of the levelling process for a binary system of U–O at each iteration (1 mol U, 2.2 mol O, 298.15 K, 1 atm) [5].

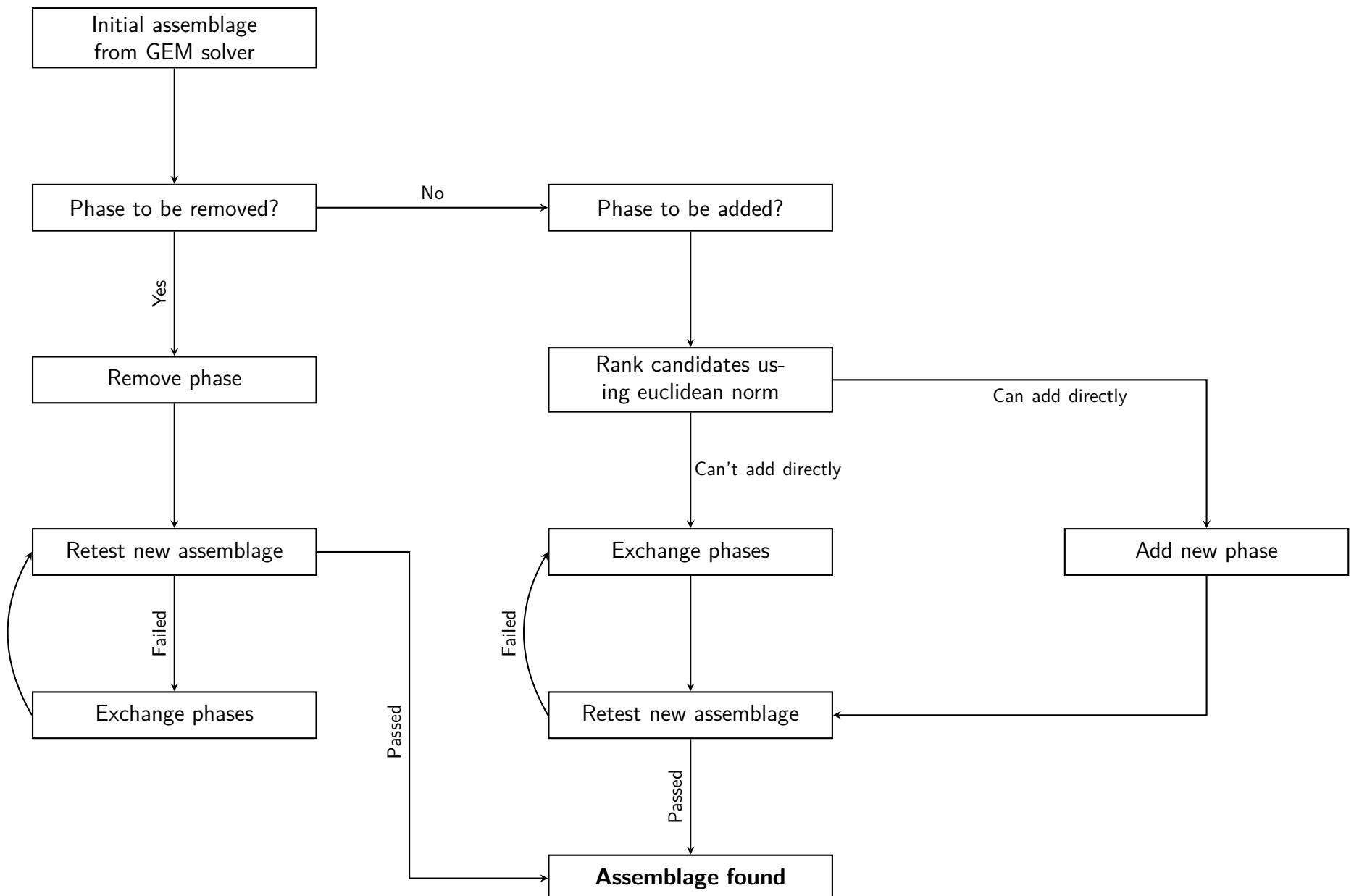


Figure 6.5: Illustration of the methodology for updating the phase assemblage. Adapted from Piro [6].

6.4.3. Convergence criterion

The convergence of the solver is tested in accordance with conditions for convergence described in chapter ???. The relative error of the mass balance and Gibbs' criterion is calculated and the solver converges when both of these are within the specified tolerance. In addition, it must be tested that the mole numbers are not negative for any species in the system. The charge neutrality constraint must also be respected. To minimise the computational cost, it is also possible to test convergence only when the functional norm has been satisfied to a specified tolerance.

Two issues that can prevent convergence were foreseen for a thermodynamic equilibrium solver. First, when the objective function has multiple roots, for example due to miscibility gap, and second when the slope of the objective function is extremely small or zero. These two issues can result in non-real numbers or divergence and possible failure of the iterative solver. The numerical dampening through Wolfe/Armijo conditions and the use of levelling as an initialisation method helps in avoiding the ill-behaviour and promotes numerical stability and enhances performance characteristics. The proposed algorithm of the thermodynamic solver with both local and global iterations has been presented in figure 6.6

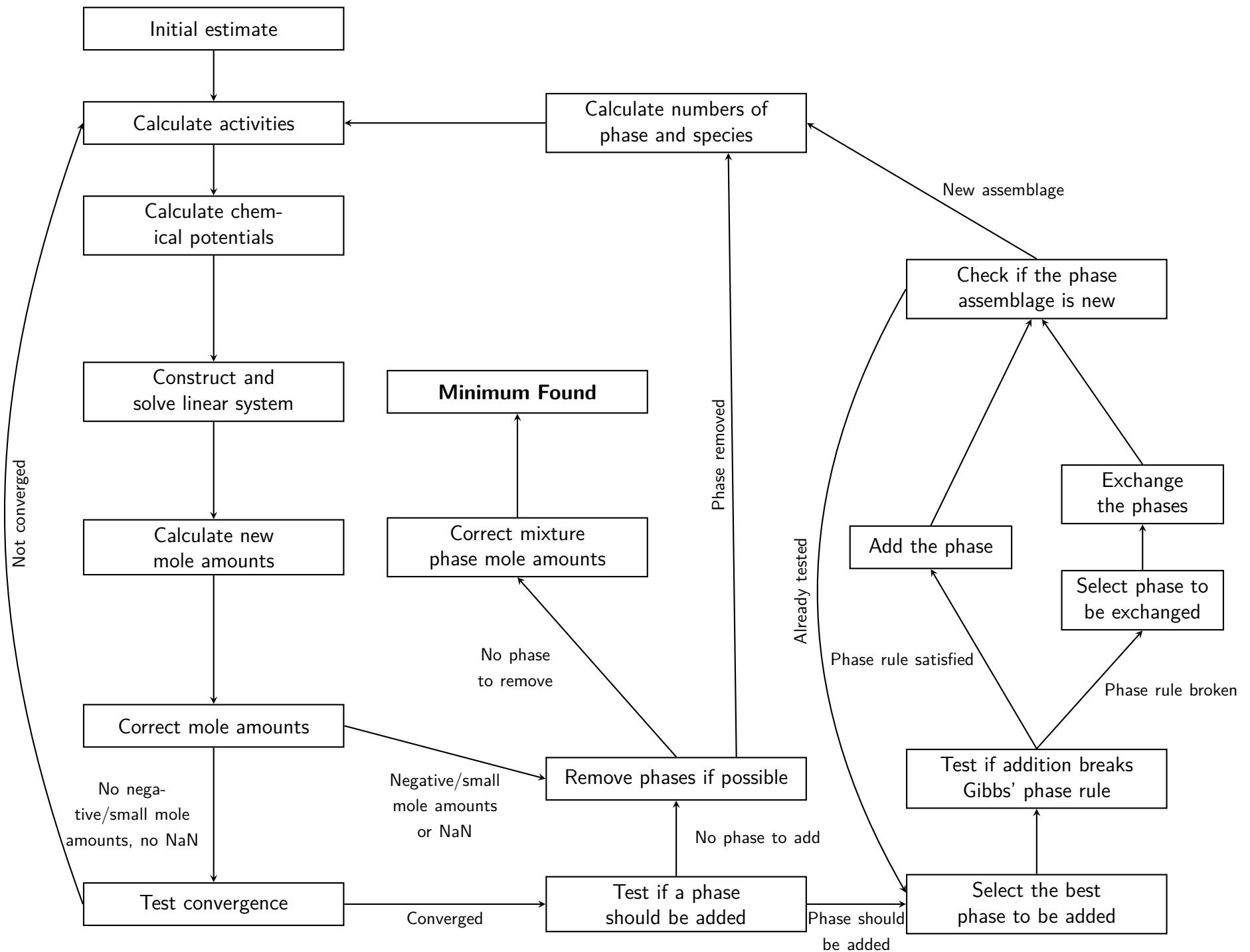


Figure 6.6: Illustration of the Gibbs energy minimisation algorithm. After Loukusa [99].

6.4.4. Interpreting the results

Though the developed algorithms are relatively very robust, there are certain classes of problems where the rank-deficiency in the stoichiometric matrices is inherent. In such cases, special care must be taken in interpreting the results computed by thermodynamic equilibrium codes. The author of this thesis co-authored a letter to the editor of Journal of Nuclear Materials explaining how one must be careful in interpreting the chemical potentials for molten salts systems. The letter by Piro et al.



On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts

Keywords:
 Molten salt
 MSR
 Modified quasi-chemical model
 Thermodynamic

In an earlier Letter to the Editor of the Journal of Nuclear Materials (JNM) [1], situations were explored whereby the chemical potentials computed by an equilibrium thermodynamics code could potentially be misleading. The intent of that letter was to acknowledge specific situations that may unintentionally lead to the misinterpretation of results that may be well understood by a specialist, but may perhaps be less obvious to a non-specialist. A closely related situation may also arise from the results produced by thermodynamic calculations involving the Modified Quasi-chemical Model (MQM), which is a sophisticated model often used to represent molten salts. With the increasing interest in Molten Salt Reactor (MSR) research [2], particularly with thermodynamic modelling and related multi-physics simulations, it seems prudent to have a follow-up discussion regarding the interpretation of chemical potentials computed by equilibrium thermodynamic codes in the context of molten salts. This Letter to the Editor of JNM is intended to better inform the user of such thermodynamic software using models specific to molten salts who may be a non-specialist. Furthermore, these matters may be of important interest when integrating thermodynamic calculations in multi-physics codes to prevent numerical instabilities.

In one particular scenario explored by Piro et al. [1], the fictive A-B system was considered with 2 mol of A and 3 mol of B. For this specific situation, only the A_2B_3 phase is stable at equilibrium. As shown in Fig. 1, the system is homogeneous and the lowest common tangent line (representing the equilibrium state, also called the "Gibbs Plane" [3]) is tangent to this phase; however, the line is not uniquely defined. This is shown graphically in Fig. 1, whereby a line cannot be uniquely defined by a single point. The tangent line could conceivably be drawn between A_2B_3 and either $B_{(s)}$ or α (with zero moles); however, there is no basis for selecting zero moles of one phase or the other.

For this particular scenario, the system is under-determined when the system components¹ are taken as A and B. One may be under the false impression that the chemical potentials of A and B have been determined, whereas these are in fact undefined due to the misidentification of the system components – for this particular situation, the system components A and B should be re-defined to a single system component: A_2B_3 . As the International Union of Pure and Applied Chemistry defines the term 'component': "The number of components in a given system is the minimum number of independent species necessary to define the composition in all the phases of a system" [4]. Since the minimum number of species required to define this system is one (i.e., A_2B_3), the system components should be re-defined from A and B to A_2B_3 for this particular scenario.

Due to the mathematical nature of the MQM model, one can easily misinterpret calculated chemical potentials of some components for similar reasons. The MQM class of models, which has been advanced primarily by Pelton et al. [5–8], has been used with great success to model various fluoride [9–12] and chloride salts [9,13] for nuclear applications. This model is currently implemented in FACTSAGE [14] and THERMOCHIMICA [15]. The fundamental premise of this model is to shift focus from the interaction of species to the interaction of pairs of species (or quadruplets) in an effort to capture short range ordering. For example, if one has a solution model comprised of species C and D, then one would be concerned with interactions of C-C, D-D, and C-D pairs. Equilibrium calculations are centred on the chemical potentials of the pairs (or quadruplets) rather than the species.² Furthermore, the model involves two sub-lattices, which do not include vacancies; therefore, every phase component (or 'compound end member') is necessarily a compound and not a pure element. The importance of this feature of the model is that the representation of the phase in composition space is limited by the compounds – not the elements – and will be further explained in the following paragraphs.

One can model a familiar material of interest to the MSR community, LiF–BeF₂ (aka. "FLiBe"), with MQM. The model produced by Beneš and Konings [16] assigns the species as LiF and BeF₂, which produces the following pairs: LiF–LiF, BeF₂–BeF₂, and LiF–BeF₂. A thermodynamic database of the Li–Be–F system may include other phases in addition to this molten salt, such as various stoichiometric solid phases and an ideal gas mixture. Some of these non-salt species may not necessarily correspond to LiF or BeF₂.

¹ The terms 'phase component' and 'system component' are used here to differentiate a component of a phase (synonymous with 'species' or 'compound end member') from a component of a system, which may be a pure element, a compound, or electron (corresponding to an ionic phase).

² Note that internal to a Gibbs energy minimizer, the number of moles of the pairs are used as independent variables rather than those of the species. This is an important point to enable effective execution of equilibrium calculations, as explained by Pelton et al. [5].

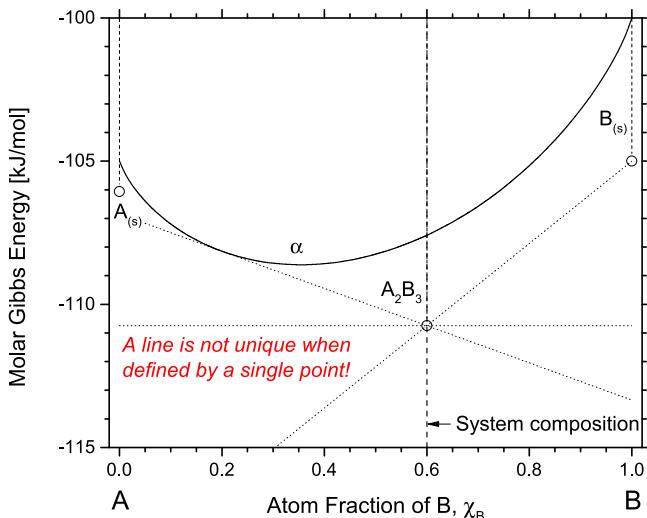


Fig. 1. The fictive A-B system is shown with the overall composition identified, which intersects the A_2B_3 phase. The lowest common tangent line intersects this phase, but is not uniquely defined. Copied from Piro et al. [1].

which may include the pure elements (e.g., $F_{2(g)}$).

Suppose one were to define the system components by the chemical elements (i.e., Li, Be, and F) while assigning mass quantities to the system that precisely correspond to LiF and BeF_2 , and a specified temperature and pressure that together yield a homogeneous system with only a molten salt being stable. This would be a typical calculation using an equilibrium solver. The composition space of this system is illustrated in Fig. 2. In this situation, there are three phase components (i.e., LiF-LiF , $\text{BeF}_2-\text{BeF}_2$, and LiF-BeF_2) and three system components (i.e., Li, Be, and F); however, one cannot uniquely define the Gibbs Plane because the three points are co-linear in three dimensional space. In more mathematical terms, the Hessian matrix is rank deficient.

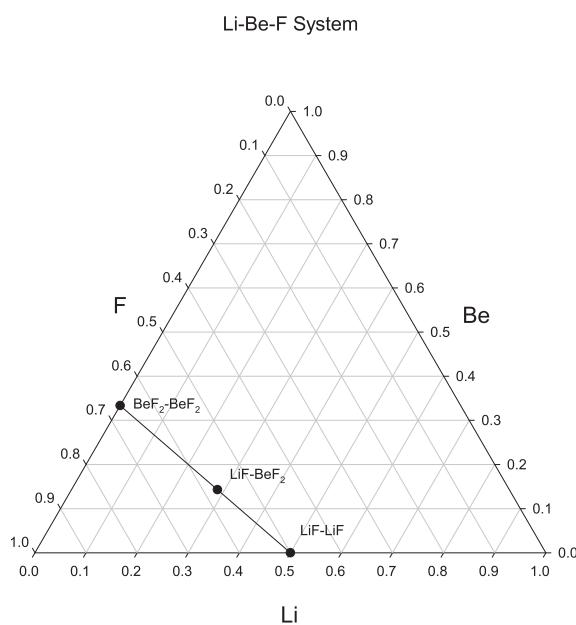


Fig. 2. A ternary plot of the Li-Be-F system with the three pair fractions corresponding to LiF-BeF_2 are indicated. A three dimensional Gibbs plane cannot be defined by three points because they are colinear.

Since the Gibbs Plane is used to define all chemical potentials in the system and it is not uniquely defined for this scenario, not all chemical potentials in the system are uniquely defined. The only uniquely defined chemical potentials in this system lie on the LiF-BeF_2 line and anything outside from that is not unique. Of particular interest to the MSR community, the fluorine potential – and the corresponding thermochemical activity of fluorine – is not uniquely defined for this situation. This scenario is analogous to the one shown in Fig. 1, whereby one could potentially compute a fluorine potential, but it would not be uniquely defined. The issue here is that the user may receive from the software a numerical value of the chemical potential or thermochemical activity of fluorine that is meaningless and misleading. A more mathematically rigorous proof is provided in the Appendix, which shows that the Hessian matrix used in Gibbs energy minimization is under-determined for this situation. It may be possible to still computationally solve the Hessian, but that would only be possible due to very minor machine imprecisions.

Note that one would have a uniquely defined system for this situation if the system components were instead defined as LiF and BeF_2 . Alternatively, one could also have a uniquely defined system if there was a slight surplus or deficit of one of the chemical elements, which would effectively shift the system off the line shown in Fig. 2. In that situation, conservation of mass would require another phase to be stable in addition to the salt. Graphically, one could interpret that situation as a three-dimensional Gibbs plane defined by three points that are co-linear (corresponding to the salt, akin to Fig. 2) in addition to some additional point(s) (representing a secondary phase).

To summarize, the MQM model has been effectively used to capture the thermodynamic behaviour of various salts for MSR applications. To avoid potentially misinterpreting calculated chemical potentials and other thermodynamic quantities, which may be non-unique, recommendations are made to the user to be conscientious of the appropriateness of selecting the system components. If the overall system composition can be defined by a reduced set of compounds that do not correspond directly to the chemical elements, then the user should define them as such. While these matters may be familiar and clear to a thermodynamics specialist, the intent of this letter is to assist non-specialists in interpreting and executing such calculations, particularly those involved with MSR research.

Acknowledgements

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Appendix

Mathematically, Gibbs energy minimization is a constrained non-convex optimization problem with the objective of determining a unique combination of system potentials that yields a minimum in Gibbs energy of the system while satisfying mass balance constraints and the Gibbs phase rule under isothermal isobaric conditions. The objective is often achieved using the method of Lagrange multipliers that simultaneously minimizes the integral Gibbs energy and the residuals of mass balance equations. This results in a system of linearized equations that can be written in matrix form as [17]:

$$\mathbf{H} \cdot \boldsymbol{\pi} = \boldsymbol{\zeta} \quad (1)$$

where $\boldsymbol{\pi}$ and $\boldsymbol{\zeta}$ denote the unknown and constraint vectors respectively, and the Hessian matrix (\mathbf{H}) can be written as [17,18]:

$$\mathbf{H} = \begin{bmatrix} r_{j=1,k=1} & \dots & r_{j=1,k=C} & \phi_{j=1,\lambda=1} & \dots & \phi_{j=1,\lambda=\Lambda} & v_{j=1,\omega=1} & \dots & v_{j=1,\omega=\Omega} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ r_{j=C,k=1} & \dots & r_{j=C,k=C} & \phi_{j=C,\lambda=1} & \dots & \phi_{j=C,\lambda=\Lambda} & v_{j=C,\omega=1} & \dots & v_{j=C,\omega=\Omega} \\ \phi_{\lambda=1,j=1} & \dots & \phi_{\lambda=1,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \phi_{\lambda=\Lambda,j=1} & \dots & \phi_{\lambda=\Lambda,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ v_{\omega=1,j=1} & \dots & v_{\omega=1,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ v_{\omega=\Omega,j=1} & \dots & v_{\omega=\Omega,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \end{bmatrix} \quad (2)$$

where C is the number of system components, λ is an index of a solution phase, of which there are Λ in the system, ω is an index of a stoichiometric phase, of which there are Ω in the system, $v_{i,j}$ is the stoichiometric coefficient of component j in species i , and $r_{j,k}$ and $\phi_{j,\lambda}$ can be expressed as follows:

$$r_{j,k} = \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)} v_{i,j} v_{i,k}, \quad (3)$$

$$\phi_{j,\lambda} = \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)} v_{i,j}. \quad (4)$$

N_{λ} is the number of species in phase λ , and $n_{i(\lambda)}$ is the number of moles of species i in solution phase λ . Clearly, $r_{j,k} = r_{k,j}$ and $\phi_{j,\lambda} = \phi_{\lambda,j}$, which yields a symmetric matrix for \mathbf{H} .

The example of the FLIBe system discussed above is used to illustrate the under-determined nature of the Hessian matrix with improperly chosen system components. Consider a homogeneous system in which the only phase present is a solution phase represented by the MQM model. Suppose the system composition falls somewhere along the $\text{BeF}_2 - \text{LiF}$ composition line illustrated in Fig. 2, and thus the phase components are LiF-LiF , $\text{BeF}_2-\text{BeF}_2$, and LiF-BeF_2 , and the system components are Li, Be, and F. For this case $C = 3$, $\Lambda = 1$, $N_1 = 3$, and $\Omega = 0$. This results in a 4×4 Hessian matrix as follows:

$$\mathbf{H} = \begin{bmatrix} r_{1,1} & r_{1,2} & r_{1,3} & \phi_{1,1} \\ r_{1,2} & r_{2,2} & r_{2,3} & \phi_{2,1} \\ r_{1,3} & r_{2,3} & r_{3,3} & \phi_{3,1} \\ \phi_{1,1} & \phi_{2,1} & \phi_{3,1} & 0 \end{bmatrix}. \quad (5)$$

The stoichiometry matrix ν is:

$$\nu = \begin{bmatrix} 2 & 0 & 2 \\ 0 & 2 & 4 \\ 1 & 1 & 3 \end{bmatrix}. \quad (6)$$

where the rows represent LiF-LiF , $\text{BeF}_2-\text{BeF}_2$, and LiF-BeF_2 , and the columns represent Li, Be, and F. Taking the current estimate of the number of moles of each species to be the arbitrary values n_1 , n_2 , and n_3 , \mathbf{H} is then:

$$\mathbf{H} = \begin{bmatrix} 4n_1 + n_3 & n_3 & 4n_1 + 3n_3 & 2n_1 + n_3 \\ n_3 & 4n_2 + n_3 & 8n_2 + 3n_3 & 2n_2 + n_3 \\ 4n_1 + 3n_3 & 8n_2 + 3n_3 & 4n_1 + 16n_2 + 9n_3 & 2n_1 + 4n_2 + 3n_3 \\ 2n_1 + n_3 & 2n_2 + n_3 & 2n_1 + 4n_2 + 3n_3 & 0 \end{bmatrix}. \quad (7)$$

This Hessian is rank-deficient, with the first three columns

linearly dependent, and thus has a determinant of 0. Therefore, any attempt to solve the corresponding system of linear equations will fail. Note that in practice it is possible that the system of equations can be solved with a sufficient numerical error associated with machine precision, which will yield some mathematically meaningless results. In this case, one must rely heavily on the quality and robustness of the linear equation solver employed.

If one were to instead take the system components as LiF and BeF_2 , C is reduced to 2, and the Hessian is of the 3×3 form:

$$\mathbf{H} = \begin{bmatrix} r_{1,1} & r_{1,2} & \phi_{1,1} \\ r_{1,2} & r_{2,2} & \phi_{2,1} \\ \phi_{1,1} & \phi_{2,1} & 0 \end{bmatrix}. \quad (8)$$

In this case, the stoichiometry matrix is:

$$\nu = \begin{bmatrix} 2 & 0 \\ 0 & 2 \\ 1 & 1 \end{bmatrix}. \quad (9)$$

where the rows represent LiF-LiF , $\text{BeF}_2-\text{BeF}_2$, and LiF-BeF_2 , and the columns LiF and BeF_2 . The Hessian is then:

$$\mathbf{H} = \begin{bmatrix} 4n_1 + n_3 & n_3 & 2n_1 + n_3 \\ n_3 & 4n_2 + n_3 & 2n_2 + n_3 \\ 2n_1 + n_3 & 2n_2 + n_3 & 0 \end{bmatrix}. \quad (10)$$

This matrix is non-singular, and its determinant is:

$$\text{Det}(\mathbf{H}) = -4(n_1 + n_2 + n_3)(4n_1 n_2 + n_1 n_3 + n_2 n_3). \quad (11)$$

This determinant is always non-zero, as the values n_1 , n_2 , and n_3 must all be greater than zero and real. This example illustrates how an under-determined system of equations representing a phase represented in MQM form can be converted to a full-rank system by reducing the number of system components to a more appropriate form.

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6.5. Global Optimisation

As described in section 5.4, computing the minimum driving force of a thermodynamic system requires solving a non-convex constrained optimisation problem. The conditions for thermodynamic equilibrium discussed in section 5.2 require that the chemical potentials of all the species must lie on or above the Gibbs plane, which passes through the element potentials Γ_j . Thus metastable phases must lie above the Gibbs plane and the difference between the Gibbs plane and the plane tangent to a metastable phase is referred to as the *driving force* [19] or *tangent plane distance function* [19, 118]. The driving force for phase ϕ is represented by ΔG_ϕ and is computed as [4]:

$$\Delta G_\phi = \min_{\lambda} \sum_{i=1}^{N_\lambda} x_i \left(\mu_i - \sum_{j=1}^C \nu_{ij} \Gamma_j \right), \quad (6.12)$$

which is subject to conservation of mass and the following linear equality and inequality constraints:

$$\sum_{i=1}^{N_\phi} x_i = 1, \quad x_i > 0, \quad \forall i \in \phi. \quad (6.13)$$

The sufficient condition for equilibrium requires that the driving force ΔG_ϕ computed with equation (6.12) is positive for all phases believed to be metastable and zero for all the stable phases. According to Hillert [165], the driving force of metastable phases can be evaluated at each iteration to determine whether or not it should be added into the system. However, this function can be non-convex and requires the evaluation of a global minimum. Though the open literature on computing these methods appears rather exhaustive, few authors have discussed generalised global minimisation schemes for the phase equilibria problem. The majority of articles focus either on relatively small systems, such as liquid-vapour equilibria, or are aimed at only a handful of calculations. Some notable exceptions to this include those of Hillert [162], Lukas et al.[166], Sundman [128], Piro and Simunovic [4], and Otis et al. [129]. Since both the robustness and computational efficiency of Yellowjacket–GEM are of concern, a number of global optimisation methods were tested through a set of carefully constructed test problems representative of some common scenarios in equilibrium thermodynamics. Though no global optimisation method can guarantee the ability to find the true global minimum, sufficient confidence can be achieved for the problem under consideration under well-defined parameters.

6.5.1. Test Problems

To objectively test the reliability and performance of various global optimisation algorithms, the methods must be benchmarked against a set of test problems representative of the requirements from the solver. While most of the open literature focusses on a single problem and tries to optimise the algorithm for the problem, such an approach is not ideal for the development of Yellowjacket–GEM. Instead the focus here has been to select an algorithm that can work reasonably well for wide variety of problems with a large number of components. The reasoning behind such an approach is that a wide variety of excess mixing models are encountered in computational thermodynamics applied to nuclear materials. To test the algorithms under consideration, eight test cases representing different thermodynamic models and system sizes, and are summarised in table 6.1.

Table 6.1: Summary of test cases used for comparing global optimisation algorithms.

Label	Size	Problem Description
A	2	Fictive binary system with a miscibility gap and a stoichiometric phase from Piro and Simunovic [4].
B	2	Pd–Rh binary system with a shallow FCC miscibility gap phase from Kaye <i>et al.</i> [167].
C	2	Fictive binary system with three convex phases with one phase having a negative driving force from Piro and Simunovic [4].
D	3	Pu–U–O ternary system from Guéneau <i>et al.</i> [168] containing an ideal gas phase, a non-ideal liquid phase, many stoichiometric phases and a $(\text{U}_y \text{Pu}_{1-y})\text{O}_{2\pm x}$ fluorite phase. Involves a multi-sublattice model and a charge balance constraint.
E	3	Al–Cr–Co ternary system used as reference problem by Otis <i>et al.</i> [129].
F	5	Hexagonal closed packing (HCP) phase in the quinary system containing noble metal fission products Mo–Pd–Tc–Ru–Rh from Kaye <i>et al.</i> [167].
G	10	Fictive high-dimensional systems with minefield of miscibility gaps based on Piro and Simunovic [4].
H	30	Piro and Simunovic [4].

1. Problem A

A fictive binary A–B system based on Piro and Simunovic [4] has been considered as the first test problem. As shown previously in section 5.4, it consists of solution phase α and a stoichiometric phase A_3B_2 which can possibly coexist and while the stoichiometric phase A_3B_2 and solution phase α are initially predicted to be stable, as represented by the dashed tangent line in figure 6.7, they are in fact metastable and a miscibility gap would yield a lower value of the integral Gibbs energy of the system, G_{sys} . The α phase

is represented by a substitutional solution model with the reference Gibbs energies of the components being $g_A^\circ = -100 \text{ J mol}^{-1}$, $g_B^\circ = -300 \text{ J mol}^{-1}$ and the excess energy given by $g_\alpha^{\text{ex}} = 21000x_Ax_B + 7000x_Ax_B^2$. The temperature of the system was fixed at $T = 1000 \text{ K}$ and the pressure at $P = 1 \text{ atm}$.

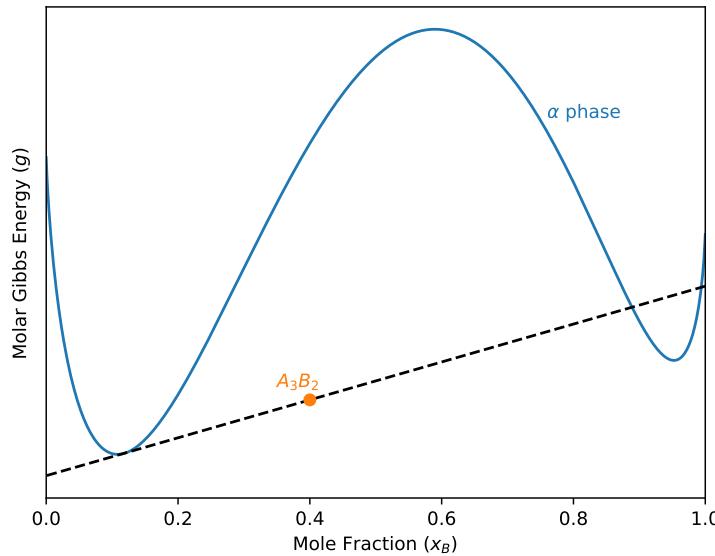


Figure 6.7: Fictive system with miscibility gap showing a possible false positive from thermodynamic equilibrium solver.

2. Problem B

The binary Pd–Rh system from Kaye et al. [167] has been selected as the second test problem. It consists of a shallow miscibility gap in the FCC phase which is assumed to be properly identified by the solver but the global optimisation algorithm must confirm that the driving force, ΔG_{FCC} , of the miscibility gap phase is indeed zero. The phase is represented by a substitutional solution model with the reference Gibbs energies of the components being $g_{\text{Pd}}^\circ = -16480 + 9.02T \text{ J mol}^{-1}$, $g_{\text{Rh}}^\circ = -26568 + 11.88T \text{ J mol}^{-1}$ and the excess energy given by $g_{\text{FCC}}^{\text{ex}} = x_{\text{Pd}}x_{\text{Rh}}(21247 + 2199x_{\text{Rh}} - (2.74 - 0.56x_{\text{Rh}})T)$. The temperature of the system was fixed at $T = 1100 \text{ K}$ and the pressure at $P = 1 \text{ atm}$.

3. Problem C

Another fictive binary system, from Piro and Simunovic [4], with components C–D can have three possible solution phases, the δ phase as shown in figure 6.9. At temperature $T = 1100 \text{ K}$, pressure $P = 1 \text{ atm}$ and composition $x_{\text{D}} = 0.6$, the δ phase is believed to be metastable but one must confirm that the combination of β and γ is most stable

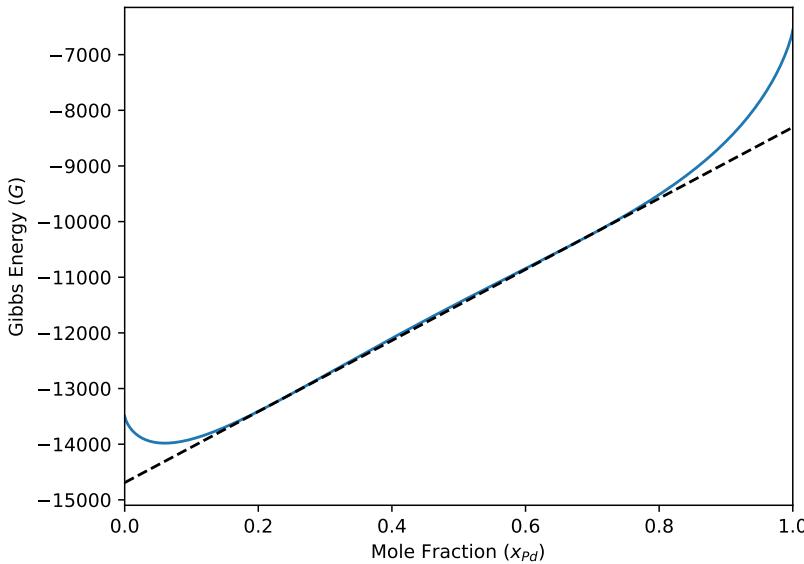


Figure 6.8: FCC phase miscibility gap in Pd–Rh binary system from Kaye et al. [167] shows a correctly identified miscibility gap which must be verified by the global optimisation algorithm.

or if a different combination is more stable. However, it can be seen that inserting the δ phase into the system and replacing one of the other two phases would yield a lower value of the integral Gibbs energy of the system, G_{sys}° . For this system, $g_{\text{C}(\beta)}^{\circ} = 0 \text{ J mol}^{-1}$, $g_{\text{D}(\beta)}^{\circ} = 12471 \text{ J mol}^{-1}$, $g_{\text{C}(\gamma)}^{\circ} = 16628 \text{ J mol}^{-1}$, $g_{\text{D}(\gamma)}^{\circ} = 4157 \text{ J mol}^{-1}$, $g_{\text{C}(\delta)}^{\circ} = 26604 \text{ J mol}^{-1}$ and $g_{\text{D}(\delta)}^{\circ} = 33256 \text{ J mol}^{-1}$. The molar Gibbs energies of mixing are $g_{\beta}^{\text{ex}} = 41570x_{\text{C}}x_{\text{D}} - 58198x_{\text{C}}x_{\text{D}}^2$, $g_{\gamma}^{\text{ex}} = -5238x_{\text{C}}x_{\text{D}}$ and $g_{\delta}^{\text{ex}} = -59445x_{\text{C}}x_{\text{D}} - 74826x_{\text{C}}x_{\text{D}}^2$.

4. Problem D

Mixed oxide fuel (MOX) is a nuclear fuel which is manufactured by mixing plutonium recovered from used reactor fuel with depleted uranium and the Pu–U–O ternary system from Guéneau et al. [168] has been selected as a test problem. The thermodynamic assessment of the system contains an ideal gas, a non-ideal liquid, and a $(\text{U}_y \text{Pu}_{1-y})\text{O}_{2\pm x}$ fluorite phase modelled using CEF with three sublattices and is an ionic phases where the first sublattice contains actinoid cations and the second and third sublattices contain oxygen anions mixing with vacancies. The global optimisation algorithm must respect the charge neutrality constraint thus distinguishing this problem from others. The system composition, as in [4], is 0.93 mol of U, 0.07 mol of Pu and 2 mol of O maintained at temperature $T = 1000 \text{ K}$ and hydrostatic pressure $P = 1 \text{ atm}$. The global optimisation algorithm must verify that the $(\text{U}_y \text{Pu}_{1-y})\text{O}_{2\pm x}$ fluorite phase is only stable phase at equilibrium.

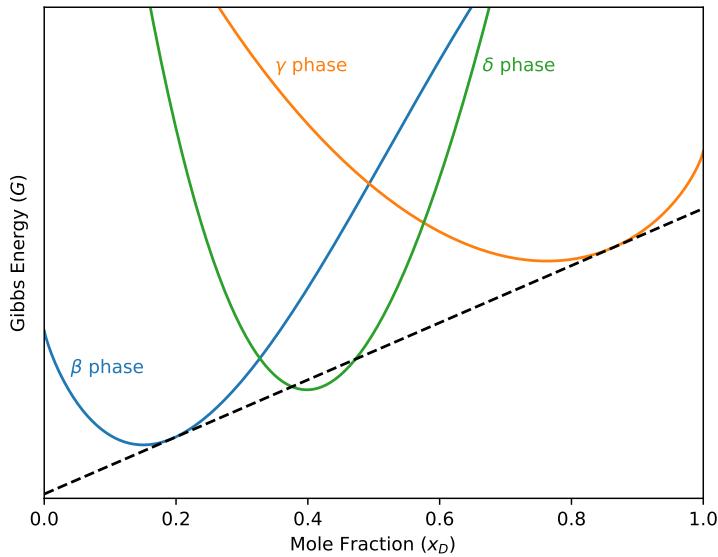


Figure 6.9: Fictive system with three phases showing a false positive from thermodynamic equilibrium solver wherein a wrong phase is believed to be present at equilibrium.

5. Problem E

Otis et al. [129] demonstrated that for the Al–Co–Cr ternary system modelled by Liu et al. [169] poses a challenge to thermodynamic equilibrium codes. In particular, it was shown that at temperature $T = 1523$ K, a ternary miscibility gap can be ignored when considering the metastable BCC phase only. The phase was modelled with a three-sublattice CEF model with the elements mixing on the first and second sublattices. Considering the challenges posed by the BCC phase in the system, the system was selected as a test problem with the system containing 0.5 mol of Al, 0.2 mol of Co and 0.3 mol of Cr at $T = 1000$ K and $P = 1$ atm. The global optimisation algorithm must identify the existence of a miscibility gap.

6. Problem F

The quinary Mo–Pd–Tc–Ru–Rh system from Kaye et al. [167] is considered as the sixth test problem for comparing global optimisation algorithms. The system is relevant to nuclear reactor accident simulations as the components are noble metal fission products and their behaviour is critical to source term analyses. The system includes ideal gas, non-ideal liquid and four solid solution phases with face centred cubic (FCC), body centred cubic (BCC), hexagonal closed packed (HCP) and tetragonal crystal structures in addition to several stoichiometric phases. The liquid and solid solution phases were all modelled using substitutional solution models and, as in [4], the system contains 1 mol of each component and is maintained at a temperature $T = 1000$ K and hydrostatic pressure

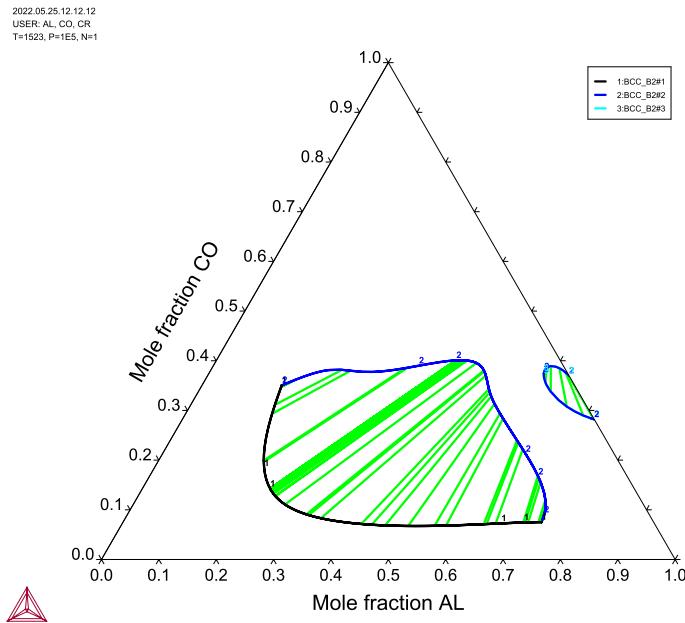


Figure 6.10: Al–Co–Cr phase diagram calculated with Thermo-Calc version 2018b with an increased point density. With only BCC phase enabled, the existence of the miscibility gaps is shown in the central portion but as shown by Otis et al. [129], the miscibility gap is lost using the default Thermo-Calc parameters.

$P = 1$ atm. Examining the HCP phase only, the HCP– $\text{Mo}_9\text{Pd}_{11}$ phase combination is assumed to be stable and the global optimisation algorithms must identify the presence of a miscibility gap which yields a lower integral Gibbs energy of the system. The stable phase assemblage should be HCP–HCP miscibility gap co-existing with $\text{Mo}_9\text{Pd}_{11}$.

7. Problems G & H

The cases until now considered relatively simpler and smaller systems which are easily visualisable and verifiable but a true representation of nuclear materials must consider a large number of system components. The last two test problems have been designed to test the global optimisation methods for a very large number of species. The fictive phases constructed for the high-dimensional tests are modelled using a three-sublattice CEF model with the first sublattice consisting of a large number of cations and the other two sublattices consisting of two anionic constituents mixing together. This results in two problems with 100 end members and 400 end members and is representative of irradiated molten salts. The fictive phases were constructed following the methodology of Piro and Simunovic [4]. The phases were assumed to have 10 and 30 components with 1–4 constituents per component. The cations were assigned a charge of +2 or +3 and the anions were assigned a charge of -1 (halides) or 0 (vacancy). The reference molar Gibbs energy of each end member was $g_i^\circ = \mathcal{U}(200, 450)$ kJ mol⁻¹. As in [4],

excess mixing parameters were created such that one cation would mix with the following cation in the list of constituents on the first sublattice with a mixing parameters ${}^0L = \mathcal{U}(-100000, 100000)$ and ${}^1L = \mathcal{U}(-1000, 1000)$.

6.5.2. Grid Sampling

Sampling from a equispaced grid has been widely adopted in thermodynamic equilibrium codes as a strategy for testing equilibria by performing numerous evaluations of the objective function at regular intervals in the domain [82, 128, 170–172]. The method was developed in the 1970s and 1980s as a brute force method to verify global minimum for phase diagram construction problems and does not scale well for large systems. As shown in figure 6.11, in the grid construction method, the surface of ΔG_ϕ is discretised with each point treated as a stoichiometric compound and the ensemble of these compounds collectively approximates the driving force surface [4]. In the example figure, the arbitrary binary system consists of a solution phase and a stoichiometric phase and the domain for the solution phase has been sampled at nine equispaced grid points.

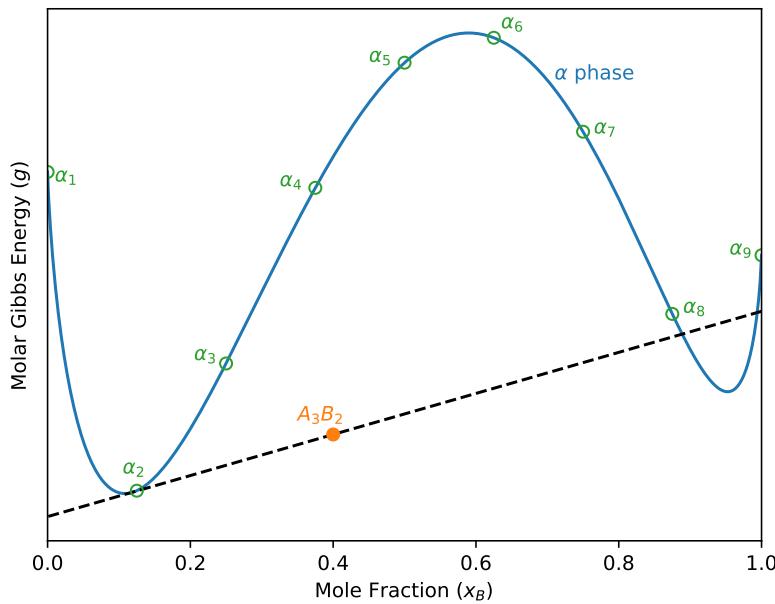


Figure 6.11: Demonstration of the grid construction method for fictive binary system in test problem A. The domain has been sampled at nine equispaced grid points and the pure stoichiometric phase A_3B_2 is found to be in equilibrium with the solution phase giving a false positive.

The discretisation of the grid plays a key role in the efficacy of this method and it has been shown by Chen et al. [172] that the grid must be sufficiently resolved to avoid missing critical features such as the minimum between grid points α_8 and α_9 in figure 6.11. However,

this requirement leads to performance concerns as too small a grid leads to an increase in the computational cost while too large a grid can lead to false positives in the optimisation process. Piro and Simunovic [4] have demonstrated how uniformly spaced grid for a phase ϕ in N_ϕ dimensional Euclidean phase (each dimension corresponds to a species in phase ϕ) can result in an enormously large number of grid points depending on the grid size. In the example with nine grid points, it becomes clear from figure 6.11 that global minimum would not be found but increasing the number of grid points will lead to an exponential increase in the cost. In conclusion, the rapid increase in the computational cost with the reduction in grid size and a questionable performance in terms of reaching a global maximum tilts the scales against this method. Despite the fact, this method was tested with three separate grid spacings ($\delta = 0.1, 0.01, \text{ and } 0.001$) to serve as benchmarks and to numerically show the rapid increase in computational time.

6.5.3. Spatial branch & bound (sBB)

The Branch and Bound (BB or B&B), attributed to Land and Doig [173] who introduced it in 1960 for discrete programming, is a widely used algorithmic paradigm for finding optimal solutions to optimisation problems. As illustrated in 6.12, the algorithm systematically enumerates all the candidate solutions by sequentially pruning out non-feasible solution candidates through a recursive approach of partitioning the domain and finding an upper and a lower bound for each subdomain. In 1969, Falk and Soland [174] proposed one of the first BB algorithms that could be applied to an continuous objective function with separable concave portions with a closed and convex set of constraints and a bounded feasibility region. The BB algorithm involves two procedures to solve global optimisation problems:

1. *Branching*: The domain S is partitioned into two or more smaller disjoint domains S_1, S_2, \dots , such that $S = S_1 \cup S_2 \cup \dots$. Thus, the partitioned objective function can be considered a convex approximation of the objective function within the subdomain S_i .
2. *Bounding*: The upper and lower bound of the objective function are found within a subset of the domain S . In the classical Branch and Bound method, a subdomain can be removed from the analysis if the lower bound of the objective function in it is greater than the upper bound of the objective function in any other subdomain.

McDonald and Floudas [175] applied the BB algorithm to solve thermochemical equilibrium problems and Piro and Simunovic [4] proposed a modified version of the classical BB for the thermochemistry library ThermoChimica which uses a different initialisation procedure and relaxation scheme for the bounds. Furthermore, instead of relying on pruning, every subdomain

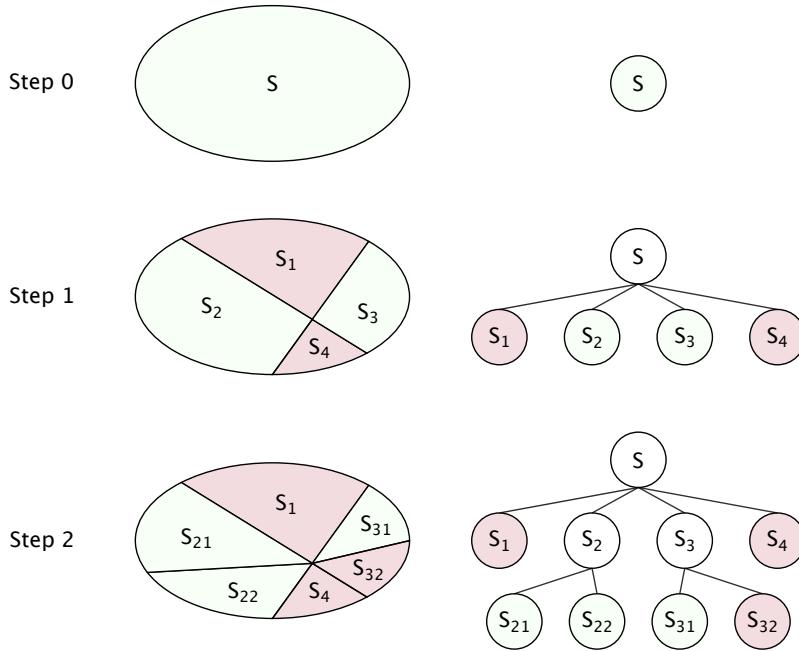


Figure 6.12: Illustration of the Branch and Bound (BB) class of algorithms. At each step, the domain is partitioned into a set of unexplored subdomains (denoted as nodes in a dynamic tree) which represent potential regions of optimal solution. By estimating the upper and lower bound on each subdomain, regions of infeasibility can be eliminated.

is evaluated till stopping criteria are met and if necessary, recursive partitioning technique is applied. The approach adopted by Piro and Simunovic [4] partitions the domain for each phase ϕ into N_ϕ subdomains and the driving force ΔG_ϕ given by equation (5.56) is minimised in each subdomain. Their approach results in a Hessian which can be represented as a symmetric arrow matrix and by exploiting the structure of this matrix, the combination of x_i that minimises ΔG_ϕ can be easily determined. To solve the matrix, Gaussian elimination can be performed on the just the bottom row followed by back substitution. Furthermore, instead of storing a Hessian, the diagonal vector and a scalar representing the far right column can be stored. However, the implementation of this method warrants the use of an appropriate line search algorithm to ensure that the Wolfe conditions are satisfied and that the local system stays within the feasible region $0 < x_i < 1$. In addition, the step length must be suitably constrained to avoid missing any local minimums [4]. While the method works reasonably well, there are situations where it fails to correctly identify the true global minimum.

One of the best known method for solving non-convex nonlinear programming (NLP) problems is the *spatial Branch and Bound* (*sBB*) [176, 177]. The branching, as already mentioned, is done by taking a continuous variable $v_i \in [v_i^l, v_i^u]$ and choosing β ($v_i^l \leq \beta \leq v_i^u$) to create two subproblems with domains $[v_i^l, \beta]$ and $[\beta, v_i^u]$. When solving either subproblem, the original

lower and upper bounds can be replaced by tighter bounds by taking the advantage of the reduced domain. This process, from McCormick [178], is called *spatial branching*. In this work, a *Symbolic Reformulation sBB* [176, 179, 180] has been used through the Couenne (Convex Over and Under ENvelopes for Nonlinear Estimation) open-source software [181, 182]. Couenne has been developed to solve global optimisation problems (**P**) of the form [181]:

$$\begin{aligned} \min \quad & f(x) \\ \text{s.t.} \quad & g_j(x) \leq 0 \quad \forall j \in M \\ & x_i^l \leq x_i \leq x_i^u \quad \forall i \in N_0 \\ & x_i \in \mathbb{Z} \quad \forall i \in N_i^0 \subseteq N_0, \end{aligned} \tag{6.14}$$

where $f : \mathbb{R}^n \rightarrow \mathbb{R}$ and, $\forall j \in M$, $g_j : \mathbb{R}^n \rightarrow \mathbb{R}$ are multivariate functions, $n = |N_0|$ is the number of variables, and $x = (x_i)_{i \in N_0}$ is the n-vector variables. In the context of equilibrium thermodynamics, the problem in the form conformant to the above equation is as follows:

$$\begin{aligned} \min \Delta G_\phi(x_i) = & \sum_{i=0}^{N_\phi} \left(\tilde{\mu}_i - \sum_{j=1}^C \nu_{ij} \tilde{\Gamma}_j \right) \\ \text{s.t.} \quad & \sum_{i=1}^{N_\phi} x_i = 1 \quad \forall i \in N_\phi \\ & \sum_{i=1}^{N_\phi} \nu_{ie^-} x_i = 0 \quad \forall i \in N_\phi \\ & 0 \leq x_i \leq 1 \quad \forall i \in N_\phi. \end{aligned} \tag{6.15}$$

Couenne implements linearisation, branching, heuristics and bound reduction and reformulates the problem by introducing a set of auxiliary variables. The reformulation of problem represented by equation (6.14) results in the following form (**P'**) [181]:

$$\begin{aligned} \min \quad & x_{n+q} \\ \text{s.t.} \quad & x_i = \vartheta_i(x) \quad \forall i \in \{n+1, n+2, \dots, n+q\} \\ & x_i^l \leq x_i \leq x_i^u \quad \forall i \in N \\ & x_i \in \mathbb{Z} \quad \forall i \in N_i \subseteq N, \end{aligned} \tag{6.16}$$

where $N = \{1, 2, \dots, n+q\}$ is the new variable index set which is a union of the original index set $\{1, 2, \dots, n\}$ and the auxiliary index set $\{n+1, n+2, \dots, n+q\}$. N_i denotes the index set of integer variables and the value of the last auxiliary variable, x_{n+q} , is the value of the

objective function.

sBB algorithms rely on the generation of rigorous lower and upper bounds for the objective function value over any given variable subdomain. Generation of a upper bound is relatively simple as any feasible point of problem (P) serves as an upper bound to the function at global minimum. In practice, it is best to chose the local minimiser of equation (6.14) as the upper bound. When the reformulated problem (P') is in factorable form, the feature can be used to derive valid bounds and exact solution or one can use linear and quadratic approximations of f and g_j . Detailed descriptions of sBB algorithms are found in literature [180, 183] and the specifics to implementation in Couenne are described in [181] but the method, illustrated in algorithm 1, is briefly described here.

1. Reformulation

A general method for allowing the formation of convex relaxation for any continuous twice differentiable function was given in [184–186] and a tighter relaxation framework was developed by Smith and Pantelides [180]. The goal of reformulation is to construct an equivalent formulation (P') to problem (P) such that it contains only linear constraints and special non-linear definitions. Since convex relations of many transcendental functions (such as logarithms, exponentials, etc.) exist and most algebraic expressions, including the ones encountered in equilibrium thermodynamics, are made up of binary operations of arithmetic and the unary operators, it is possible to construct convex relaxations of any algebraic expression. For doing this, additional variables can be introduced in the problem. For example, in test problem A, the non-linear terms in the excess mixing part can be reformulated as a linear problem by introducing variables $w_1 = x_A x_B$ and $w_2 = x_A x_B^2$. Such a process can be generalised and automated using the standard binary tree representation of algebraic expressions [176]. The reformulated problem (P') is equivalent to the original problem (P) but all the non-linearities are described by sets corresponding to bilinear product, linear fractional, simple exponentiation and univariate function terms. Because the two problems are equivalent, a convex relaxation of (P') is also a valid relaxation of (P). Hence, reformulation allows constructing a convex relaxation of any problem and the sBB determined optimal solution of (P') is also the optimal solution to (P).

2. Linearisation

If one considers the constraint $x_j = \vartheta_j(x)$ created during reformulation and set $B = [x^l, x^u]$ defining bounds on the variables, a ϑ_j -linearisation is a system of linear inequalities $A^j x \geq b^j$ such that $X_{LP} := x \in B : A^j x \geq b^j \supseteq x \in B : x_j = \vartheta_j(x)$. If a ϑ_j -

Algorithm 1: sBB algorithm for the MINLP problem (\mathbf{P}) [181]**Input:** Problem (\mathbf{P})

```

Define set  $L$  of subproblems,  $L \leftarrow \{\mathbf{P}\}$ ;
Define upper bound  $z^u$  for  $\mathbf{P}$ ,  $z^u \leftarrow \infty$ ;
while  $L \neq \emptyset$  do
    Choose  $\mathbf{P}_k \in L$ ;
     $L \leftarrow L \setminus \{\mathbf{P}_k\}$ ;
    Apply bound tightening to  $\mathbf{P}_k$ ; /* Bound tightening */
    if  $\mathbf{P}_k$  is feasible after bound tightening then
        Generate a linear relaxation  $\mathbf{LP}_k$  of  $\mathbf{P}_k$ ; /* Linearisation */
        repeat
            | Solve  $\mathbf{LP}_k$  to get an optimum  $\bar{x}^k$  with objective value  $\bar{z}^k$ ;
            | Refine linearisation  $\mathbf{LP}_k$ ;
        until  $\bar{x}^k$  is feasible for  $\mathbf{P}_k$  or  $\bar{z}^k$  does not improve;
        if  $\bar{x}^k$  is feasible for  $\mathbf{P}_k$  then
            |  $z^u \leftarrow \min\{z^u, \bar{z}^k\}$ ;
        end
        Find a local optimum  $\hat{z}^k$  of  $\mathbf{P}_k$ ; /* Upper bound calculation */
         $z^u \leftarrow \min\{z^u, \hat{z}^k\}$ ;
        if  $\bar{z}^k \leq z^u - \epsilon$  then
            | Choose a variable  $x_i$ ; /* Branching variable selection */
            | Choose a branching point  $x_i^b$ ; /* Branching point selection */
            | Create subproblems:
            |    $\mathbf{P}_{k-}$  with  $x_i \leq x_i^b$ ,
            |    $\mathbf{P}_{k+}$  with  $x_i \geq x_i^b$ ;
            |    $L \leftarrow L \cup \{\mathbf{P}_{k-}, \mathbf{P}_{k+}\}$ ;
        end
    end
end

```

Output: $z_{\text{out}} \leftarrow z^u$, an optimal solution of (\mathbf{P})

linearisation is created for each constraint x_j , a linear problem $\mathbf{LP}_k := \min x_{n+q} : Ax \geq b$ is a linear relaxation of \mathbf{P}_k where \mathbf{P}_k is a root node of \mathbf{P} obtained through branching. The optimal solution \bar{x} of \mathbf{LP}_k provides a lower bound for the problem. If the solution of \mathbf{LP}_k becomes infeasible for \mathbf{P}_k , the lower bound can be improved by either branching or refinement of \mathbf{LP}_k , i.e. by amending linearisation inequalities [181]. Couenne uses a variant of the projection error rule for refinement [181].

3. *Bound tightening*

According to Smith and Pantelides [180], sBB can achieve convergence without any

bound tightening but the rate of convergence can be improved by using it. The goal of bound tightening is to reduce the interval $[x_i^l, x_i^u]$ without causing the optimal value of the problem to change and it allows reduction of the feasible set and an improved linearisation. One way of propagating the effects of constraints to variable bounds in optimality-based bounds tightening (OBBT) [176, 183, 187] but faster-feasibility bounds tightening (FBBT) are also available albeit resulting in weaker bounds [176, 183, 188, 189]. In OBBT, two convex optimisation problems are solved:

$$x_i^l = \min_x x_i, \quad \text{subject to convex relaxation constraints,} \quad x^l \leq x \leq x^u, \quad (6.17)$$

$$x_i^u = \max_x x_i, \quad \text{subject to convex relaxation constraints,} \quad x^l \leq x \leq x^u. \quad (6.18)$$

OBBT can be applied to every variable x_i separately and when feasible the convex relaxation constraints can be updated but at each iteration it will solve $2N$ optimisation problems making it extremely expensive and suitable only for initial bound tightening steps [180]. FBBT, on the other hand, considers each constraint of the reformulated problem individually [188]. At any sBB node k , if the local minimum $\hat{x}^k \in [x^l, x^u]$ of the convex relaxed problem \mathbf{CP}_k is known, FBBT is applied to fictitious bounding box $B \cap x \in \mathbb{R}^{n+q} : x_i \leq \tilde{x}_i$, where $\tilde{x}_i \in (x_i^l, \hat{x}_i^k)$ is suitably chosen. If the resulting problem become infeasible or if its lower bound becomes larger than the best upper bound, then $[\tilde{x}_i^k, x_i^u]$ is a valid tightening . On the other hand, if $\tilde{x}_i \in (\hat{x}_i^k, x_i^u)$ is chosen and FBBT applied to the analogous bounding box results in infeasibility, then $[x_i^l, \tilde{x}_i^k]$ is valid.

4. Branching

Branching is critical to the performance of sBB and an effective strategy can help minimise the size of the sBB tree. The goal of branching is to choose a branch variable and corresponding branch point to be used to partition the domain. In doing so, the goal must be to improve the lower bound of the resulting subproblems and to eliminate as large an infeasible region as possible. In doing so, one must also try to keep the sBB balanced and together the three requirements are often conflicting and the implementations can be optimised to emphasise on one aspect or the other. Branching may be required when the lower bound \bar{x}_{n+q}^k of an sBB node \mathbf{P}_k is smaller than the best known feasible solution and the relaxation \mathbf{LP}_k cannot be further refined. To objectively select the branching variable and point, Belotti et al. [181] define the ϑ_i -infeasibility of auxiliary variable x_i at node k as $U_i(\bar{x}^k) = |\bar{x}_i^k - \vartheta_i(\bar{x}^k)| / (1 + \|\nabla \vartheta_i(\bar{x}^k)\|_2)$. The scaling of the error term in numerator with the norm of the gradient avoids selecting a variable x_i with a small bound interval $[x_i^l, x_i^u]$ but with a large $|\bar{x}_i^k - \vartheta_i(\bar{x}^k)|$ as it is unlikely to improve linearisation

if used for branching.

(a) Branching variable selection

In Couenne, integer variables have higher priority than continuous variable but since the driving force function results in a strictly NLP problem, continuous variables become the only candidate for branching. Defining the *dependence set*, $D(x_i)$, as the set of variables in $\vartheta_i(x)$ (these are the variables in x that x_i directly depends on), the infeasibility of variable x_i can be propagated to $D(x_i)$. In Couenne, Belotti et al. [181] define the non-linear infeasibility as:

$$\Omega_i^N(\bar{x}^k) = \mu_1 \sum_{j \in E(i)} U_j(\bar{x}^k) + \mu_2 \max_{j \in E(i)} U_j(\bar{x}^k) + \mu_3 \min_{j \in E(i)} U_j(\bar{x}^k),$$

where for variable x_i , the set $E(i) = j \in N : x_i \in D(x_j)$. Parameter $\mu_k \geq 0$, $k = 1, 2, 3$ ¹ and $\mu_1 + \mu_2 > 0$ ensures that \bar{x}^k is infeasible if and only if $\Omega_i^N(\bar{x}^k) > 0$ for at least one variable x_i . In Couenne $(\mu_1, \mu_2, \mu_3) = (0.1, 1.3, 0.8)$ [181]. The strategy, however, can often be ineffective and Couenne also has implementations of *Violation Transfer* proposed by Tawarmalani and Sahinidis [190] and an extension of the *reliability branching* technique introduced by Achterberg et al. [191]. In violation transfer, violations of non-convexities by the current solution are assigned to problem variables followed by transfer of violations to $D(x_i)$. The violations are then weighted to account for branching priorities and potential for convex relaxation improvement. The variable that leads to the maximum weighted violation is selected as the branching variable [190]. Since, the reliability branching strategy was not used in Yellowjacket–GEM, a discussion of it is omitted and can be found in [182].

(b) Branching point selection

For a continuous variable x_i appearing in a single expression $x_j = \vartheta_j(x_i)$, the goal of sBB is to keep the resulting tree balanced. This makes areas of the linearisations a reasonable metric for selecting the branching point as shown in figure 6.13. In Couenne, three branching point selection strategies are implemented.

In the *LP-based strategy*, the branching point is set so that \bar{x}^k can become infeasible in both the subproblems. While simple to implement, as shown in subfigure (a) of figure 6.13, it can result in unbalanced subproblems. To avoid this, for variable $x_i \in [x_i^l, x_i^u]$, the branching point can be set as a convex combination of \bar{x}_i^k and the midpoint of bound interval, $x_i^m = (x_i^l + x_i^u)/2$ (see subfigure (b) of figure 6.13).

¹Parameters μ_k defined here have no correlation to the chemical potential μ_i .

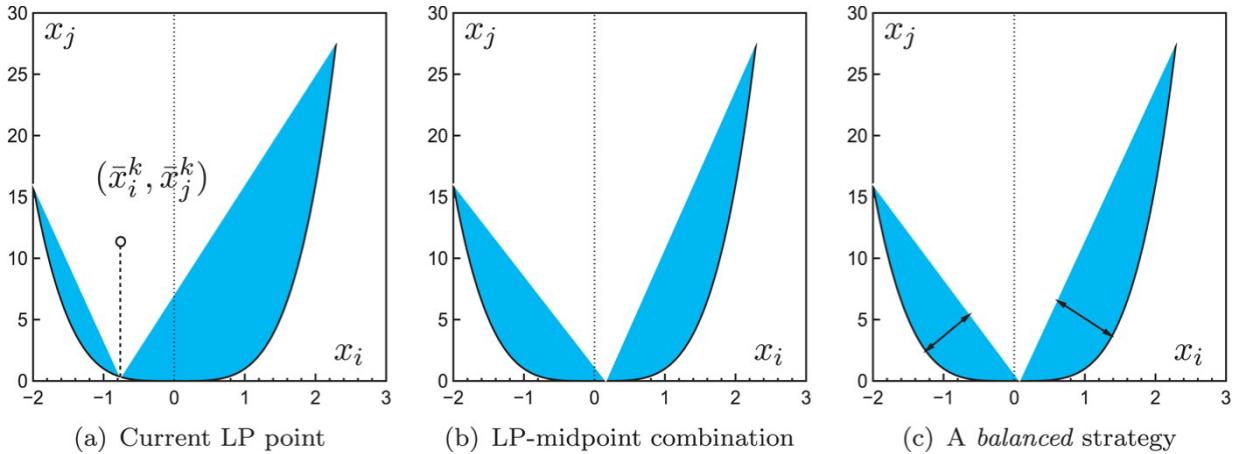


Figure 6.13: Strategies for selecting a branching point as implemented in Couenne: (a) branching on current LP solution \bar{x}_i^k , (b) Convex combination of LP point \bar{x}_i^k and midpoint of bound interval, (c) Balancing the areas of the two resulting linearisations. Figure from Belotti et al. [181].

Hence, a selection strategy guaranteeing a minimum distance from variable bounds is as follows [177]:

$$x_i^b = \max \{x_i^l + b, \min \{x_i^u - b, \alpha \bar{x}_i^k + (1 - \alpha) x_i^m\}\},$$

where $0 < \alpha < 1$ and $b = \beta(x_i^u - x_i^l)$ for $0 < \beta < 0.5$ and α and β are set to 0.25 and 0.2 respectively [181] and the strategy tries to balance the half-intervals of x_i . Alternatively, if a local minimum \hat{x}^k is known, \hat{x}_i^k can be chosen as a branching point since the resulting convexification will return a solution \bar{x}^k that is very close to \hat{x}^k [188].

In *expression-based strategies*, one can aim to reduce the sum of the areas of the resulting convexifications as shown in subfigure (c) of figure 6.13. Several methods for such strategy can be adopted [192, 193] but a balanced strategy implemented in Couenne finds the branching point using a binary search on the interval $[x_i^l, x_i^u]$ that minimises the difference between the maximum area $u'(x_i)$ and maximum area $u''(x_i)$ [181]:

$$x_i^b \in \arg \min \left| \max_{x_i \in [x_i^l, x_i^u]} u'(x_i) - \max_{x_i \in [x_i^l, x_i^u]} u''(x_i) \right|,$$

where u' and u'' are the distance between the upper envelope line of ϑ_j and $(x_i, \vartheta_j(x_i))$ on the subdomains LP' and LP'' resulting from branching. The method balances the maximum distance between the points on $\vartheta_j(\cdot)$ and the upper envelope

[182].

Together, the reformulation of the problem and the sBB algorithm result in a rigorous solution framework for global optimisation problem. Since the driving force functions are smooth and differentiable, they are well formulated for the method. Though the reformulation results in an increase in the size of the problem, it doesn't become a major issue for determining the minimum of the driving force.

6.5.4. Particle swarm optimisation

Particle swarm optimisation (PSO) is a stochastic search algorithm inspired by the flocking behaviour of birds. First proposed by Kennedy and Eberhart [194, 195], PSO is a population based method which relies on the premise of social sharing of information among a bird flock seeking food. PSO is relatively simple to describe and implement and its apparent competence in finding optimal solutions in complex search spaces has made it a widely studied search algorithm [196]. In PSO, a population of candidate solutions, dubbed particles, moves around the search space as a function of the position and velocity of the particle and the movement of each particle is influenced by its best known local position and guided towards the best global position as other particles find better solutions.

At each iteration t , the velocity vector of particle i in the swarm gets updated according to the following equation [197]:

$$\mathbf{v}_i^{t+1} = \omega \mathbf{v}_i^t + \psi_1 R_{1i}^t (\mathbf{p}_i^t - \mathbf{x}_i^t) + \psi_2 R_{2i}^t (\mathbf{g}^t - \mathbf{x}_i^t), \quad (6.19)$$

where \mathbf{v}_i^t and \mathbf{x}_i^t are the velocity and position at iteration t . The inertia weight is given by ω and ψ_1 and ψ_2 are real acceleration coefficients known as cognitive weight and inertia weight respectively. Together, the weights control the impact of global and individual best positions on the particle's velocity and trajectory. Kennedy and Eberhart [195] originally assigned the same value of 2 to social and cognition parts but fine-tuning the parameters is critical to performance and convergence of PSO, particularly when dealing with multimodal problems [198–200]. R_1 and R_2 are uniformly distributed vectors used to maintain an adequate level of diversity in the swarm population and \mathbf{p}_i^t and \mathbf{g}^t represent the best known position of particle i and the global best position of the swarm at iteration t . In turn, the position of each particle i at every iteration t can be updated according to the following equation [197]:

$$\mathbf{x}_i^{t+1} = \mathbf{x}_i^t + \mathbf{v}_i^t. \quad (6.20)$$

Algorithm 2: PSO algorithm for objective function $f : \mathbb{R}^n \rightarrow \mathbb{R}$

Input: Objective function f , Search space $\mathbf{x}_i = [\mathbf{x}_i^l, \mathbf{x}_i^u]$, Number of particles N_p

```

for Particle  $i \in \{1, 2, \dots, N_p\}$  do
    Initialise initial position,  $\mathbf{x}_i \leftarrow \mathcal{U}(\mathbf{x}_i^l, \mathbf{x}_i^u)$ ;
    Initialise particle's best known position,  $\mathbf{p}_i \leftarrow \mathbf{x}_i$ ;
    if  $f(\mathbf{p}_i) < f(\mathbf{g})$  then
        | Update global best position,  $\mathbf{g}_i \leftarrow \mathbf{p}_i$ ;
    end
    Initialise the particle velocity,  $\mathbf{v}_i \leftarrow \mathcal{U}(-|\mathbf{x}_i^u - \mathbf{x}_i^l|, |\mathbf{x}_i^u - \mathbf{x}_i^l|)$ ;
end

while Termination criteria is not met do
    for Particle  $i \in \{1, 2, \dots, N_p\}$  do
        Pick random vectors,  $\mathbf{R}_1, \mathbf{R}_2 \leftarrow \mathcal{U}(0, 1)^n$ ;
        Update particle velocity,  $\mathbf{v}_i^{t+1} \leftarrow \omega \mathbf{v}_i^t + \psi_i R_{1i}^t (\mathbf{p}_i^t - \mathbf{x}_i^t) + \psi_i R_{2i}^t (\mathbf{g}^t - \mathbf{x}_i^t)$ ;
        Update particle position,  $\mathbf{x}_i^{t+1} = \mathbf{x}_i^t + \mathbf{v}_i^t$ ;
        if  $f(\mathbf{x}_i^{t+1}) < f(\mathbf{p}_i)$  then
            | Update particle's best known position,  $\mathbf{p}_i^t \leftarrow \mathbf{x}_i^{t+1}$ ;
            if  $f(\mathbf{p}_i^t) < f(\mathbf{g})$  then
                | Update global best position,  $\mathbf{g}^t \leftarrow \mathbf{p}_i^t$ ;
            end
        end
    end
end

```

Output: $x_{\text{out}} \leftarrow \mathbf{g}^t$, an optimal solution of f

The PSO algorithm, illustrated algorithm 2, has several advantages compared to other continuous optimisation methods. First, PSO is a problem independent algorithm which only needs the objective function to evaluate the fitness of each candidate solution. In doing so, PSO does not make any assumptions about the continuity and differentiability of the objective function. Second, the evolution of particles is random and therefore the gradients of the objective function need not be calculated. Lastly, PSO does not need a good initial estimate or a-priori knowledge of the objective function search space [196]. These factors have led PSO to gain a widespread appeal and it has shown good performance in several domains like function optimisation, artificial neural network training, fuzzy system control, etc. Unfortunately, for complex multimodal problems, the conventional PSO algorithm can get trapped in local optima, considerably compromising the convergence rate. This leads to poor performance and accuracy, and imposes restrictions on applicability to a wide range of practical problems [201, 202]. While a-priori tuning can help improve performance, it is a time-intensive process but also

assume that the optimal parameter configuration does not change over time. However, as shown by Leonard and Engelbrecht [203], the parameter values well-suited for exploration are not well-suited for exploitation and vice-versa. To achieve the two fold characteristic of good convergence speed and to avoid stagnating in local optima, several variations of PSO have been developed [204–208]. Another limitation of PSO is in constrained optimisation problem as it lacks an explicit constraint-handling mechanism. Several methods such as penalty function, feasibility-based rules method and the constraint-preserving method have been proposed with the penalty method being the most commonly used [209, 210]. While detailed discussions on handling these problems are available in open literature, the specific approach in the context of this work is discussed in the following text.

1. Constraint handling

As previously stated, several strategies have been explored to impose the constraints in PSO. One of the simplest constraint-handling mechanism is that of resetting the particles that escape the feasible region [211–213]. Minimisation of a non-stationary multi-stage assignment penalty function was proposed by Parsopoulos and Vrahatis [214] and the results were promising albeit at the cost of a very complex process for determining penalty. In the feasibility-based approaches such as that by Pulido and Coello [215], a candidate solution is chosen leader based on Deb's comparison rules [216]. The constraint handling strategy implemented in Yellowjacket–GEM is based on the method by Hu and Eberhart et al. [211]. To make the solution more plausible, all the equality constraints are modified into inequality constraints to specified tolerance, i.e., the constraints on sum of mole fractions and the charge neutrality constraints are reformulated as:

$$\left| \sum_{i=1}^{N_\phi} x_i - 1 \right| < \epsilon_1, \quad (6.21)$$

$$\left| \sum_{i=1}^{N_\phi} \nu_{ie^-} x_i \right| < \epsilon_2. \quad (6.22)$$

The initialisation step is then modified to impose the constraints and once a feasible initial solution is found, the algorithm can progress. At every iteration t , each particle is checked for feasibility. If the updated position x_i^{t+1} results in the bounds being violated, the step length is updated based on the following equation:

$$\mathbf{x}_i^{t+1} = \mathbf{x}_i^t + \alpha \mathbf{v}_i^t, \quad (6.23)$$

where $\alpha \in \mathcal{U}(0.1, 0.9)$ is a randomly generated constriction vector used to scale the step length. Handling the constraints, however is less straightforward. Once the position of each particle has been updated, the feasibility of each particle is verified and if it is found to violate the feasibility condition, Deb's comparison rules [216] are applied as follows:

- (a) If all candidate solutions are infeasible, the candidate closest to feasibility is selected as the best candidate and the remaining particles are restored to previous feasible position. The best known position of these particles is not changed.
- (b) If some candidates are feasible, their personal best is updated and the global best solution is selected from the feasible particles. The particles in infeasible regions are restored to the previous feasible solution.
- (c) If all candidates are feasible, the same process as usual is followed.

2. Particle initialisation

One of the parameters in PSO that can potentially affect the convergence rate is the number of particles and their initial positions. While the particle position x_i is often initialised randomly from a uniform sampling in $[x_i^l, x_i^u]$, it has been shown by Woronow [217] that, when compared to normalised exponential distribution, normalised uniform distributions produce a poorer coverage of composition space. Otis et al. [129] employed a set of different sampling strategies such as Halton sequence, Sobol sequence and their variations to come up with an efficient sampling strategy for PyCalphad. Furthermore, Piro and Simunovic [4] found that PSO often fails to capture the optimal solutions located close to the domain edges and special considerations must be taken when the optimal solution may exist close to the boundaries. To best see the effect of particles' initial position on the performance of PSO, a number of different options were tested. First, the number of particles, N_p , was selected from a finite set $\{N_\phi, 2N_\phi\}$ and second, the particles were initialised using both normalised uniform and normalised exponential sampling. In addition, when $N_p = 2N_\phi$, a hybrid strategy was also used where N_ϕ particles were initialised using the sampling methods while the remaining N_ϕ particles were fixed at the corners of the domain. The reasoning behind this approach is that the particles closer to the edges should enable the spare closer to the edges to be properly explored. Also, more advanced sampling methods were not selected as, with well-tuned hyperparameters, PSO is expected to efficiently scan the domain unlike when only sampling is used and one must make sure that the features are not missed if the samples are not well picked.

3. Particle dynamics

Parameter tuning can have a significant impact on the performance of PSO and a large number of *Adaptive PSO* (APSO) algorithms have been proposed in literature to overcome the problem of a-priori tuning of the parameters. A comparative analysis of many such algorithms has been performed by Harrison et al. [202]. Amongst one of the promising APSO algorithms is *APSO based on velocity information* (APSO-VI) proposed by Xu [201] which adapts the inertia weight based on the current velocity of the particles. The concept of APSO-VI is borrowed from Yasuda et al. [218] and aims to evolve the velocity to be close to an *ideal* velocity. In APSO-VI the average velocity of swarm is defined as [201]:

$$\bar{v}^t = \frac{1}{nN_p} \sum_{i=1}^{N_p} \sum_{j=1}^n |v_{ij}^t|, \quad (6.24)$$

where n and N_p represent the problem dimension and the number of particles in the swarm respectively. The size of the average velocity reflects the size of the particle search space and to better explore the search space, one should maintain a larger average velocity with longer time, during the early stage of the optimisation. On the other hand, during the latter stage, it is important to keep a small average velocity to find the optimum solution efficiently [201]. One can then define an ideal velocity at iteration t , which decreases with time, as follows:

$$v_{\text{ideal}}^t = v_s \left(\frac{1 + \cos \left(\frac{\pi t}{T_{\text{end}}} \right)}{2} \right), \quad (6.25)$$

where $v_s = (x^u - x^l)/2$ is the initial ideal velocity, T is the maximum number of iterations and $T_{\text{end}} = 0.95T$ is the time in which 95% of search is completed. As visualised in figure 6.14, the ideal velocity profile matches the requirements for an effective exploration of the search space. The inertia weight can then be dynamically adapted at each iteration based on the average velocity in relation to the ideal velocity [202] using:

$$\omega^{t+1} = \begin{cases} \max \{ \omega^t - \Delta\omega, \omega_{\min} \} & \text{if } \bar{v}^t \geq v_{\text{ideal}}^{t+1} \\ \min \{ \omega^t - \Delta\omega, \omega_{\max} \} & \text{if } \bar{v}^t < v_{\text{ideal}}^{t+1} \end{cases}, \quad (6.26)$$

where ω_{\min} and ω_{\max} are the minimum and maximum inertia weights and $\Delta\omega$ is the inertia weight step size. It has been shown by Harrison et al. [219] that decreasing the ideal velocity decrease the inertia weight such that it remains within convergent range. Xu fixed the parameters $\omega_{\min} = 0.3$, $\omega_{\max} = 0.9$, $\Delta\omega = 0.1$, and $\psi_1 = \psi_2 = 1.49$ [201] and, in this work, APSO-VI has been adopted, albeit with slightly different parameter values.

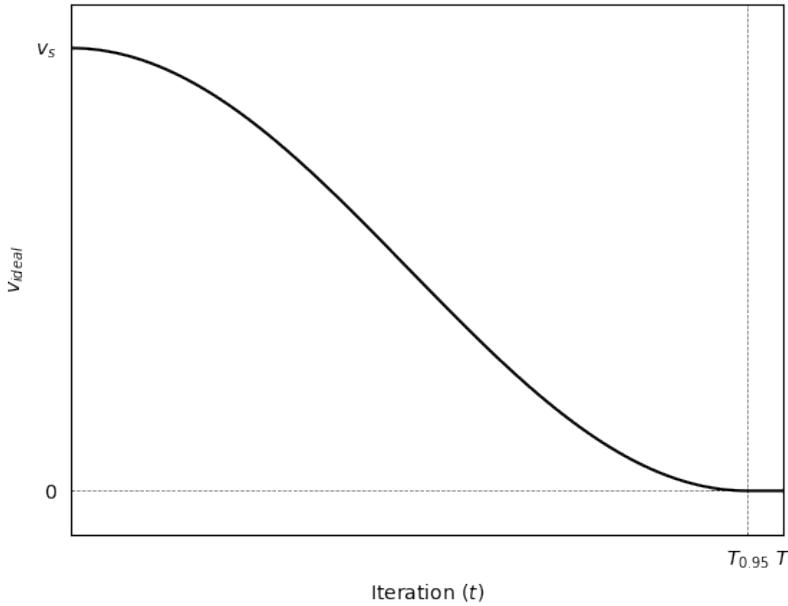


Figure 6.14: Schematic of ideal velocity profile in APSO-VI.

In Yellowjacket–GEM, the APSO-VI hyperparameters were selected to be $\omega_{min} = 0.2$, $\omega_{max} = 0.9$, $\Delta\omega = 0.1$, $\psi_1 = 1.5$ and $\psi_2 = 2$. These values provided good convergence rates while reasonably exploring the search space and are similar to those previously used in thermodynamic equilibrium application such as by Piro and Simunovic [4] and Myint et al. [139].

6.5.5. Implementation and analysis

All global optimisation methods have their advantages and disadvantages and no global optimisation method is universally superior to others. While the deterministic methods are good at converging to a local minimum, they are often prone to high computational expenses. The stochastic methods, on the other hand, tend to cover the search space more effectively but face difficulty at finding the global minimum [4]. The global optimisation methods discussed in literature have mostly been problem centric and there has been a lack of a comprehensive and rigorous analysis of these methods applied to a variety of thermodynamic equilibrium problems. Since the global optimisation methods are critical to the performance of Yellowjacket–GEM, an experimental approach was adopted to select method to be used. While the goal of the global minimiser can be restricted to identifying whether or not a phase has a negative driving force, in terms of comparison, the aim was to correctly identify the minimum of driving force in each

of the eight test cases described in section 6.5.1.

Since, the convergence criteria for Couenne and the APSO-VI implementation differ, they must be clarified. In Couenne, the convergence is based on the feasibility tolerance. If a constraint $g_i(x) \leq 0$ within this tolerance, it is deemed satisfied [182]. The Couenne solve requires several options to be specified. The ones of particular concern here were that related to branching for which violation transfer was selected and FBBT was applied to bound tightening. Since OBBT is computationally expensive, it was disabled and Couenne was allowed to use heuristics through interior point optimisation. The tolerance was left to the default value of 10^{-6} .

In APSO-VI, the convergence criterion is more complicated due to the stochastic nature of the algorithm. Guaranteeing that all the particles will converge to the same value is impossible without significantly compromising performance. Apart from a preset maximum number of iterations $T = 100$, the algorithm is deemed to converge if 95% of the particles converge to a small distance of the global best position. For this, the Euclidean distance of each particle from the best known global solution is calculated using $S_i^t = \|x_i^t - g^t\|$ and if $S_i^t \leq 10 - 6$ for $0.95N_p$ particles, the algorithm is terminated as converged. For calculating the Euclidean distance, only feasible solutions are considered and if a feasible global best is not identified, the algorithm is marked as failed.

For comparison, each implementation of the method was executed a hundred times on a 2020 M1 MacBook Air with 8 GB of memory. The methods were alternated in ABC...ABC... pattern to avoid bias and the total time for all the runs was considered. The average time of all the times in the interquartile range was selected as the performance metric while the number of times the algorithm correctly identified the minimum or absence of negative driving force was the metric of reliability. No runs were discarded for the reliability metric. The results of a comparative analysis are shown in figures 6.15 and ???. The results demonstrate that the equispaced grid sampling method is only effective with very small resolutions leading to a very rapid increase in the cost. On the other hand, the APSO is a lot more robust but they do show that a larger number of particles can better scan the space. Despite their efficiency, the robustness of the APSO is slightly lower than the sBB algorithm which converges to the correct results for each test case but does so at the cost of increase in computational time.

The grid sampling method was able to find the minimum in all the test cases albeit only when the grid resolution was increased to $\delta = 0.00$ and with a significant impediment on performance. In particular, one must be careful about the charge neutrality constraints with this approach. When dealing with ionic phases, many of the samples using this strategy will result in infeasibility due to the charge neutrality constraint getting violated. This can potentially

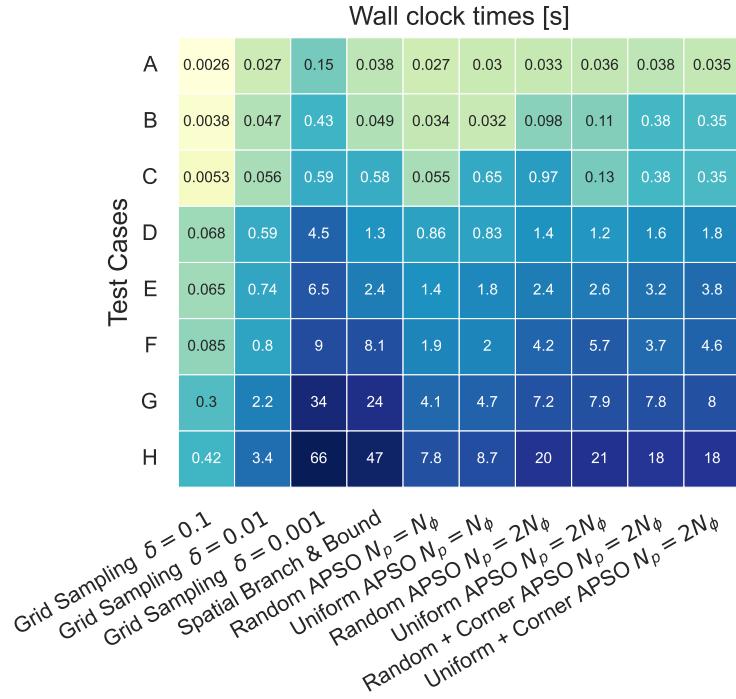


Figure 6.15: Comparison of computational performance of various global optimisation algorithms for the test cases. The wall clock time is the average time of the results in interquartile range for 100 calculations of each method and case combination

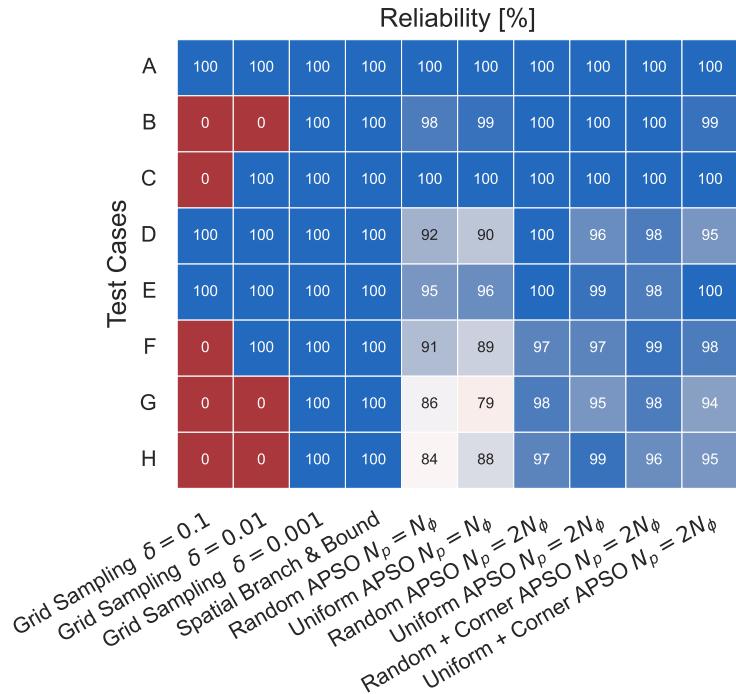


Figure 6.16: Comparison of reliability of various global optimisation algorithms for the test cases. The reliability is the number of times the correct results were shown by a method out of the 100 calculations.

compromise the method's reliability as a feasible point satisfying the charge constraint might never be found. In the implementation here, the objective function was evaluated at every sample point despite some of them being infeasible.

Among the tested options, sBB proves to be the most reliable though at a cost to performance. This is expected for the well behaved driving force functions. One way of reducing the computational cost of sBB is to terminate the solver as soon as an upper bound becomes negative or a feasible solution with negative driving force has been identified. This however has not been implemented in Yellowjacket–GEM. The stochastic methods on the other hand exhibit fairly good computational performance though with a slightly lower reliability. In the experiments, the loss of reliability is attributable to reaching maximum iterations and in a small number of cases to converging to an infeasible value. Moreover, the impact of the number of particles in the swarm is clearly visible. With $N_p = N_\phi$, the space is not sufficiently scanned leading to a lower overall reliability. In such a scenario, increasing the number of particles seems to be the best choice but one must take cognisance of the fact that this can increase the computational time and might also require adjusting the convergence criteria. Initialising the particles on the corners did not have as big an impact as the number of particles. This can be attributed to the test cases itself where the optimal solution in most cases was not close to any edge and therefore no significant benefit was obtained from the particles scanning the space closer to the boundaries.

In the context of Yellowjacket, both the sBB and APSO algorithms have been integrated into the code and the user will have the option of specifying the desired method. In cases where reliability is of the utmost and the system is deemed too complex, one could select sBB as the global optimisation algorithm while in cases where the system is deemed to be not very complicated or where there is a possibility of a-posteriori checking the results and / or augmenting global optimisation results with other information such as that from the grain information available in phase field.

6.5.6.

6.6. Summary

A number of algorithms for different parts of a thermodynamic equilibrium solver were presented in this chapter. Many of these algorithms have already been implemented in other codes available in the literature and GEM and levelling are relatively mature algorithms with little to no scope of improvement. This is evident from the fact that most of the development efforts since the original GEm method has relied on auxiliary operations such as initialisation, etc. However,

this does not mean that improvements can not be made. The development of an advanced thermodynamic solver leaves the door open for incremental gains on many of these algorithms. For example, the post-levelling and temporal series estimates for initialisation will be more carefully analysed and implemented during this work in order to minimise the computational cost of the non-linear step. The work on non-linear step will focus on improving the convergence rate by focussing the attention on the line-search and phase update algorithms. Finally, two of the major areas that stand to benefit from this work are global optimisation methods and integration with multiphysics framework MOOSE. The rigorous application based study of global optimisation methods which will be performed during this work is expected to provide a definitive answer to the question of reliability, efficiency and robustness of various candidate methods for application to thermodynamic equilibrium problems. The optimum method will then be implemented to achieve the best possible performance. Regarding MOOSE integration, this work will try to minimise the costs associated with thermodynamic equilibrium calculations, which significantly impede performance of multiphysics simulations, by minimising thermodynamic computation costs themselves and reducing overheads related to coupling which also contribute towards the performance impediment.

7

Results and Discussions

This chapter presents the applications. Write intro. Describe problems in more detail

7.1. GEM - Phase Field Coupling

The objective of Yellowjacket development was to allow concurrent coupling of GEM with the phase field module in MOOSE. To achieve this a two step process was adopted. The first step was an offline coupling where GEM calculations are used to pre tabulate the Gibbs energy and chemical potential data. The data is then used to generate interpolated functions using the `PiecewiseLinearInterpolationMaterial` object in MOOSE. The next step was to move towards a full coupling for which a `UserObject` has been developed and is currently being tested. The `UserObject` will allow direct incorporation of GEM calculation in the phase field module and other codes. A phase field simulation was performed at the University of Florida¹ to demonstrate the current capabilities. In the model, the corrosion of Ni metal by a LiF–NiF₂ salt at 1150K was simulated with values for the Gibbs energy supplied by the Gibbs energy minimiser. As shown in figure 7.1, the use of GEM allows capturing the excess mixing effects which were not captured by the dilute solution Nernst model used previously. Since the excess energies can have significant contributions for larger systems such as ones with impurities, being able to capture the additional contributions can significantly improve the fidelity.

The result of Ni leaching into the molten salt has been shown in figure 7.2. In the simulation, the corrosion of Ni by LiF–NiF₂ was simulated under oxidising conditions. The mole fraction of Ni in the molten salt phase was fixed as $x_{\text{Ni}} = 0.001$.

¹The phase field calculations were performed by Chaitanya Bhave, University of Florida.

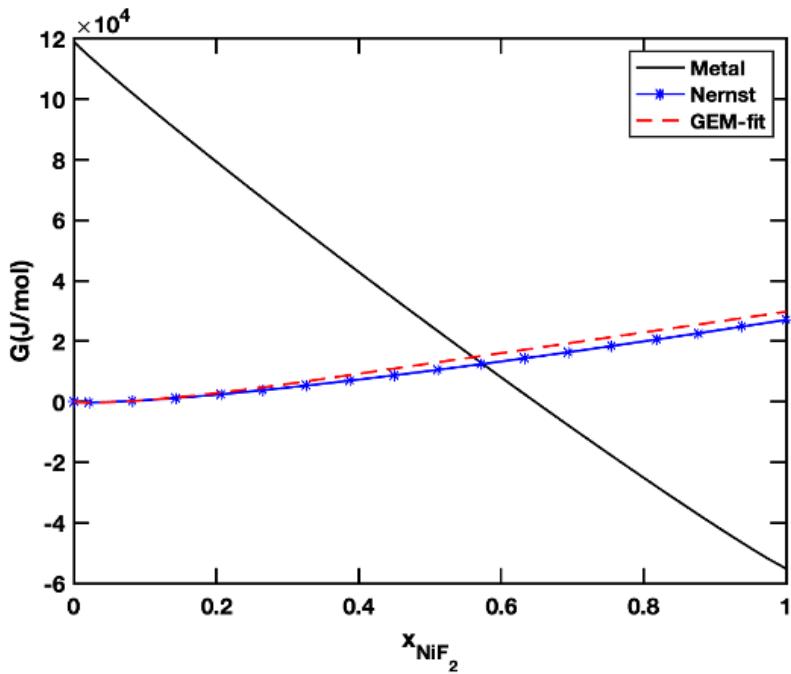


Figure 7.1: Comparison of Gibbs energy predicted by the Gibbs energy minimiser vs. the dilute Nernst energy model used previously.

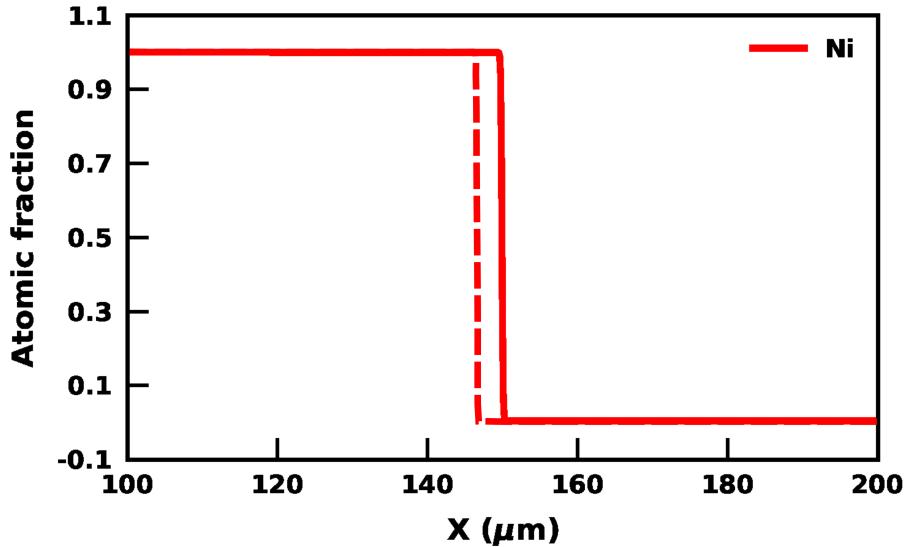


Figure 7.2: Simulation of Ni corrosion by $\text{LiF}-\text{NiF}_2$ salt. Initially, the domain contained Ni in the left half of the domain and molten salt in the right half with the interface shown by the solid vertical line at the centre of the domain. At the end of the simulation, denoted by the dashed vertical line, the oxidising conditions lead to the leaching of Ni from the metal into the molten salt as exhibited by the interface shifting to the left.

7.1.1. Phase Equilibrium Calculations

To demonstrate the capabilities of Yellowjacket-GEM, the $\text{NaF}-\text{CsF}$ binary system was selected. This system has been recently re-evaluated experimentally by Lipkina *et al.* [220] and the phase

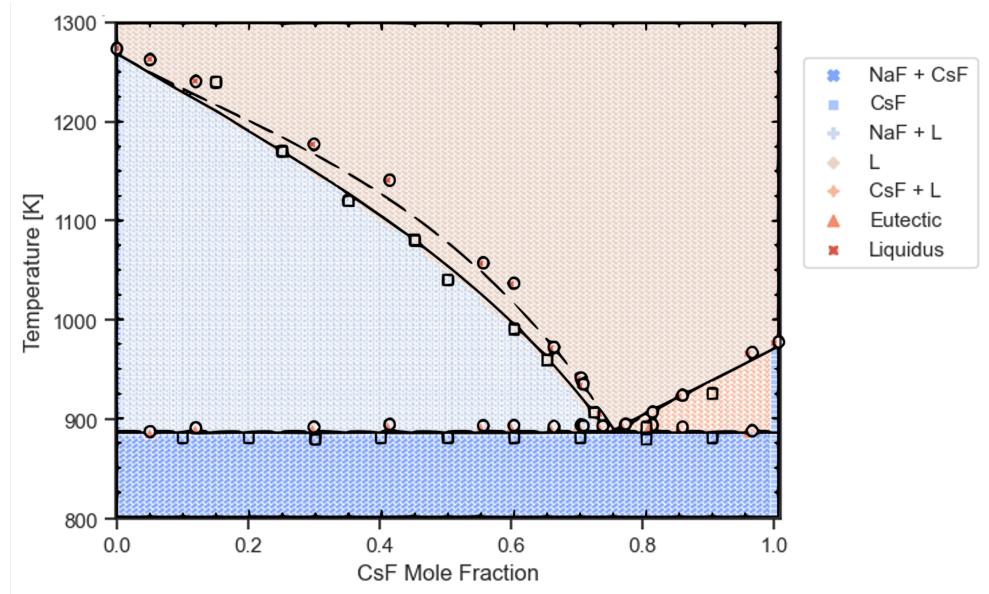


Figure 7.3: Yellowjacket prediction of NaF–CsF phase diagram with the original phase diagram overlayed on top.

diagram was reproduced using Yellowjacket–GEM and compared to the experimental results. The calculations from Yellowjacket are shown in figure 7.3 and show excellent agreement with the experimental data for the eutectic points. There is, however, a departure between the liquidus points calculated by Lipkina *et al.* and the ones predicted by Yellowjacket. This is a direct consequence of the database used in the calculations as it has not been updated to reflect the recent experimental results. In fact, as shown by the solid black line, the calculations match the results of the previously available experimental data. The example not only highlights the capability of Yellowjacket–GEM but also shows a need for the re-evaluation of the NaF–CsF thermodynamic model currently used in the databases.

7.1.2. Vapour Pressure in MSR

Another demonstration of capabilities of GEM focuses on the change of vapour pressure of elements in gas phase and the element potential evolution in MSR. For the purpose of demonstration, a fictive system representative of a molten salt system (FLiBe) with some dissolved fissile material (U) and some fission products (Nd, Ce, La, Cs, Rb) was simulated to undergo an unmitigated increase in temperature. Such a scenario can be relevant in source term analyses and is of particular interest for MSR design and deployment. The predicted vapour pressures are shown in figure 7.5 and the predicted element potentials are shown in figure 7.6. One must note that the results are purely for capability demonstration and must not be treated as physically relevant. However, they do exhibit cases where one might find the use of Yellowjacket–GEM

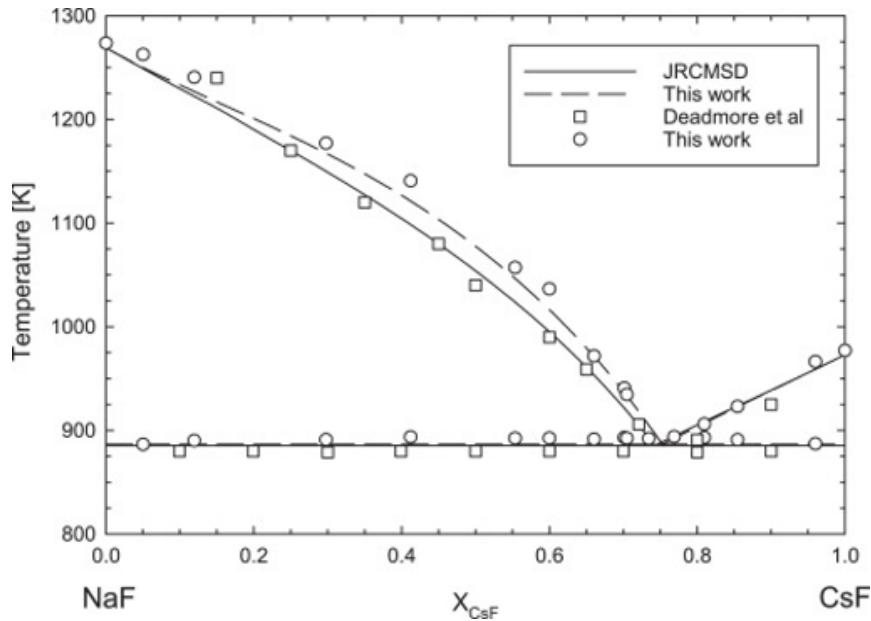


Figure 7.4: Reference NaF–CsF phase diagram from Lipkina *et al.* [220].

relevant.

7.2. Verification

To ensure that accuracy of results, a significant effort was put into verification of Yellowjacket-GEM results by comparison with commercial code FactSage. For this, a representative system was selected (the system composition is the same as that used by Poschmann *et al.* [157]) and the relative difference of the mole fractions of each quadruplet was compared between Yellowjacket and FactSage. As shown in figure 7.7, the results are in excellent agreement with FactSage and the maximum relative difference is of the order of $1e - 5$.

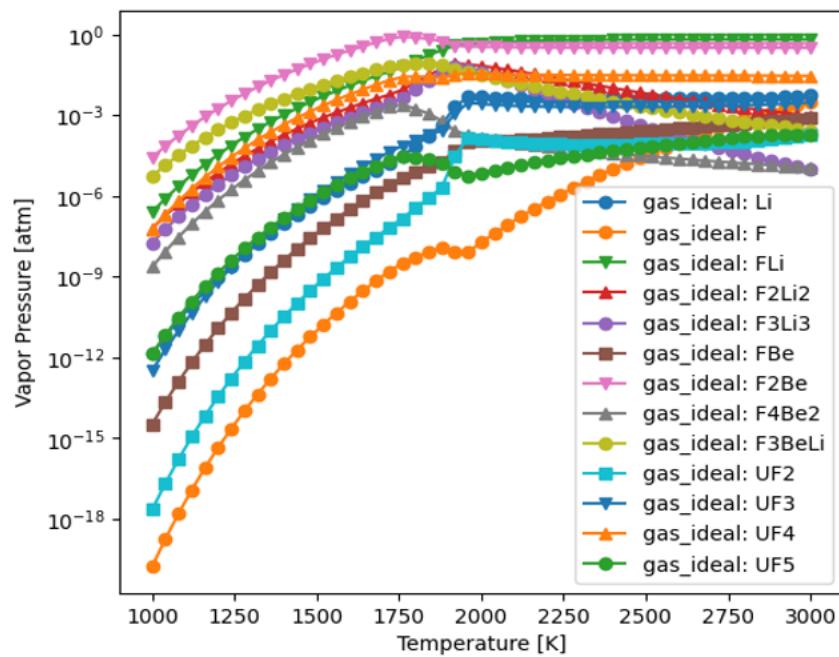


Figure 7.5: Vapour pressure prediction in molten salt system.

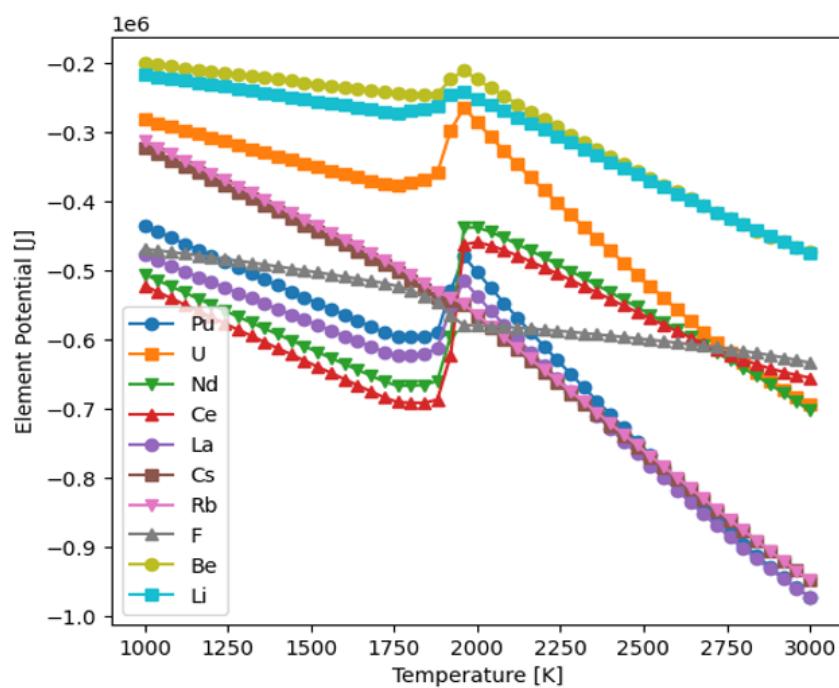


Figure 7.6: Element potential evolution in MSR.

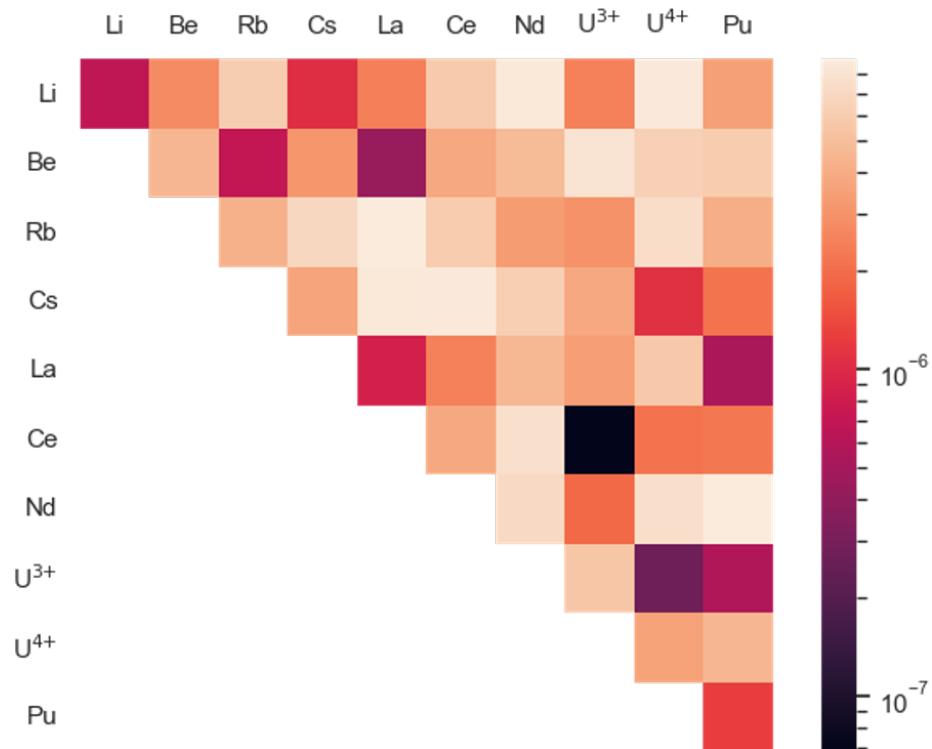


Figure 7.7: Relative difference of mole fraction of quadruplets when compared to FactSage

8

Conclusions

This chapter summarises the conclusion

9

Recommendations

This chapter summarises the expected outcomes from this research work along with a proposed timeline for the implementation of the different subtasks that form the part of the work. The current progress towards the development of the Gibbs energy minimiser has also been presented along with a demonstration problem, which is then followed by a brief publication plan.

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List of Publications

Peer Reviewed Journal Articles

1. **P. Bajpai**, M. Poschmann, M.H.A. Piro, *Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models*, *Journal of Phase Equilibria and Diffusion*, 42 (2021) 333-347.
2. M. Poschmann, **P. Bajpai**, B.W.N. Fitzpatrick, M.H.A. Piro, *Recent developments for molten salt systems in Thermochimica*, *Calphad*, 75 (2021) 102341.
3. **P. Bajpai**, M.H.A. Piro, *Corrigendum to 'The thermochemistry library Thermochimica'*, *Computational Materials Science*, 198 (2021) 110659.
4. M.H.A. Piro, M. Poschmann, **P. Bajpai**, *On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts*, *Journal of Nuclear Materials*, 526 (2019) 151756.
5. **P. Bajpai**, M.H.A. Piro, D. Schwen *Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models*, In preparation, to be submitted to *Journal of Global Optimization*.

Peer Reviewed Conference Proceedings

1. **P. Bajpai**, M. Poschmann, D. Andrš, C. Bhave, M. Tonks and M. Piro, *Development of a new thermochemistry solver for multiphysics simulations of nuclear materials*, *TMS 2020 Supplemental Proceedings, TMS 2020 - 149th Annual Meeting & Exhibition*, San Diego, February 23-27, 2020.
2. **P. Bajpai**, M. Poschmann, D. Andrš and M. Piro, *Progress in developing a new thermochemistry code for corrosion modelling and multiphysics simulation of nuclear fuels*, *39th Annual Conference of the Canadian Nuclear Society and 43rd Annual CNS/CNA Student Conference*, Ottawa, June 23-26, 2019.

Conference / Workshop Talks & Posters

1. **P. Bajpai**, C. Bhave, M. Poschmann, D. Schwen, M. Tonks and M. Piro, *Yellowjacket Gibbs Energy Minimiser: Computing Thermochemical Equilibrium for Multiphysics Simulations of Molten Salt Reactors*, 15th International Conference on CANDU Fuel, Ajax, Canada, August 21-24, 2022..
2. **P. Bajpai**, C. Bhave, M. Poschmann, D. Schwen, M. Tonks and M. Piro, *Yellowjacket: Coupling Gibbs Energy Minimisation with Phase Field Method for Corrosion Modelling in Molten Salt Reactors*, Workshop for the Molten Salt Thermal Properties Working Group, Virtual, November 15-17, 2021.
3. **P. Bajpai**, C. Bhave, M. Poschmann, D. Schwen, M. Tonks and M. Piro, *Yellowjacket: Coupling Gibbs Energy Minimisation with Phase Field Method for Corrosion Modelling in Molten Salt Reactors*, NuFuel 2021, Bangor, United Kingdom, March 15-18, 2021.
4. **P. Bajpai**, C. Bhave, M. Poschmann, D. Andrš, M. Tonks and M. Piro, *Yellowjacket: A New MOOSE-based Corrosion Modelling Application for Molten Salt Reactors*, TMS 2021 - 150th Annual Meeting & Exhibition, Virtual, March 15-18, 2021.
5. **P. Bajpai**, M. Poschmann, D. Andrš, C. Bhave, M. Tonks and M. Piro, *Development of a new thermochemistry solver for multiphysics simulations of nuclear materials*, TMS 2020 - 149th Annual Meeting & Exhibition, San Diego, United States, February 23-27, 2020.
6. **P. Bajpai**, M. Poschmann, D. Andrš and M. Piro, *Progress in developing a new thermochemistry code for corrosion modelling and multiphysics simulation of nuclear fuels*, 39th Annual Conference of the Canadian Nuclear Society and 43rd Annual CNS/CNA Student Conference, Ottawa, Canada, June 23-26, 2019.